

JACK E. FERNANDEZ | ROBERT D. WHITAKER

AN INTRODUCTION TO
**CHEMICAL
PRINCIPLES**

8961437

06

F363-2



E8961437

AN INTRODUCTION TO **CHEMICAL** **PRINCIPLES**

MACMILLAN PUBLISHING CO., INC.
NEW YORK

COLIER MACMILLAN PUBLISHERS
LONDON

Copyright © 1975, MACMILLAN PUBLISHING CO., INC.

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.

A portion of this material has been adapted from *Modern Chemical Science*, copyright © 1971 by Jack E. Fernandez.

MACMILLAN PUBLISHING CO., INC.
866 Third Avenue, New York, New York 10022

COLLIER-MACMILLAN CANADA, LTD.

Library of Congress Cataloging in Publication Data

Fernandez, Jack E (date)
An introduction to chemical principles.

1. Chemistry. I. Whitaker, Robert D., joint
author. II. Title.

QD31.2.F48 540 74-80

ISBN 0-02-337070-X

Printing: 1 2 3 4 5 6 7 8

Year: 5 6 7 8 9 0

贈閱

AN INTRODUCTION TO **CHEMICAL PRINCIPLES**



JACK E. FERNANDEZ **ROBERT D. WHITAKER**

University of South Florida, Tampa

To

ALBERT
BARRY
CAMPBELL
DALLAS
JACK
MARINA
RICHIE
RUDY
RUTH
SYLVIA

REFACE

First year college chemistry courses have come to mean many different things to different people. The diverse backgrounds of entering college students and their varied purposes in taking the course have created problems for instructors and textbook writers alike. As teachers with combined experience of over thirty years, we have long been interested in these problems. This textbook is our attempt to find a solution. Its originality lies more in the integration of ideas, principles, and theories than in a new selection of topics. This book is designed to serve that wide range of students who come to their first year college chemistry course with only an average or no high school chemistry background. Additionally, there is sufficient versatility of material so that this text can meet the needs of the students who will follow their first course with courses in organic and analytical chemistry as well as those students taking first year chemistry as a terminal course.

The text is divided into four broad areas:

- Part 1. Elementary Ideas
- Part 2. Chemical Structure
- Part 3. Chemical Dynamics
- Part 4. Chemistry in the Service of Man

The fundamentals of chemistry are covered in Parts 1, 2, and 3. Part 4 is a special topics section that can be utilized, at the discretion of the instructor, either as collateral material as the underlying principles are developed or as independent study for the better student. The section can even be eliminated entirely without loss of critical principles.

The objective of our approach is to emphasize relationships among important chemical principles. Students who have had no previous course in chemistry should experience little difficulty in grasping the fundamental concepts because mathematical sophistication is not a goal nor is it assumed on the part of the student.

We have tried to make the coverage truly *general*. We have therefore included some concepts that are not usually covered in a freshman text. These are included, not because they are new or unusual, but rather because they aid in understanding and in giving the student a better idea of the scope of chemistry. Some such concepts are molecular symmetry and stereochemistry, polymer structure, reaction mechanisms, nuclear and chemical technology, and chemicals that affect life. By the same token, we have omitted some concepts traditionally covered where our experience has convinced us that they are neither essential nor helpful to the student's grasp of fundamental principles and facts.

Three concepts omitted are *gram atomic weight*, *equivalent weight* and its associated concentration term *normality*, and *electronegativity*. We feel that these ideas are more confusing than helpful to the beginning student. If one takes the broad view of the mole concept, then surely the idea of a *mole of atoms* need not be obscured by the introduction of gram atomic weight. Equivalent weight was an interesting early solution to the historic problem of obtaining relative atomic masses. However, the use of equivalent weights in our opinion creates unnecessary confusion in dealing with the far more important concept of atomic weight. Normality, while a convenient concentration term in the analytical laboratory, is certainly a nonessential for beginning chemistry. The concept of electronegativity appears to be passing out of the vocabulary of research chemists. Although it does possess considerable explanatory utility, beginning students are

often too prone to seize upon electronegativity as the ultimate explanation for all phenomena. We, therefore, have used the directly measurable quantitative properties of ionization energy and electron affinity to develop the qualitative idea of the relative ability of an atom to attract electrons without reference to the pseudo-quantitative concept of electronegativity.

In all numerical examples the correct numbers of significant figures and proper units have been employed. Significant figures and unit analysis are not discussed in great detail but the instructor can emphasize them if he chooses. Both of these topics along with fairly complete discussions of other mathematical skills are treated in Appendix A for easy reference and assignment.

Our approach in Part I is to begin with common experience and proceed slowly in an experimental route through the introductory concepts and language of chemistry. Our aim in the first three chapters is to define some chemical terms and to develop the most fundamental ideas upon which atomic theory will be based. The next three chapters develop kinetic molecular theory through a study of gases and phase changes. The remaining chapters of Part I present a gradual development of atomic theory culminating in its application to chemical bonding. Throughout Part I, we have attempted to provide as far as possible an integration of these concepts. An approach found in many other books is to present kinetic molecular theory, atomic structure, stoichiometry, periodicity, and bonding as separate topics to be mastered independently. We feel that each of these is understood best in terms of the others. For this reason we have attempted to develop the concepts of periodicity, atomic structure, and bonding in a parallel fashion, beginning with the operational viewpoint and leading to the theoretical. Moreover, these same topics are carried over to Parts 2 and 3 where their development and application continue along with the introduction of new concepts.

Part 2 begins at Chapter 13 with a subject that is both fundamental to molecular considerations and interesting to students—stereochemistry. This subject is a logical extension of atomic theory and bonding and forms one of the pillars upon which subsequent study of molecular structure rests. The most recent stereochemical conventions have been adopted.

Chapters 14 through 18 comprise a study of chemical structure that is divided into covalent, metallic, and ionic bond types. Within each of these bond types, the role of stereochemistry is examined as a means of relating structure to observable properties. Such ideas as physical properties, chemical energy, and reactivity can thus be correlated with structure. Of course, periodicity and atomic and bonding theory provide the basis.

The general scheme of Part 3 is to present equilibrium as the fundamental way to view chemical changes. The introductory chapter on chemical equilibrium serves to link the generalized concept of chemical equilibrium with simple types of physical equilibria. Le Chatelier's principle is presented and is shown to be a necessary consequence of the existence of an equilibrium constant. Separate chapters cover electrolytic dissociation, oxidation-reduction, acid-base reactions, and equilibria important in analytical chemistry. Quantitative treatments of weak acids and bases, buffer systems, and multiple equilibria are considered in detail in several sections of Chapter 22, but these sections may be deleted in terminal courses without loss of continuity.

Chemical kinetics is presented in Chapters 24 and 25. The striking differences among reaction rates and the effect of temperature serve as the starting point. The idea of mechanism is then discussed as a logical explanation of reactions and their rates using the kinetic molecular paradigm. Finally, reaction rate theory

is developed from Arrhenius' early ideas of activation and is refined by a consideration of collision theory.

Chapter 25 uses collision theory as the basis to investigate various chemical reactions from a mechanistic point of view. Some examples are presented to show how chemists "tailormake" molecules. The importance of an understanding of reaction mechanism in this effort is emphasized.

Chapter 26 is a brief introduction to the chemistry of the most important organic functional groups. It serves to prepare the way for the next chapter, which is an attempt to deal with life as a complex chemical system. The emphasis is on how this chemistry differs from simpler chemistry. Life chemistry is thus shown to be different in organization rather than in principle.

The final chapter of this section treats nuclear reactions. Of special importance in this chapter is the fascinating story of the scientific revolution that culminated in the practical use of atomic energy.

Several points that are felt to be novel should be stressed. First, in dealing with chemical dynamics, organic chemistry is not treated separately from other "chemistries." In keeping with the idea that this book is a truly "general" textbook, reactions traditionally reserved to an organic section are presented where they serve to illustrate an important principle or merely to show some interesting chemistry. Likewise, coordination compounds are treated simply as additional examples of the variety of molecular geometry. Descriptive chemistry is not isolated from principles because principles in chemistry are not developed in isolation but, rather, are shown to spring from a consideration of "real" chemistry and "real" reactions.

Part 4 is an attempt to deal with the interface between the science of chemistry and its application to modern life. Much has been said and written in recent years about the need for relevance in science courses. Our response to this concern is to present some chemical topics that bear directly on man and over which man has increasingly to make direct value judgments. These topics need not be deferred to the end of the course. Instead they may be assigned at any time after the necessary groundwork had been laid.

A suggested sequence for the use of Part 4 as collateral material is as follows:

<i>Section in Part 4</i>	<i>Can Be Used Any Time Following Chapter</i>
29-1 Nylon	16 Polymers
29-2 Nylon Starting Materials	26 Organic Chemicals
29-3 Sulfur	3 Pure Substances
29-4 Sulfuric Acid	19 Chemical Equilibrium
29-5 Iron from Its Ore	11 Periodic Properties of the Elements
29-6 Sodium and Aluminum	21 Oxidation and Reduction
29-7 Electrolytic Copper Refining	21 Oxidation and Reduction
29-8 Cryogenics	6 Kinetic Molecular Theory
29-9 Cryogenic Liquids	6 Kinetic Molecular Theory
29-10 Synthetic Diamonds	6 Kinetic Molecular Theory
30 Chemicals That Affect Life	26 Organic Chemicals
31 Origin of Life	16 Polymers
32 Nuclear Technology	28 Nuclear Reactions
33 Energy	6 Kinetic Molecular Theory

The mathematical manipulations of Appendix A are designed to allow the student to acquire on his own the manipulative skills necessary for beginning chemistry. Students with only minimal backgrounds in algebra should be able to handle the mathematics in the text after a thorough review of this appendix.

Appendix B gives rules for the systematic naming of organic compounds and coordination compounds.

Appendix C—"Qualitative Inorganic Analysis"—is a treatment of the traditional "qual scheme." The analysis of some common anions and cations is presented to serve several purposes: (1) To afford a convenient means for the student to acquire a working knowledge of some descriptive chemistry, (2) to provide a direct interaction between text material and laboratory practice, and (3) to emphasize the application of equilibrium theory. This section presents both theory and actual laboratory directions. This material is suitable for use at any time after Chapter 23.

We wish to acknowledge Ginger Weir for typing the manuscript.

J. E. F.
R. D. W.

PART

ELEMENTARY IDEAS

1

CHEMISTRY—A PROLOGUE

- 1-1. Introduction 3
- 1-2. Contemporary Chemistry 4
- 1-3. Energy as a Chemical Resource 4
- 1-4. Chemistry and Health 4
- 1-5. Sources of Chemical Raw Materials 5
- 1-6. Chemistry as an Intellectual Achievement 5
- 1-7. Social Implications of Chemistry 6

2

CLASSIFICATION OF MATTER AND ENERGY

- 2-1. States of Matter 7
- 2-2. Measurement of Temperature 7
- 2-3. Metric System 8
- 2-4. Physical Changes and Physical Properties 11
- 2-5. Mixtures and Solutions 14
- 2-6. Compounds and Elements 16
- 2-7. Chemical Change 16
- 2-8. Conservation Laws 17
- 2-9. Energy 18
- Problems 21

3

PURE SUBSTANCES—ELEMENTS AND COMPOUNDS

- 3-1. Introduction 24
- 3-2. Decomposition of Compounds 24
- 3-3. Percentage Composition 25
- 3-4. Laws of Chemical Composition 27

3-5.	Dalton's Atomic Theory	27
3-6.	Chemical Symbols	28
3-7.	Chemical Formulas and Equations	29
3-8.	Avogadro's Number—Moles	30
3-9.	Calculation of Percent Composition—Simplest Formula	32
3-10.	Naming of Compounds	34
	Problems	35

4

PROPERTIES AND BEHAVIOR OF GASES

4-1.	Basic Definitions	38
4-2.	Pressure	39
4-3.	Basic Gas Laws	40
4-4.	Combined Gas Law	44
4-5.	Gay-Lussac and Combining Volumes of Reacting Gases	45
4-6.	Avogadro's Law	46
4-7.	Ideal Gas Law	48
4-8.	Dalton's Law of Partial Pressures	52
	Problems	56

5

KINETIC THEORY OF GASES

5-1.	Basic Postulates	59
5-2.	Molecular Velocities	60
5-3.	Derivation of the Perfect Gas Law	62
5-4.	Graham's Laws of Diffusion and Effusion	65
	Problems	67

6

KINETIC MOLECULAR THEORY AND LIQUIDS AND SOLIDS

6-1.	Validity of Gas Laws	69
6-2.	Condensed Phases of Matter	70
6-3.	Extension of Kinetic Molecular Theory to Condensed Phases	72

6-4. Kinetic-Molecular Interpretation of Phase Equilibria 76

6-5. Kinetic-Molecular Theory as a Scientific Theory 80

Problems 81

7

STOICHIOMETRY

7-1. Conservation Laws 84

7-2. Chemical Equations and Moles 85

7-3. Heat of Reaction 86

7-4. Problems Involving Chemical Reactions 88

7-5. Molarity 90

Problems 91

8

ATOMIC CONCEPTS

8-1. Inadequacies of Dalton's Atoms 93

8-2. Early Electrochemical Observations 93

8-3. Electric Discharges Through Gases 96

8-4. Millikan and the Charge on the Electron 99

8-5. Alpha, Beta, and Gamma Rays 100

8-6. Discovery of the Nucleus 101

8-7. Periodicity and the Periodic Table 103

Problems 105

9

THE ATOMIC NUCLEUS

9-1. Discovery of X Rays 109

9-2. Discovery of Radioactivity 109

9-3. Atomic Numbers 110

9-4. The Mass Spectrograph—Isotopes 112

Problems 114

10

ELECTRONIC THEORY OF ATOMIC STRUCTURE

- 10-1. Early Work on the Nature of Light 116
- 10-2. Theory of Electromagnetic Radiation 118
 - 10-3. Planck's Quantum Theory 120
 - 10-4. Photoelectric Effect 121
 - 10-5. Atomic Bright-Line Spectra 123
 - 10-6. Bohr's Theory of the Atom 124
 - 10-7. Extensions of Bohr's Theory 127
 - 10-8. Electron Distributions in Atoms 130
 - 10-9. Wave Properties of Matter 131
- 10-10. Schrodinger's Wave Mechanical Theory 133
- 10-11. Physical Interpretation of Wave Functions 135
 - Problems 136

11

PERIODIC PROPERTIES OF THE ELEMENTS

- 11-1. Modern Periodic Law 139
- 11-2. Ionization Potentials 140
- 11-3. The Alkali Metals 141
- 11-4. Alkaline Earth Metals 143
- 11-5. Group III Representative Elements 145
- 11-6. Group IV Representative Elements 147
- 11-7. Group V Representative Elements 147
- 11-8. Group VI Representative Elements 148
- 11-9. Group VII Representative Elements—The Halogens 148
 - 11-10. Noble Gases 149
 - 11-11. Transition Metals 150
 - 11-12. Inner Transition Metals 151
- Problems 152

12

CHEMICAL BONDING

- 12-1. Electrical Conductivity and Physical Properties 155
 - 12-2. Nature of Conductors 156
 - 12-3. Nature of Nonconductors 158
 - 12-4. Nature of Metallic Conductors 159
 - 12-5. Ionic Bonding 160
 - 12-6. Covalent Bonding 161
 - 12-7. Bonding in Metals 164
 - 12-8. Covalent Bonding and Orbital Overlap 165
 - 12-9. Electron Repulsion and the Shapes of Molecules 166
 - 12-10. Hybridization of Orbitals 170
 - 12-11. Problem of Electron Delocalization 171
 - 12-12. Bonding as a Periodic Property 173
 - Problems 175
-

PART 2

CHEMICAL STRUCTURE

13

STEREOCHEMISTRY—THE SHAPES OF MOLECULES

- 13-1. Constitutional Isomers 181
- 13-2. Stereoisomers I—Cis-trans Isomers 182
- 13-3. Stereoisomers II—Chiral Molecules 185
- 13-4. Symmetry—A Criterion of Chirality 186
- 13-5. Optical Activity and Chirality 189
- 13-6. Hydrogen Bonding 191
- 13-7. Tetrahedral Geometry 193
- 13-8. Diffraction Analysis Techniques 195
- Problems 197

14

COVALENT ARCHITECTURE I. GEOMETRICAL VARIATIONS

A. TETRAHEDRAL GEOMETRY 199

14-1. Hydrocarbons 199

14-2. Cyclic Hydrocarbons 201

14-3. Molecular Strain and Chemical Energy 202

14-4. Unsaturation 204

14-5. The Benzene Molecule 206

B. OCTAHEDRAL GEOMETRY 207

14-6. Structure Elucidation 207

14-7. Ferrocene and Metallocenes 210

C. SQUARE PLANAR GEOMETRY 211

14-8. Nonmetal Compounds 211

14-9. Transition Metal Complexes 212

Problems 215

15

COVALENT ARCHITECTURE II. ELEMENTS OF THE FIRST THREE PERIODS

15-1. Hydrogen 218

15-2. Beryllium and Magnesium 219

15-3. Boron and Aluminum 222

15-4. Carbon and Silicon 225

15-5. Nitrogen and Phosphorus 231

15-6. Oxygen and Sulfur 240

15-7. The Halogens 246

15-8. The Noble Gases 250

15-9. Periodic Trends 250

Problems 251

16

COVALENT ARCHITECTURE III. POLYMERS

16-1. Characteristics of Polymeric Substances 254

16-2. Problem of Molecular Weight 254

16-3.	Classification According to Physical Behavior	255
16-4.	Preparation of Polymers	255
16-5.	Effect of Molecular Structure on Physical Properties—Crystallinity	258
16-6.	Energy Transformations in Polymer Orientation	259
16-7.	Factors That Affect Polymer Strength	259
16-8.	Stereoregular Polymers	261
16-9.	Linear Rigid Polymers	261
16-10.	Proteins and Amino Acids	262
16-11.	Proteins Structure	265
16-12.	Deoxyribonucleic Acid (DNA)— Molecular Structure and Genetic Replication	269
	Problems	272

17

METALLIC STRUCTURES

17-1.	Crystal Systems	274
17-2.	Close-packed Structures	276
17-3.	Body-centered Cubic Structure	279
17-4.	Alloys	280
17-5.	Metallic Bonding	282
	Problems	285

18

STRUCTURES OF IONIC COMPOUNDS

18-1.	Rock Salt—An Important MX Structure	286
18-2.	Fluorite—An Important MX ₂ Structure	287
18-3.	Antifluorite—An Important M ₂ X Structure	288
18-4.	The Calculation of Lattice Energies	288
18-5.	Solvation Effects	291
	Problems	291