

# Introduction to Chemistry

Charles E. Mortimer

### TO L.R.M. AND E.H.M.

D. Van Nostrand Company Regional Offices: New York Cincinnati

D. Van Nostrand Company International Offices: London Toronto Melbourne

Copyright © 1977 by Litton Educational Publishing, Inc.

Library of Congress Catalog Card Number: 76-58670 ISBN: 0-442-25569-1

All rights reserved. No part of this work covered by the copyright hereon may be reproduced or used in any form or by any means—graphic, electronic, or mechanical, including photocopying, recording, taping, or information storage and retrieval systems—without written permission of the publisher. Manufactured in the United States of America.

Published by D. Van Nostrand Company 450 West 33rd Street, New York, N.Y. 10001

### Preface

Designing an introductory chemistry course for college students is difficult. The subject is large and growing. Today's students have widely different interests, academic backgrounds, and abilities. The course must take into account the requirements of diverse career objectives. A text should help instructors respond to their particular problems. INTRODUCTION TO CHEMISTRY was written as an alternative to CHEMISTRY: A CONCEPTUAL APPROACH and in response to some instructors' suggestions as to how their needs could be met, especially in the organization of topics.

The beginning chapters offer a gradual introduction to the subject. Atomic structure and chemical bonding, which some students find abstract and difficult, are postponed until the students are better able to handle them. The principles of stoichiometry, which are central to an understanding of all chemical concepts, are introduced in Chapter 2. The early introduction of this topic permits it to be expanded and reinforced throughout the entire course. The basic principles of thermochemistry, which also are of fundamental importance, are introduced in Chapter 3. The early and systematic discussion of thermochemistry prepares the way for the use of energy concepts (such as lattice energy, ionization energy, and bond energy) in the development of later topics that focus in other directions. The topical order of INTRODUCTION TO CHEMISTRY should facilitate the design of a good laboratory program closely correlated to classroom work.

At the same time, the format of this book is intended to permit relatively wide latitude in course organization. Instructors should not feel constrained to present all the material in this book in the exact order in which it is given.

In recent years, the career goals as well as the mathematical and scientific backgrounds of students who enroll in introductory chemistry have become more diverse than ever. Instructors, therefore, can assume no uniform level of attainment on the part of entering students. In INTRODUCTION TO CHEMISTRY, each concept is developed slowly and thoroughly in a way that should make it understandable to a student who has had no prior exposure to chemistry. Important terms are set in boldface type the first time they are used. Numerous problems are solved as examples. Step-by-step directions for the solution of basic types of problems are set off in boxes. Students will find this boxed material useful for initial assignments and also for reference in later work. The use of calculus is avoided.

Approximately one thousand chapter-end problems of varying difficulty are included. Similar problems are grouped together, and the problems of a chapter are arranged in the order in which the topics are discussed in that chapter. An-

swers to selected numerical problems are given in Appendix G. A Solutions Manual containing worked-out solutions for mathematical problems and an Answer Booklet containing answers only are available. The Student Self-Study Guide, by Michaeleen P. Lee, is keyed to the text and designed to be used independently by students.

Historical anecdotes appear throughout the text to enliven the material. They illustrate that chemistry is a human endeavor, that the science grows and changes, that creative imagination plays a role in the development of chemical thought, and that a full understanding of any phenomenon is never obtained—truth is only approached.

The growing acceptance of the International System of Units (SI) makes it important that students be introduced to this official metric system. With the exception of the United States, all the major industrial powers of the world have adopted SI units exclusively. In the interest of world-wide scientific communication and international trade, sooner or later the United States must convert. Many scientific groups and agencies (including the National Bureau of Standards) have recommended or officially adopted SI units. Some upper level chemistry and physics books use the units and the secondary schools of some states have begun to use SI units.

The rules for the use of the International System appear in Le Système International d'Unités, published by the International Bureau of Weights and Measures, which is available in an English translation prepared jointly by the National Bureau of Standards, of the United States, and the National Physical Laboratory, of the United Kingdom.\* In INTRODUCTION TO CHEMISTRY, the joule, rather than the calorie is used for energy measurements. The ångstrom unit is not employed. Nanometers  $(1 \text{ nm} = 10^{-9} \text{ m})$  are used in place of ångstrom units for the wavelengths of spectral lines (4500 Å = 450 nm), and picometers  $(1 \text{ pm} = 10^{-12} \text{ m})$  are used for bond distances (1.98 Å = 198 pm). The standard atmosphere, which may be used with SI units for the present, is employed instead of the pascal, which is the SI unit of pressure. Since the International Committee of Weights and Measures considers it preferable to avoid the use of the torr, this unit is not employed to express the results of pressure measurements.

I sincerely thank the following for their suggestions and comments: David Herlocker, Western Maryland College, George B. Kauffman, California State University, Fresno, Michaeleen P. Lee, Bucks County Community College, Karl Marhenke, Cabrillo College, and Louise S. Shive, Muhlenberg College.

Suggestions for the improvement of this book will be welcomed.

Charles E. Mortimer

<sup>\*</sup>Page, Chester H., and Vigoureux, Paul, ed. *The International System of Units (SI)*, National Bureau of Standards Special Publication 330, U.S. Government Printing Office, Washington, D.C. (1972).

### Contents

### 1. INTRODUCTION 1

1.1	The Development of N	иоа	ern Chemistry		4
1.2	Elements, Compounds	, ar	nd Mixtures	6	
1.3	The Metric System	9			
1.4	Scientific Notation	12			
1.5	Significant Figures	13			
1.6	Chemical Calculations		16		

### 2. STOICHIOMETRY 22

Problems 20

2.1 Dalton's Atomic Theory 2	22
------------------------------	----

2.2 Formulas 25

### viii CONTENTS

3.

4.

5.

5.2

The Proton 110

2.3	The Mole 27
2.4	Derivation of Formulas 30
2.5	Percentage Composition of Compounds 33
2.6	Chemical Equations 36
2.7	Problems Based on Chemical Equations 37
	The Symbols of Chemistry 42
	Problems 44
THER	MOCHEMISTRY 48
3.1	Energy Measurement 48
3.2	Temperature and Heat 49
3.3	Calorimetry 52
3.4	Thermochemical Equations 54
3.5	The Law of Hess 56
3.6	Enthalpies of Formation 58
3.7	Bond Energies 61
	Count Rumford and the Nature of Heat 64
	Problems 65
GASE	S 70
4.1	Pressure 71
4.2	Boyle's Law 73
4.3	Charles' Law 75
4.4	Amontons' Law 77
4.5	Ideal Gas Law 79
4.6	Gay-Lussac's Law of Combining Volumes
	and Avogadro's Principle 82
4.7	Avogadro's Principle as a Basis for Atomic
	and Molecular Weights 85
4.8	Stoichiometry and Gas Volumes 86
4.9	Kinetic Theory of Gases 89
4.10	Dalton's Law of Partial Pressures 90
4.11	Graham's Law of Effusion 93
4.12	Molecular Speeds 95
4.13	Real Gases 97
4.14	Liquefaction of Gases 98
	The Discovery of Gases 100
	Problems 101
ATON	IIC STRUCTURE 107
5.1	The Electron 108

	5.4 5.5 5.6 5.7 5.8 5.9 5.10 5.11 5.12 5.13 5.14	The Nuclear Atom 112 Atomic Number and the Periodic Law 114 Atomic Symbols and Isotopes 116 Atomic Weights 118 Electromagnetic Radiation 120 Atomic Spectra 122 Wave Mechanics 125 Quantum Numbers 128 Orbital Filling and Hund's Rule 133 Derivation of Electron Configurations 136 Half-Filled and Filled Subshells 140 Scientists and the Atom 143 Problems 144
6.	PROF	PERTIES OF ATOMS AND THE IONIC BOND 149
	6.1 6.2 6.3 6.4 6.5 6.6 6.7 6.8	Types of Elements 150 Atomic Size 151 Ionization Energy 153 Electron Affinity 155 The Ionic Bond 157 Lattice Energy 158 Types of Ions 161 Ionic Radius 163 Problems 165
7.	THE (	COVALENT BOND 168
	7.1 7.2 7.3 7.4 7.5 7.6 7.7 7.8 7.9	The Lewis Theory 168  Formal Charge 170  Transition Between Ionic and Covalent Bonding 178  Electronegativity 180  Resonance 183  Hybrid Orbitals 185  Electron Pair Repulsion Theory 191  Molecular Orbitals 197  Molecular Orbitals in Polyatomic Molecules 204  The Dualistic Theory and the Theory of Types 208  Problems 209
8.		APPLICATIONS OF BONDING THEORY 214  Oxidation Numbers 214

Nomenclature of Binary Compounds 218

5.3 The Neutron 111

8.2

9.

10.

8.3 8.4 8.5 8.6 8.7 8.8 8.9 8.10 8.11	Arrhenius Acids and Bases 219  Nomenclature of Acids, Bases, and Salts 222  Stoichiometry of Neutralization Reactions 224  Equivalent Weights and Normal Solutions 226  The Strength of Oxyacids and Structure 229  Hydrides 232  Oxides 237  Halides 241  Notes on Nomenclature 243  Problems 244
LIQUI	DS AND SOLIDS 248
9.1 9.2 9.3 9.4 9.5 9.6 9.7 9.8 9.9 9.10 9.11 9.12 9.13 9.14 9.15	Intermolecular Forces of Attraction 248 The Hydrogen Bond 251 The Liquid State 254 Evaporation 255 Vapor Pressure 256 Boiling Point 258 Heat of Vaporization 259 The Freezing Point 262 Vapor Pressure of a Solid 263 Phase Diagrams 264 Properties of Solids 267 Cubic Unit Cells 269 X-Ray Diffraction of Crystals 273 Metallic and Ionic Crystal Lattices 275 Crystal Defects 277 The Case of the Disappearing Diamonds 278 Problems 280
SOLU <sup>*</sup>	TIONS 286
10.1 10.2 10.3 10.4	Nature of Solutions 287 The Solution Process 288 Hydrated Ions 289 Heat of Solution 291
10.5 10.6 10.7	Effect of Temperature and Pressure on Solubility Concentrations of Solutions 292 Vapor Pressure of Solutions 299
10.8 10.9 10.10	Boiling Point and Freezing Point of Solutions 302 Osmosis 305 Solutions of Electrolytes 307

	10.11	Interionic Attractions in Solutions 309 The Story of Water 311 Problems 313
11.	REAC	TIONS IN AQUEOUS SOLUTION 318
	11.1 11.2 11.3 11.4	Oxidation-Reduction Reactions 318 Equivalent Weights of Oxidants and Reductants 325 Solutions of Oxidizing and Reducing Agents 327 Metathesis Reactions 328 Cleopatra's Pearls 333 Problems 334
12.	ACIDS	AND BASES 339
	12.1 12.2 12.3 12.4 12.5 12.6	The Arrhenius Concept 340 The Solvent System Concept 341 The Brønsted – Lowry Concept 342 Strengths of Brønsted Acids and Bases 344 Hydrolysis 347 The Lewis Concept 349 Problems 353
13.	CHEM	ICAL KINETICS 356
	13.1 13.2 13.3 13.4 13.5	Reaction Rates 357  Molecular Collisions and Reaction Rate 359  Temperature and Reaction Rate 361  Catalysts 364  Surface Area in Heterogeneous Reactions 369
	13.6 13.7 13.8	Concentration and Reaction Rates 369 Rate Equations and Temperature 372 Reaction Mechanisms and Rate Equations 375 The Exact Truth 380 Problems 380
14.	CHEM	ICAL EQUILIBRIUM 384
	14.1 14.2 14.3 14.4	Reversible Reactions and Chemical Equilibrium 385 Equilibrium Constants 388 Equilibrium Constants Expressed in Pressures 392 Le Chatelier's Principle 396 Poisoned Brandy and Sodium Carbonate 399 Problems 400

15.	IONIC	C EQUILIBRIA 404
	15.1 15.2 15.3 15.4 15.5 15.6 15.7 15.8 15.9 15.10 15.11 15.12 15.13	Amphoterism 435 Hydrolysis 437
16.	ELEC	TROCHEMISTRY 452
	16.1 16.2 16.3 16.4 16.5 16.6 16.7 16.8 16.9 16.10 16.11 16.12	
17.	ELEM	ENTS OF CHEMICAL THERMODYNAMICS 487
	17.1 17.2 17.3 17.4 17.5 17.6 17.7 17.8	First Law of Thermodynamics 488 Enthalpy 489 Second Law of Thermodynamics 492 Gibbs Free Energy 494 Standard Free Energies 496 Absolute Entropies 497 Free Energy and Chemical Equilibrium 498 Electrochemical Measurement of $\Delta G^{\circ}$ and $\Delta S^{\circ}$ 502 Kelvin and the Age of the Earth 505 Problems 506

18.	THE	NONMETALS 512
	18.1 18.2 18.3 18.4 18.5 18.6 18.7 18.8 18.9 18.10	The Group VII A Elements 513 Compounds of the Halogens 515 The Group VI A Elements 517 Compounds of the Group VI A Elements 520 The Atmosphere 525 Air Pollution 528 The Group V A Elements 530 Compounds of the Group V A Elements 532 Carbon and Silicon 538 Boron 544 Hydrogen 546 Problems 548
19.	META	LS AND METALLURGY 552
	19.1 19.2 19.3 19.4 19.5	The Metallic Bond 553  Natural Occurrence of Metals 557  Metallurgy: Preliminary Treatment of Ores 558  Metallurgy: Reduction 560  Metallurgy: Refining 565  Earths 567  Problems 568
20.	СОМЕ	PLEX COMPOUNDS 570
	20.1 20.2 20.3 20.4	Structure 571  Nomenclature 576  Isomerism 577  The Bonding in Complexes 581  The Arrangement of Atoms in Space 591  Problems 592
21.	ORGA	ANIC CHEMISTRY 595
	21.1 21.2 21.3 21.4 21.5 21.6 21.7 21.8	The Alkanes 596 The Alkenes 601 The Alkynes 603 Aromatic Hydrocarbons 604 Reactions of the Hydrocarbons 607 Alcohols and Ethers 611 Carbonyl Compounds 616 Carboxylic Acids and Esters 619

21.9 Amines and Amides

	21.10	Polymers 624 The Time Or the Person 627 Problems 628	
22.	ВІОСН	HEMISTRY 632	
	22.4	Fats and Oils 641 Nucleic Acids 643 Enzymes 649	
23.	NUCL	EAR CHEMISTRY 656	
	23.1 23.2 23.3 23.4 23.5 23.6 23.7	The Nucleus 657 Radioactivity 660 Rate of Radioactive Decay 665 Radioactive Disintegration Series 669 Nuclear Reactions 670 Nuclear Fission and Fusion 674 Uses of Isotopes 677 Were the Alchemists Fakers? 680 Problems 681	
APP	ENDIX	A INTERNATIONAL SYSTEM OF UNITS (SI)	85
		SI Base Units 685 SI Supplementary Units 685 SI Prefixes 685	
APP	ENDIX	B VALUES OF SOME CONSTANTS AND CONVERSION FACTORS 687	
		Physical Constants 687 Conversion Factors 688	
APP	ENDIX	C NOTES ON MATHEMATICAL OPERATIONS	689
		Exponents 689 Scientific Notation 690 Logarithms 691 Quadratic equations 692	

622

APPENDIX D LOGARITHMS 694

APPENDIX E STANDARD ELECTRODE POTENTIALS AT 25°C 696

A1 23 C 030

Acid Solution 696
Alkaline Solution 698

APPENDIX F EQUILIBRIUM CONSTANTS AT 25°C 699

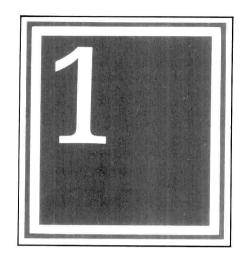
Ionization Constants 699 Solubility Products 700

APPENDIX G ANSWERS TO SELECTED NUMERICAL

PROBLEMS 702

INDEX 705

## Chapter



### Introduction

Until the early years of the nineteenth century, the tendency to specialize in a particular branch of the sciences was not strong. Scientists commonly followed their interests no matter where they led. John Dalton (1766–1844) is best known for his atomic theory. But the scientific interests of Dalton ranged widely and included topics in botany, meteorology, chemistry, physiology, and physics.

As scientific knowledge grew, scientific specialization increased. In the first half of the nineteenth century, such specialization became the norm. Some older scientists resisted the change. Michael Faraday (1791–1867), whose major accomplishments are in the chemistry of electrolysis and the physics of electricity and magnetism, refused to be called a physicist, a chemist, or any other kind of -ist; he regarded himself as a natural philosopher.

By the beginning of the twentieth century, science had become highly organized. The interests of the various branches of science, however, fre-

1

quently overlap. Ernest Rutherford (1871–1937), who is noted for his investigations into the nature of radioactive decay and the nuclear structure of the atom, considered himself to be a physicist. Rutherford, a man with a keen sense of humor, once wrote to a chemist friend that the authors of some articles that were critical of Rutherford's work were "damned fools, whom I think must once have been chemists."

In 1908, Rutherford, who was then a professor of physics at the University of Manchester, was awarded a Nobel prize. The prize was awarded, however, in chemistry, not physics! When the awards were presented, a banquet was given in Stockholm in honor of the prize winners. At the banquet, Rutherford made a speech in which he said that he had observed many transformations in his scientific work, but not one was as rapid as his own transformation from physicist to chemist.

The boundaries of the various branches of science are indistinct. The interests of the branches coincide at times, and they share common scientific concepts and methods. A precise definition of chemistry, therefore, is impossible.

Nevertheless, there is a common, if somewhat vague, understanding of what chemistry includes. Chemistry is usually defined as the science that deals with the composition, properties, and transformations of matter. Since matter is anything that occupies space and has mass, the scope of chemistry is enormous. This book should provide an introduction to chemistry and its unifying principles.

### 1.1 THE DEVELOPMENT OF MODERN CHEMISTRY

Modern chemistry, which emerged late in the eighteenth century, took hundreds of years to develop. The story of its development can be divided roughly into five periods.

 Practical arts (--- to 600 BC) The production of metals from ores, the manufacture of pottery, brewing, baking, and the preparation of medicines, dyes, and drugs are ancient arts. Archaeological evidence proves that the inhabitants of ancient Egypt and Mesopotamia were skilled in these crafts, but how and when they developed is not known.

These arts, which are chemical processes, became highly developed during this period. The development, however, was *empirical*, that is, based on practical experience alone without reference to underlying chemical principles. The Egyptian craftsman knew how to obtain copper by heating malachite ore with charcoal. He did not know, nor did he seek to know, why his process worked and what actually occurred in the fire.

- 2. Greek (600 BC to 300 BC) The philosophical aspect (or theoretical aspect) of chemistry began in classical Greece about 600 BC. The foundation of Greek science was the search for principles through which an understanding of nature could be obtained. Two theories of the Greeks became very important in the centuries that followed.
  - a. A concept that all substances are composed of four elements (earth, air, fire, and water) in various proportions originated with Greek philosophers of this period.
  - b. A theory that matter consists of separate and distinct units called atoms was proposed by Leucippus in the fifth century BC.

Plato proposed that the atoms of one element differ in shape from the atoms of another. Furthermore, he believed that atoms of one element could be changed (or transmuted) into atoms of another by changing the shape of the atoms.

The concept of transmutation is also found in Aristotle's theories. Aristotle (who did not believe in the existence of atoms) proposed that the elements, and therefore all substances, are composed of the same primary matter and differ only in the forms that this primary matter assumes. To Aristotle, the form included not only the shape but also the qualities (such as color and hardness) that distinguish one substance from others. He proposed that changes in form constantly occur in nature and that all material things (animate and inanimate) grow and develop from immature forms to adult forms. (Throughout the middle ages, men believed that minerals could grow and that mines would be replenished after minerals were removed from them.)

3. Alchemy (300 BC to 1650 AD) The philosophical tradition of ancient Greece and the craft tradition of ancient Egypt met in Alexandria, Egypt (the city founded by Alexander the Great in 331 BC), and alchemy was the result of the union. The early alchemists used Egyptian techniques for the handling of materials to investigate theories concerned with the nature of matter. Books written in Alexandria (the oldest known works on chemical topics) contain diagrams of chemical apparatus and descriptions of many laboratory operations, for example, distillation, crystallization, and sublimation.

The philosophical content of alchemy incorporated elements of astrology and mysticism into the theories of the earlier Greeks. A dominant interest of the alchemists was the transmutation of base metals, such as iron or lead, into the noble metal, gold. They believed that a metal could be changed by changing its qualities (notably its color) and that such changes occur in nature - that metals strive for the perfection represented by gold. Furthermore, the alchemists believed that these changes could be brought about by means of a very small