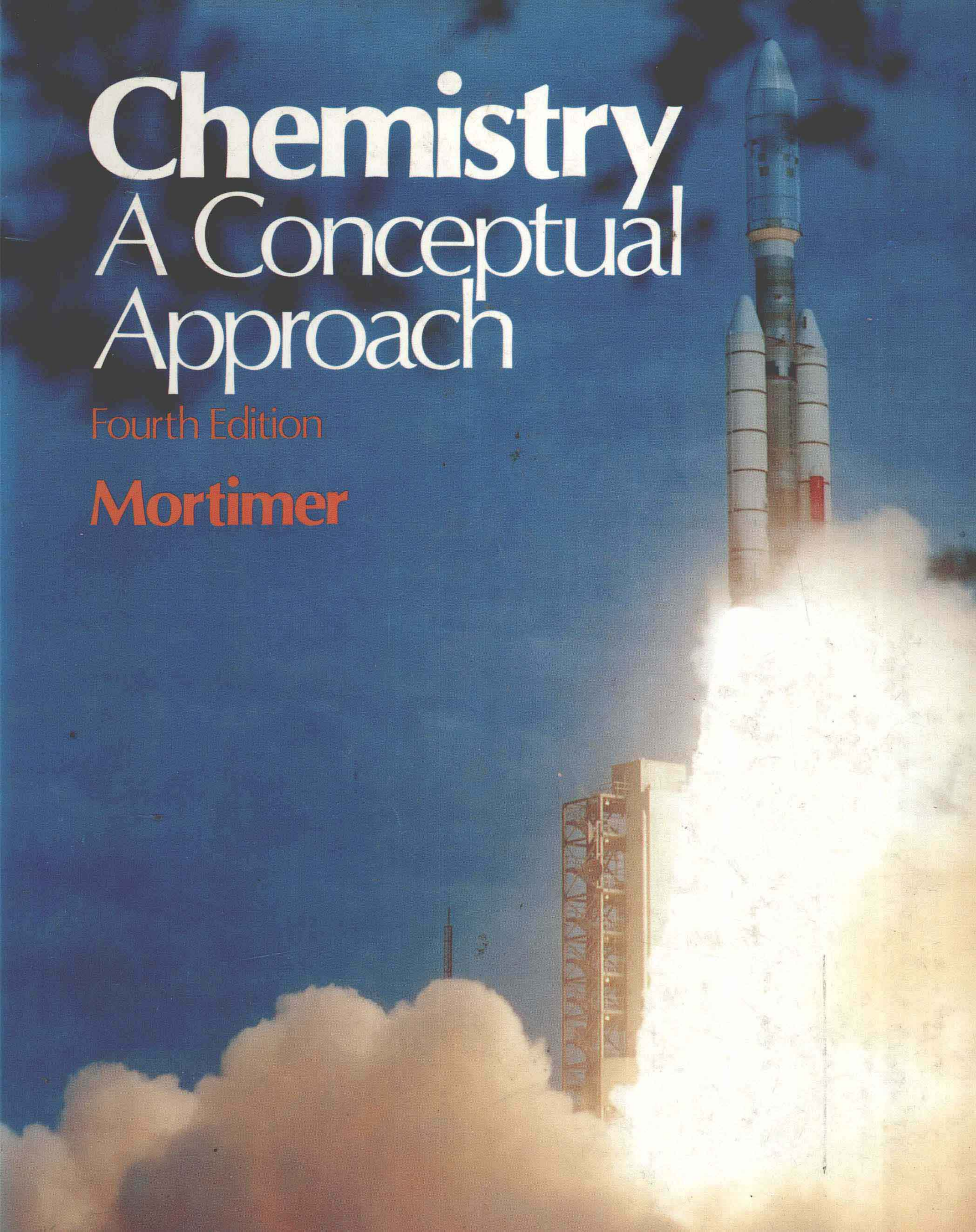
Chemistry
A Conceptual Approach

Fourth Edition

Mortimer



CHEMISTRY

A Conceptual Approach

FOURTH EDITION

Charles E. Mortimer

MUHLENBERG COLLEGE

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Preface

The philosophy underlying CHEMISTRY: A CONCEPTUAL APPROACH has stood the test of twelve years of classroom use. Beginning college students can attain a true understanding of chemical principles with the help of a text whose approach is to explain chemistry, not just to present chemical facts. With each successive edition, I have renewed and strengthened my commitment to provide students with just such a text. Thus, the special character that distinguishes this FOURTH EDITION from previous ones is really an expression of my original goal to explain each concept as fully as necessary for understanding, simplifying where needed, but never distorting.

The special character to which I refer reflects a development of my thinking regarding the needs of today's students. My own experience in teaching freshman chemistry, as well as the teaching experience of many users of my book who have kindly sent me their suggestions, convinced me that this revision should have as its primary goal to make this book more than ever a source of help as well as of information. In past editions, I have concentrated on improving the text's clarity and precision. This time, I have, in addition, concentrated on improving another aspect: helpfulness. I have reexamined every statement in the text and constantly asked myself, "Can I give the student more help in understanding this point?" The result of this long and painstaking process is the most student-oriented edition of CHEMISTRY: A CONCEPTUAL APPROACH.

This effort to help the student more than ever has resulted in some important changes. The treatment of Chemical Kinetics is entirely new. The new chapter starts by defining rate in terms of change in concentration with respect to time and develops the relationship between concentration and reaction rates. Thus the student is introduced to kinetics by way of easily visualized, experimentally based concepts before the more abstract topics of molecular collisions and temperature effects are taken up.

Many changes have made the book more helpful. The Stoichiometry chapter now takes into account the need that many students have for help in problem solving. The new chapter explains the mole concept much more carefully. More detailed directions for working out problems are given throughout.

In the Chemical Bonding chapter, students will benefit from a new section giving step-by-step directions for drawing Lewis dot structures. I have reorganized the chapter on Molecular Geometry by treating VSEPR theory before taking up hybrid orbitals. This arrangement makes it much easier for the student to understand the need for hybridization. In certain places, I have deleted unnecessary rigor. For example, by simplifying the treatment of Bohr's atomic theory, I have removed what for some students was an early stumbling block. The new, expanded introductory chapter prepares the student better for the quantitative study of chemistry by explaining the basics of chemical calculations and reinforcing the explanation with a set of problems. The changes that have been made in these early chapters are of particular importance. For many students, the introductory college chemistry course is the first rigorous exposure to a quantitative science, and they need help in adjusting early in the course. This edition gives much more of this kind of help, without in any way "watering down" the content.

The problem sets have been revised. Over 1100 problems are now included. For the first time, problems are grouped into sections and are labeled according to the chapter sections to which they correspond. Problems that are particularly challenging are marked with an asterisk.

The basic organization of the book has proved workable and has been retained. To be useful to a large number of instructors, a textbook must be readily adaptable to many different course syllabi. This edition continues to have this flexibility. Many users of this book prefer to start the course with stoichiometry (Chapter 5), and some incorporate topics from nuclear chemistry (Chapter 21) into the treatment of atomic structure (Chapter 2).

The growing acceptance of the International System of Units (SI) makes it important that the scientists, engineers, and technicians of the future use this official metric system in their scientific education. For the most part, the units used in this edition conform to the standards formulated by the International Bureau of Weights and Measures and adopted by the National Bureau of Standards. In some cases, units that are not SI units have been retained. For example, the standard atmosphere is used as the unit of pressure instead of the SI unit, the pascal; the liter is used rather than the SI designation for the same volume, the cubic decimeter. Both of these usages are currently acceptable to the International Bureau of Weights and Measures.

Supplementary study aids have become increasingly popular in introductory chemistry courses. I am delighted that in this edition I have once more the collaboration of Donald and Louise Shive as authors of the new *Student Self-Study Guide*. The earlier edition of this Guide proved extremely successful and helped many thousands of students to improve their study habits and develop their problem-solving skills. A *Solutions Manual* provides worked-out solutions for mathematical problems in the text. An *Answer Booklet* gives the answers to all mathematical problems (the text itself gives answers to selected problems in Appendix G).

I sincerely thank the following persons for their suggestions and comments: Robert C. Brasted, University of Minnesota; S. A. Carrano, Fairfield University; Maxwell L. Eidinoff, Queens College; David W. Herlocker, Western Maryland College; Frank A. Kanda, Syracuse University; Robert Kren, University of Michigan–Flint; Betty Leventhal, University of Toronto; George Moriber, Brooklyn College; W. D. Perry, Auburn University; J. W. Viers, Virginia Polytechnic Institute and State University.

I will welcome suggestions for improvements of this edition.

Charles E. Mortimer

Contents

Introduction

Chemistry may be defined as the science that is concerned with the characterization, composition, and transformations of matter. This definition, however, is far from adequate. The interplay between the branches of modern science has caused the boundaries between them to become so vague that it is almost impossible to stake out a field and say "this is chemistry." Not only do the interests of scientific fields overlap, but concepts and methods find universal application. Moreover, this definition fails to convey the spirit of chemistry, for it, like all science, is a vital, growing enterprise, not an accumulation of knowledge. It is self-generating; the very nature of each new chemical concept stimulates fresh observation and experimentation that lead to progressive refinement as well as to the development of other concepts. In the light of scientific growth, it is not surprising that a given scientific pursuit frequently crosses artificial, human-imposed boundaries.

Nevertheless, there is a common, if somewhat vague, understanding of the province of chemistry, and we must return to our preliminary definition; a fuller understanding should emerge as this book unfolds. Chemistry is concerned with the composition and the structure of substances and with the forces that hold the structures together. The physical properties of substances are studied since they provide clues for structural determinations, serve as a basis for identification and classification, and indicate possible uses for specific materials. The focus of chemistry, however, is probably the chemical reaction. The interest of chemistry extends to every conceivable aspect of these transformations and includes such considerations as: detailed descriptions of how and at what rates reactions proceed, the conditions required to bring about desired changes and to prevent undesired changes, the energy effects that accompany chemical changes, the syntheses of substances that occur in nature and those that have no natural counterparts, and the quantitative mass relations between the materials involved in chemical changes.

1.1 Matter

Science interprets nature in terms of energy (discussed in Section 1.3) and matter. **Matter**, the material of which the universe is composed, may be defined as anything that occupies space and has mass. **Mass** is a measure of quantity of matter. A body that is not being acted upon by some external force has a tendency to remain at rest or, when it is in motion, to continue in uniform motion in the same direction. This property is known as **inertia**. The mass of a body is proportional to the inertia of the body.

The mass of a body is invariable; the weight of a body is not. **Weight** is the gravitational force of attraction exerted by the earth on a body; the weight of a given body varies with the distance of that body from the center of the earth. The weight of a body is directly proportional to its mass as well as to the earth's gravitational attraction. At any given place, therefore, two objects of equal mass have equal weights.

The ancient Greeks originated the concept that all matter is composed of a limited number of simple substances called **elements**. The Greeks assumed that all terrestrial matter is derived from four elements: *earth, air, fire*, and *water*. Since heavenly bodies were thought to be perfect and unchangeable, celestial matter was assumed to be composed of a different element, which later came to be known as *quintessence* (from Latin, meaning *fifth element*). This Greek theory dominated scientific thought for centuries.

In 1661, Robert Boyle proposed an essentially modern definition of an element in his book *The Sceptical Chymist*:

I now mean by Elements . . . certain Primitive and Simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the Ingredients of which all those call'd perfectly mixt Bodies are immediately compounded, and into which they are ultimately resolved.

Boyle made no attempt to identify specific substances as elements. He did, however, emphasize, that the proof of the existence of elements, as well as the identification of them, rested on chemical experimentation.

Boyle's concept of a chemical element was firmly established by Antoine Lavoisier in the following century. Lavoisier accepted a substance as an element if it could not be decomposed into simpler substances. Furthermore, he showed that a compound is produced by the union of elements. Lavoisier correctly identified 23 elements (although he incorrectly included light, heat, and several simple compounds in his list).

At the present time, 106 elements are known. Of these, 85 have been isolated from natural sources; the remainder have been prepared by nuclear reactions (Section 21.5).

The 15 most abundant elements in the earth's crust, bodies of water, and atmosphere are listed in Table 1.1. This classification includes those parts of the universe from which we can obtain the elements. The earth consists of a core (which is probably composed of iron and nickel) surrounded successively by a mantle and a thin crust. The crust is about 20 to 40 miles thick and constitutes only about 1% of the earth's mass.

If the entire earth were considered, a list different from that of Table 1.1 would result, and the most abundant element would be iron. On the other hand, the most abundant element in the universe as a whole is hydrogen, which is thought to constitute about 75% of the total mass of the universe.

Whether an element finds wide commercial use depends not only upon its abundance but also upon its accessibility. Some familiar elements (such as copper, tin, and lead) are not particularly abundant but are found in nature in deposits of ores from which they can be obtained readily. Other elements that are more abundant (such as titanium, rubidium, and zirconium) are not widely used because either their ores are widespread in nature or the extraction of the elements from their ores is difficult or expensive.

Compounds are substances that are composed of two or more elements in fixed proportions. The **law of definite proportions** (first proposed by Joseph Proust in 1799) states that a pure compound always consists of

TABLE 1.1 Abundance of the elements (earth's crust, bodies of water, and atmosphere)

RANK	ELEMENT	SYMBOL	PERCENT BY MASS
1	oxygen	O	49.2
2	silicon	Si	25.7
3	aluminum	Al	7.5
4	iron	Fe	4.7
5	calcium	Ca	3.4
6	sodium	Na	2.6
7	potassium	K	2.4
8	magnesium	Mg	1.9
9	hydrogen	H	0.9
10	titanium	Ti	0.6
11	chlorine	Cl	0.2
12	phosphorus	P	0.1
13	manganese	Mn	0.1
14	carbon	C	0.09
15	sulfur	S	0.05
	all others		0.56