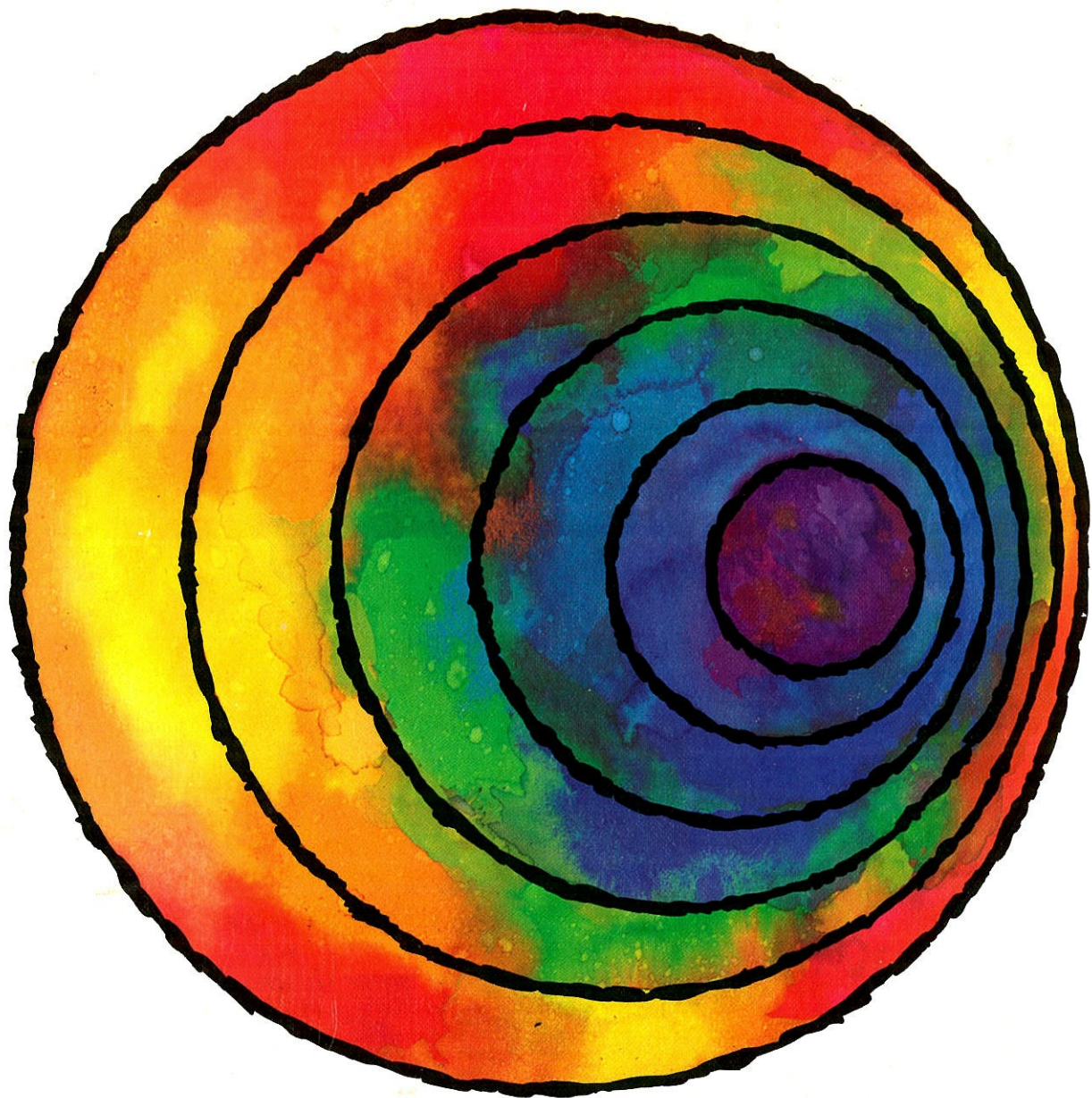


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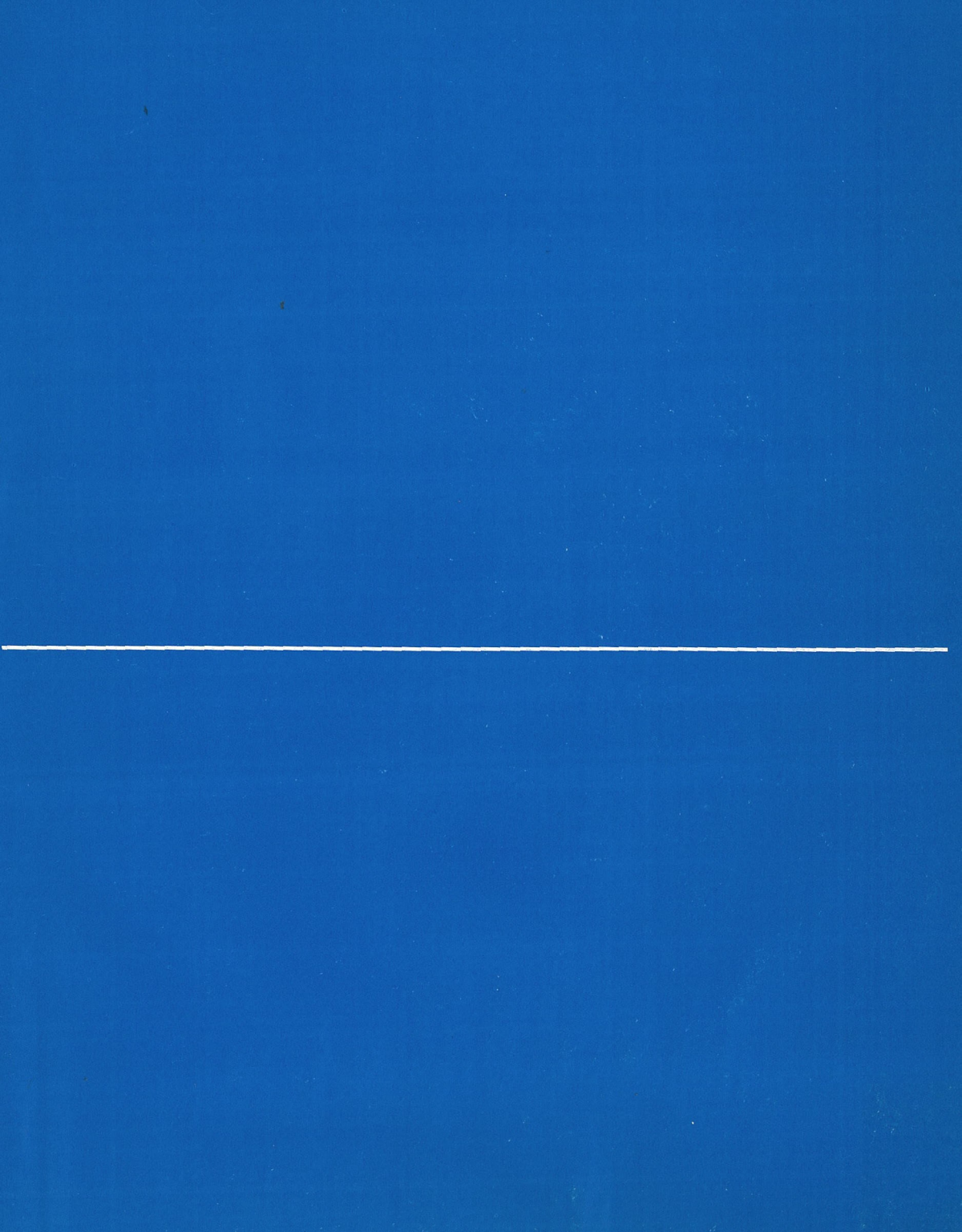


**CHEMICAL
PRINCIPLES**

THIRD EDITION

Chemical Principles

Third Edition



Chemical Principles

Third Edition

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Preface

This edition of *Chemical Principles*, like its predecessors, is designed to be used in a general university chemistry course which must provide both an overview of chemistry for nonspecialists and a sound foundation for later study for science or chemistry majors. Hence there are several survey chapters introducing different areas of chemistry, including inorganic, nuclear, organic, and biochemistry, and an attempt is made throughout the book to place chemistry in its historical and cultural setting. At the same time, the quantitative aspects of chemistry are presented in a manner consistent with their importance, in a way that will make it easy to build upon them in later courses.

This is the first complete revision of *Chemical Principles* since the first edition was published in 1969. The authors have rethought and replanned the entire book, especially the first thirteen chapters, trying to make it a better pedagogical tool without losing the special viewpoints and flavor that made the earlier editions so successful. The history and the anecdotal asides that help to make the subject palatable have been retained, but they have been better segregated from the factual material for which a student will be held responsible.

THIRD EDITION REORGANIZATION AND LEVEL

The basic material of the first six chapters has been rearranged into a more logical and more easily absorbed order. These chapters, although not formally set off from the rest of the book, actually make up one study unit on quantitative chemistry: atoms and moles, stoichiometry, heats of reaction, gas laws and the kinetic theory, chemical equilibrium and acid-base equilibrium. They have been rethought and rewritten as a block by one of the authors, with more in-text examples and new end-of-chapter problems. The mole concept, balancing of equations, and stoichiometry in general now appear in the first two chapters where they will be most useful as preparation for the laboratory. At the same time, stoichiometry, which can be one of the duller topics in chemistry, is presented along with heats of reaction as two illustrations of a fundamental physical principle: the conservation of mass and energy. A long but essential chapter on equilibrium has been broken down into two more accessible chapters: one on principles of equilibrium, and the second on acid-base equilibria in aqueous solutions. It is hoped that these five chapters will give the student a solid foundation in vocabulary and problem-solving skills without which further progress in chemistry is impossible. After a solid dose of “basic training,” Chapter 6 provides a little historical relief, with the story of how we arrived at the knowledge contained in the first five chapters.

Chapters 7 through 14 make up a second study unit on atomic structure, chemical periodicity, and chemical structure and bonding. This too has been carefully reconsidered and revised as a whole by a single author, thus the Third Edition revision helps unify the text. In response to user requests, the material on chemical periodicity and inorganic oxidation-reduction chemistry has been unified in Chapters 9 and 10.

The treatment of molecular orbitals and chemical bonding in the Second Edition had been liked by most users, but had been considered a little too high-level and difficult to get into. Now we have divided this material into two chapters, Chapter 12 on principles of the molecular orbital theory and applications to simple diatomic molecules, and Chapter 13 on polyatomic molecules and molecular spectroscopy. We have also provided a new Chapter 11 as an introduction to bonding theories, as far as one can go with electron pairing and electron pair repulsion short of quantum mechanics. The Valence Shell Electron Pair Repulsion (VSEPR) theory, which has been surprisingly neglected in this country, provides an intuitively simple and nonmathematical way of explaining the shapes of molecules. These three chapters plus the subsequent one on bonding in solids and liquids will give the student a secure grounding in the principles of bonding, molecular structure, and spectroscopy.

Chapters 15–19 make up a third study unit on thermodynamics and equilibrium. The material on the first and second laws is essentially the

same as in previous editions, but has been divided into two more digestible chapters. The statistical description of entropy has been simplified. A new chapter has been added on phase equilibria, Chapter 18. Since this is quantitative material and frequently is difficult for the beginning student, we have significantly increased the number of worked examples in the text, revised the chapter-end problems, and added new ones.

The last four chapters cover special topics that may not be included in all introductory courses: coordination chemistry, organic and biochemistry, chemical kinetics, and nuclear chemistry. After much agonized debate about principles and pedagogy, we finally decided to place these chapters at the end, where they can be used or not as the individual instructor chooses. (We hope that they will all be used.) They have all been revised and rewritten where necessary, especially the chapter on organic and biochemistry.

PEDAGOGY

Each chapter begins with a list of key concepts. This provides students with a brief overview of the chapter material, both before they start the chapter and after they finish, as a quick check on their retention of key ideas. Throughout the text of each chapter, we have concentrated on expanding the solutions to problems worked in the chapter. Problem examples relevant to each concept are presented, and solutions proceed step by step. Chapters conclude with a summary in which key terms, introduced in the chapter, are called out in boldface type. Each summary is followed by 20 to 40 self-study questions and a series of problems arranged by subject.

The Third Edition contains over 100 more end-of-chapter problems than its predecessor. Moreover, new problems have been written to parallel the development of each chapter, and all problems have been titled and grouped by subject matter. Following the more quantitative chapters, the problems have been paired, with first an odd-numbered problem and then an even-numbered problem testing the same skills. Answers to the odd-numbered problems are given in Appendix 6. Hence the even-numbered problems can be assigned as homework, and if the students cannot work a problem, they can try the preceding odd-numbered problem first as practice, checking their solution against the Appendix.

SI UNITS

After considerable debate, the authors have decided to “bite the bullet” with regard to SI units. There is a traditional attachment to the calorie as the unit of heat, and it will be a long time before the calorie is eliminated

from the scientific literature. Nevertheless, the sheer logic of SI units, their ease of use, and the way that they make obvious the connection between heat, work, and energy, all argue for a changeover now to what will be the standard units of the next generation of scientists. SI units and the logic behind them are explained in Appendix 1. The calorie is mentioned in this book because every scientist will still have to know what a calorie is, but all calculations are carried out in joules. Thermodynamic tables in Appendix 3 and elsewhere in the book have all been converted to joules. At the same time, we have refused to become overly doctrinaire and throw the baby out with the bathwater. The standard atmosphere (101,325 pascals) has been considered to be as reasonable a derived unit in gas law calculations as is the electronic charge (0.16022 attocoulomb) for expressing the charge on an ion. The careful reader will even discover angstrom units lurking here and there, and we offer no apologies. Our goal has been to train intelligent scientists and laypeople who can read, understand, and use the literature.

SUPPLEMENTS

All of the supplemental aides to the Third Edition have been revised by their authors on the basis of the new manuscript: *Programmed Reviews* by Lassila, Barrow, Kenney, Litle, and Thompson; *Relevant Problems* by Butler and Grosser; a new *Study Guide* covering the entire text by Tom Taylor; and an *Instructors' Manual* by Ben Chastain. Some or all of these may be useful adjuncts to the main textbook in your course.

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As before, our goals in writing *Chemical Principles* have been to make the material (a) correct, (b) clear, and (c) interesting, in that order. Your response to the first two editions tells us that they were reasonably satisfactory in this respect, and we hope that the Third Edition will prove to be even better.

Richard E. Dickerson

Harry B. Gray

Gilbert P. Haight, Jr.

October 1978

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