University Chemistry

FOURTH EDITION

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Preface

Bruce Mahan wrote the first edition of his *University Chemistry* for use in a course with a selected group of first-year Berkeley students who were well prepared in mathematics. This fourth edition continues in the tradition of previous editions; it is intellectually challenging and it uses mathematical reasoning where it is appropriate to the subject at hand. Although commonly described as a classic, previous editions of *University Chemistry* did have room for improvement. They contained very few problems, and lacked worked-out examples in some critical areas. There were few student aids such as key words, and little attention was paid to units and dimensions. Several third edition chapters had not been revised since the first edition appeared. Our revision scheme was based upon teaching experience with the book in a large number of schools. Part of this experience involved selected students in small courses; part involved courses with a thousand students. Some of the material used in the revision has been class-tested by Berkeley students over the past few years. Major changes are summarized in the following paragraphs.

Problems New problems have been added, doubling the total number, and particular attention has been given to including problems with a range of difficulty. The problems are classified according to the principles involved, and answers to about one half of the problems are given at the back of the book.

Units SI units are used in the text, and some popular units such as Angstroms and Debyes are also shown. Energies are uniformly given in joules, except where atomic units (hartrees) or electron volts are much more convenient to use.

Stoichiometry Mahan's emphasis in Chapter 1 on moles as the basis of stoichiometric calculations has been retained, but more emphasis is given to units and dimensions. Stoichiometry is treated as a problem in algebraic relationships, because this method properly unites stoichiometric and equilibrium calculations. There is a short introduction to conversion factors in Appendix A, and we show how they can be used in stoichiometric calculations. Solution stoichiometry is now covered by examples in Chapter 3 on solutions and in Chapter 7 on oxidation-reduction.

Gases, Liquids, and Solutions Chapter 2 on gases remains a fundamental treatment of kinetic theory, of molecular size, and of molecular interaction. The liquifaction of gases is now illustrated along with gas nonideality. Transport properties are presented on a more practical level. The chapter on solids is now at the end of the text along with other special topic chapters. Chapter 3 on liquids and solutions, again, places more emphasis on the practical properties such as the vapor pressure of water and the types of solutions; it now includes a discussion of electrolytes and of solubility rules for salts in aqueous solution. Chapter 3 introduces students to the thermodynamic concepts of enthalpy and entropy, as before, and it also now considers activity and standard states for solutes using Henry's law.

Chemical Equilibrium While equilibrium as a concept is introduced through phase equilibria in Chapter 3 on liquids, it is formally introduced in Chapter 4. Equilibrium quotients and equilibrium constants are both introduced in Chapter 4 together with the forever useful Le Chatelier's principle, and we show that free energy is the controlling factor in chemical equilibria. Ionic equilibria are treated in the heavily revised Chapter 5 using net reactions, and the charge balance and mass balance relations. Nonideality for ionic solutions is discussed both in Chapters 4 and 5, but of course, most calculations are done using molarity and ideal solution assumptions.

Bonding and Atomic Structure Chemical bonding is first discussed in a new Chapter 6, and then in revised Chapters 11 and 12. Our new chapter shows only those bonding theories that do not depend upon wavefunctions and quantum mechanics. These include valence, Lewis electron-dot diagrams, VSEPR, dipole moments, molecular structure, bond energies, potential energy diagrams, and van der Waals molecules. The concepts of bonding, nonbonding, and antibonding are also introduced. A revised Chapter 10 treats atomic structure including spectroscopy, atomic wavefunctions and configurations, quantum theory, and the Hartree-Fock method for including electron-electron repulsion. As a result, Chapter 11 includes both ionic and covalent bonds similar to the previous edition, and now also includes some molecular orbital theory along with illustrations of modern Hartree-Fock molecular orbital calculations on some simple molecules. The treatment of molecular orbitals using the Hückel approximation has been expanded and moved to the end of Chapter 11. This leaves Chapter 12 as a

systematic treatment of diatomic and triatomic molecules using qualitative molecular orbital theory. Although most courses would cover the bonding in Chapter 6, some teachers might not devote the time to bonding that is necessary to finish all of Chapters 11 and 12.

Electrochemistry, Thermodynamics and Chemical Kinetics   Although these were always strong chapters, some changes have been made. All the tables have been revised, and information has been included on the use of volt-equivalents in Chapter 7 on electrochemistry and on partial molar quantities for solution thermodynamics in Chapter 8. Chapter 9 on chemical kinetics includes a formal introduction to activated complex theory. It also makes early reference to experimental results, to better illustrate experimental kinetic techniques, and shows a modern reaction surface.

Periodic Table and Inorganic Chemistry   These extensive chapters have been modernized, but they still retain the use of thermodynamic reasoning to help explain inorganic chemistry. The newly proposed notation for the periodic table is presented, but the traditional roman numerals are still utilized. All the tabular information has been revised, and ligand field theories are now presented early in Chapter 16 on transition metals so that they can be taught separately. An effort has been made to make descriptive chemistry more interesting to students.

Special Topics   The book concludes with a series of chapters on special topics including: organic chemistry, biochemistry, nuclear chemistry, and solid state chemistry. All these chapters have been modernized and particular attention has been paid to the meshing of our organic chapter with the nomenclature used in current organic texts. Examples have been added to the nuclear chapter, illustrating both nuclear energy and half-life calculations.

Appendix   Conversion factor methods and their use with physical constants and chemical reactions are given in Appendix A. SI is explained in Appendix B, and Coulomb's law for point charges and for uniformly charged spheres is shown in Appendix C.

Data   Particular care has been taken in the selection of data in the tables. For equilibrium constants we mainly have used the values selected by Martell and Smith. For thermodynamic data we have used the recently published NBS tables, and whenever possible we also used them to calculate our standard electrode potentials. For the physical properties of the elements we have used Hultgren *et al*. This careful choice of data has two purposes: first, to let students know that there are good and poor sources of data; second, to create a text that can be used as a reference by a student for a number of years. For this same reason, we have also carefully selected the additional reading at the end of each chapter.

Supplement   The study guide for this text is authored by Barbara Sawrey of the University of California, San Diego. The study guide starts with a Chapter Zero to

help those students who have little or no previous experience in chemistry, and then continues with discussions of the material in each chapter along with additional problems and their answers.

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Part of the revision was done while I was residing in London through the courtesy of Sylvia Myers and Germaine Greer. A good deal of this revision was done on the basis of library work, and I would like to thank the staff of the Science Museum Library in London, and Dana Roth of the California Institute of Technology. Berkeley graduate students who helped with the answers given to the problems are David Eisenberg, Maria Madigan, Richard Ollman, David Shykind, and Cris Wilisch. I would also like to thank my typists, Peter Ray and Cordelle Yoder.

This revision was completed by the Addison-Wesley Publishing Company, and I would particularly like to thank my editors, Bob Rogers and Debra Hunter. The production editor was Marion Howe, and my outstanding copy editor was Susan Middleton.

Bruce Mahan died in 1982 after a long bout with amyotropic lateral sclerosis (ALS). He will be remembered by the many students who used his top-quality textbooks, and we can only hope that perhaps one of them will discover a cure for the affliction that struck him in the prime of life.

Berkeley, California   Rollie J. Myers

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