Chemical Principles

Third Edition
Sponsoring editor: Mary Forkner
Production editor: Betsey Rhame
Cover designer: Stephen Osborn
Book designer: Marjorie Spiegelman


Library of Congress Cataloging in Publication Data
Dickerson, Richard Earl.
Chemical principles.
   Includes bibliographies and index.
   1. Chemistry. I. Gray, Harry B., joint author. II. Haight, Gilbert Pierce, joint author. III. Title.
QD312.D52 1979 540 77-87336
ISBN 0-8053-2398-8

Copyright © 1979 by The Benjamin/Cummings Publishing Company, Inc.
Philippine's copyright 1979 by The Benjamin/Cummings Publishing Company, Inc.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher. Printed in the United States of America.
Published simultaneously in Canada.
Library of Congress Catalog Card No. 77-87336

ISBN 0-8053-2398-8
ABCDEFGHIJ-DO-782109

The Benjamin/Cummings Publishing Company, Inc.
2727 Sand Hill Road
Menlo Park, California 94025
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 dullest 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, Little, 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.

ACKNOWLEDGMENTS

We are grateful to the many reviewers who read the Third Edition revision with care: Marcetta Darenbourg, Leo E. Kallan, Curtis B. Anderson, Paul M. Treichel, Jean Lassila, George Miller, Caroline Eastman, Lawrence E. Wilkins, Paul Hunter, and Peter Linde. We would like to thank Ben Chastain and Mildred Johnson for yeoman service in reading every line of the new edition, and offering detailed suggestions based on their experience with the Second Edition. Gloria Joyce deserves our thanks for reducing some of our more convoluted prose to comprehensibility. Mary Forkner, as sponsoring editor, provided us with feedback from reviewers and users that led to the present book. Betsey Rhame carried out the remarkable task of producing a book that is not only complete and attractive, but right on schedule. Lastly, we offer belated thanks and recognition to James Hall, without whose steady hand there would not even have been a First Edition, let alone a Third.
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
# Table of Contents

## Chapter 1  
**Atoms, Molecules, and Ions**

1.1 The Structure of Atoms  
2  
1.2 Isotopes  
4  
1.3 Molecules  
9  
1.4 Forces Between Molecules  
12  
1.5 Molecules and Moles  
15  
1.6 Ions  
17  
  *Melting Points and Boiling Points of Salts*  
24  
1.7 Ions in Solution  
25  
1.8 Gaseous Ions  
33

## Chapter 2  
**Conservation of Mass and Energy**

2.1 Atomic Weights, Molecular Weights, and Moles  
49  
2.2 Chemical Analyses:  
  *Percent Composition and Empirical Formulas*  
49  
2.3 Chemical Equations  
55  
2.4 Calculations of Reaction Yields  
58  
2.5 Solutions as Chemical Reagents  
60  
  *Acid–Base Neutralization*  
64  
  *Acid–Base Titration*  
68
2-6 Heats of Reaction: Conservation of Energy 71  
Heats of Formation 76  
2-7 Conservation Principles 78

Chapter 3  
Gas Laws and the Kinetic Theory 93
3-1 Avogadro's Law 95  
3-2 The Pressure of a Gas 95  
3-3 Boyle's Law Relating Pressure and Volume 97  
3-4 Charles' Law Relating Volume and Temperature 102  
3-5 The Combined Gas Law 105

Standard Temperature and Pressure 108  
Ideality and Nonideality 109
3-6 The Kinetic Molecular Theory of Gases 110

The Phenomenon of Pressure and Boyle's Law 112
3-7 Predictions of the Kinetic Molecular Theory 115

Molecular Size 116  
Molecular Speeds 118

Dalton's Law of Partial Pressures 119

Other Predictions of the Kinetic Molecular Theory 123
3-8 Real Gases and Deviations from the Ideal Gas Law 125

Postscript to Gas Laws and Atomic Theory 136

Chapter 4  
Will It React? An Introduction to Chemical Equilibrium 139
4-1 Spontaneous Reactions 140  
4-2 Equilibrium and the Equilibrium Constant 141  
4-3 General Form of the Equilibrium Constant 144  
4-4 Natural Atomic Weights 147  
4-5 Units and Equilibrium Constants 153
4-6 Equilibria Involving Gases with Liquids or Solids 155  
4-7 Factors Affecting Equilibrium: Le Chatelier's Principle 159

Temperature 160  
Pressure 161  
Catalysis 163

Chapter 5  
Solution Equilibria: Acids and Bases 172
5-1 Equilibria in Aqueous Solutions 173  
5-2 Ionization of Water and the pH Scale 176  
5-3 Strong and Weak Acids 180  
5-4 Strong and Weak Bases 185  
5-5 Solutions of Strong Acids and Bases:  
Neutralization and Titration 187  
Titrations and Titrations Curves 189
Chapter 6

Are Atoms Real? From Democritus to Dulong and Petit 225
6-1 The Concept of An Element 228
6-2 Compounds, Combustion, and the Conservation of Mass 229
   Phlogiston 231
   Conservation of Mass 232
6-3 Does a Compound Have a Fixed Composition? 233
   Equivalent Proportions 234
   Combining Weights 234
6-4 John Dalton and the Theory of Atoms 236
   The Greek Atomic Theory 238
   Fixed Ratios 238
   Law of Multiple Proportion 240
6-5 Equal Numbers in Equal Volumes: Gay-Lussac and Avogadro 241
   Gay-Lussac 242
   Avogadro 242
6-6 Cannizzaro and a Rational Method of
   Calculating Atomic Weights 244
6-7 Atomic Weights for the Heavy Elements: Dulong and Petit 247
6-8 Combing Capacities, “Valence,” and Oxidation Number 250
   Postscript: Joseph Priestley and Benjamin Franklin 255

Chapter 7

The Periodic Table 257
7-1 Early Classification Schemes 258
   Döbereiner's Triads 259
   Newlands' Law of Octaves 259
7-2 The Basis for Periodic Classification 261
   The Periodic Law 264
7-3 The Modern Periodic Table 266
7-4 Periodicity of Chemical Properties as Illustrated by Binary
   Hydrides and Oxides 270
Chapter 8  Quantum Theory and Atomic Structure  279
8-1 Rutherford and the Nuclear Atom  281
8-2 The Quantization of Energy  284
   The Ultraviolet Catastrophe  287
   The Photoelectric Effect  289
   The Spectrum of the Hydrogen Atom  290
8-3 Bohr’s Theory of the Hydrogen Atom  293
   Energy Levels of a General One-Electron Atom  299
   The Need for a Better Theory  300
8-4 Particles of Light and Waves of Matter  300
8-5 The Uncertainty Principle  306
8-6 Wave Equations  309
   Vibrating String  310
   Schrödinger Equation  310
8-7 The Hydrogen Atom  312
8-8 Many-Electron Atoms  321

Chapter 9  Electronic Structure and Atomic Properties  331
9-1 Buildup of Many-Electron Atoms  332
   Relative Energies of Atomic Orbitals  333
   Orbital Configurations and First Ionization Energies  335
   Electron Affinities  344
9-2 Types of Bonding  346
   Atomic Radii  347
9-3 Electronegativity  349

Chapter 10  Oxidation-Reduction and Chemical Properties  358
10-1 Oxidation Numbers  358
    Calculating Oxidation Numbers  360
10-2 Oxidation-Reduction Reactions  362
10-3 Balancing Oxidation-Reduction Equations  365
    Oxidation-Number Method  365
    Ion-Electron (Half-Reaction) Method  366
10-4 Redox Titrations  369
10-5 Oxidation and Reduction Potentials  372
10-6 Chemical Properties: The $s$-Orbital Metals  373
    Group IA. Alkali Metals: Li, Na, K, Rb, and Cs  373
    Group IIA. Alkaline Earth Metals: Be, Mg, Ca, Sr, and Ba  375
Contents

10-7 The Filling of the d Orbitals: Transition Metals 377
   The Structure of Transition-Metal Ions 378
   Oxidation Potentials 378
   Chemical Properties of Individual Groups: Sc and Ti Groups 379
   The Vanadium Group and the Colors of Ions and Complex Compounds 380
   The Chromium Group and the Chromate Ion 381
   The Manganese Group and the Permanganate Ion 382
   The Iron Triad and the Platinum Metals 383
   The Coinage Metals 384
   The Chemistry of Photography 385
   The Low-Melting Transition Metals 385
   Trends in the Transition Metals 387

10-8 The Filling of f Orbitals: Lanthanides and Actinides 387

10-9 The p-Orbital or Representative Elements 388

Chapter 11 Lewis Structures and the VSEPR Method 399
11-1 Lewis Structures 400
   Multiple Bonds 402
   Formal Charges 403
   Some Polyatomic Molecules 405
   The Ammonium Chloride Molecule 406
   Lewis Acids and Bases 407
   Bonding to Heavier Atoms 408
   Resonance Structures 410
   The Meaning of Oxidation Numbers 415

11-2 Acidity of Oxyacids 418

11-3 The VSEPR Method and Molecular Geometry 422
   Steric Numbers Greater Than Six 428
   Exceptions to the VSEPR Rules 429

Chapter 12 Diatomic Molecules 438
12-1 Molecular Orbitals 439
   Bonding in the H₂ Molecule 440
   The Pauli Buildup Process in Molecules 445

12-2 Diatomic Molecules with One Type of Atom 448
   Paramagnetism and Unpaired Electrons 452
   Buildup of Diatomic Molecules 453

12-3 Diatomic Molecules with Different Atoms 458
   Hydrogen Fluoride and Potassium Chloride 458
   Dipole Moments 462
   A General AB Type Diatomic Molecule 463
Chapter 13  Polyatomic Molecules
13-1 Localized Molecular Orbitals for BeH₂, BH₃, and CH₄  476
13-2 Hydrogen in Bridge Bonds  481
13-3 Localized-Molecular-Orbital Theory for Molecules with Lone Electron Pairs  483
13-4 Single and Multiple Bonds in Carbon Compounds  488
13-5 Benzene and Delocalized Orbitals  494
13-6 Polar and Nonpolar Polyatomic Molecules  500
13-7 Molecular Spectroscopy  503

Chapter 14  Bonding in Solids and Liquids
14-1 Elemental Molecular Solids  522
14-2 Ionic Solids  528
14-3 Molecular Solids and Liquids  530
   Van der Waals Forces  530
   Polar Molecules and Hydrogen Bonds  535
   Polar Molecules as Solvents  540
14-4 Metals  541
   Electronic Bands in Metals  542
14-5 Nonmetallic Network Solids  546
   Semiconductors  547
14-6 The Framework of the Planet: Silicate Minerals  549
   Chain Structures  550
   Sheet Structures  552
   Three-Dimensional Networks  553

Chapter 15  Energy and Enthalpy in Chemical Systems
15-1 Work, Heat, and Caloric  562
   The Cannons of Bavaria  562
   Blood, Sweat, and Gears  563
15-2 The First Law of Thermodynamics  566
   A Different View of the First Law  570
   State Functions  570
15-3 Energy, Enthalpy, and Heat Capacity  573
15-4 The First Law and Chemical Reactions  576
15-5 Bond Energies  580
   Bond Energy of a C—C Single Bond  580
   Tabulation of Bond Energies  582
   Applications of Bond-Energy Calculations  584
   The Heat of Formation of Benzene  585
   Postscript: Count Rumford versus the World  594
### Chapter 16
**Entropy, Free Energy, and Chemical Reactions**
- 16-1 Spontaneity, Reversibility, and Equilibrium 601
- 16-2 Heat, Energy, and Molecular Motion 603
- 16-3 Entropy and Disorder 605
  - *Life in a Nine-Point Universe* 607
- 16-4 Third-Law Entropies and Chemical Intuition 610
- 16-5 Free Energy and Spontaneity in Chemical Reactions 613
  - *Free Energy Changes When External Work Is Done* 618
  - *Calculations with Standard Free Energies* 619
- 16-6 Free Energy and Concentration 622
  - *General Expressions* 627

### Chapter 17
**Free Energy and Equilibrium**
- 17-1 The Properties of Equilibrium 637
  - *Stoichiometry and the Equilibrium Constant* 640
- 17-2 Reactions Involving Gases 643
  - *Experimental Measurement of Equilibrium Constants* 643
  - *Calculation of Equilibrium Constants* 644
  - *The Partial Pressure of One Component* 645
  - *Alteration of Stoichiometry* 646
  - *Extent of Reaction* 646
- 17-3 Le Chatelier’s Principle 651
  - *The Effect of Temperature* 651
- 17-4 The Anatomy of a Reaction 652

### Chapter 18
**Equilibria Involving Liquids and Solids**
- 18-1 Melting, Evaporation, and Sublimation 663
- 18-2 Free Energy of Vaporization and Vapor Pressure 666
- 18-3 The Critical Point 669
- 18-4 Phase Diagrams 672
- 18-5 Solutions and Raoults’s Law 675
- 18-6 Colligative Properties 677
  - *Vapor Pressure Lowering* 678
  - *Boiling Point Elevation* 679
  - *Freezing Point Lowering* 681
  - *Molecular Weight Determinations* 682
  - *Osmotic Pressure* 684

### Chapter 19
**Oxidation–Reduction Equilibria and Electrochemistry**
- 19-1 Harnessing Spontaneous Reactions 695
  - *Concentration Cells* 698
- 19-2 Electrochemical Cells 700
Chapter 20

Coordination Chemistry

20-1 Properties of Transition-Metal Complexes 736
   Color 736
   Isomers and Geometry 738
   Magnetic Properties 740
   Lability and Inertness 741
   Oxidation Number and Structure 743
   Influence of the Number of d Electrons 743

20-2 Nomenclature for Coordination Compounds 745
   Isomerism 748

20-3 Theories of Bonding in Coordination Complexes 749
   Electrostatic Theory 751
   Valence Bond Theory 751
   Crystal Field Theory 755
   Ligand Field (or Delocalized Molecular-Orbital) Theory 759

20-4 Tetrahedral and Square Planar Coordination 764

20-5 Equilibria Involving Complex Ions 767

Postscript: Coordination Complexes and Living Systems 777

Chapter 21

The Special Role of Carbon

21-1 The Special Talents of Carbon 788

21-2 The Chemistry of the Neighbors of Carbon 793
   Boron 794
   Nitrogen 796
   Silicon 799
   Comparison of Boron, Nitrogen, and Silicon 802

21-3 Saturated Hydrocarbons or Alkanes 803
   Reactions of Alkanes 806
21-4 Unsaturated Hydrocarbons 808
21-5 Derivatives of Hydrocarbons: Functional Groups 810
21-6 Aromatic Compounds 819
21-7 Aromatic Compounds and the Absorption of Light 823
21-8 Carbohydrates 826
    Polysaccharides 829
21-9 Proteins and Enzymes 831
21-10 The Mechanism of Action of an Enzyme 836
21-11 Energy and Metabolism in Living Systems 842
    The Combustion of Glucose 842
    The Three-Step Process in Metabolic Oxidation 843
        Step 1: Glycolysis 843
        Step 2: Citric Acid Cycle 846
        Step 3: Terminal Oxidation or Respiratory Chain 848
    Winding the Mainspring of Life: Photosynthesis 851

Chapter 22  Rates and Mechanisms of Chemical Reactions 864
22-1 What Happens When Molecules React? 866
22-2 Measurement of Reaction Rates 870
    Following the Course of a Reaction 872
    A First-Order Rate Equation and the Decay of $^{14}$C 873
    Decomposition of $N_2O_5$ 874
    Stoichiometry and Rate Expressions 874
    The Goals of Chemical Kinetics 876
22-3 Calculating Rate Constants from Molecular Information 877
    Arrhenius' Activation Energy 877
    Collision Theory of Bimolecular Gas Reactions 879
    Activated Complexes 880
    Potential Energy Surfaces 881
    Absolute Rate Theory 889
    Comparison of Theories 890
22-4 Complex Reactions 891
    The Hydrogen-Iodine Reaction 891
    Rates and Mechanisms of Substitution Reactions 893
    Chain Reactions 895
22-5 Catalysis 898
    Homogeneous Acid Catalysis 899

Chapter 23  Nuclear Chemistry 911
23-1 The Nucleus 913
    Size and Shape 913
    Binding Energy 914
23-2 Nuclear Decay 917
    $\beta^-$ or Electron Emission 918
Orbital Electron Capture, EC  919
β+ or Positron Emission  919
α− Particle Emission  919
γ Emission During α Decay  920
Stability and Half-Life  920
23-3 Stability Series  923
Natural Radioactive Series  925
23-4 Nuclear Reactions  925
Artificial Elements  927
Fission  929
Fusion  930
23-5 Applications of Nuclear Chemistry and Isotopes  931
Chemical Markers  931
Radiometric Analysis  932
Isotope-Dilution Methods  932
Radiocarbon Dating  934
The Age of the Earth  936

Appendix 1  The Système Internationale (SI) of Units  A-1

Appendix 2  Physical Constants and Conversion Factors  A-5


Appendix 4  Significant Figures and Exponential (Scientific) Notation  A-14
Significant Figures  958
Addition and Subtraction  959
Multiplication and Division  962
Exponential Numbers or "Scientific Notation"  965

Appendix 5  A More Exact Treatment of Acid—Base Equilibria  A-25
Strong and Weak Acids: The Contribution from Dissociation of Water  969
Weak Acids and Water Dissociation  971
Weak Acids and Their Salts: Exact Treatment  973
Titration of a Weak Acid by a Strong Base  976

Appendix 6  Answers to Odd-Numbered Problems  A-35

Index  I-1