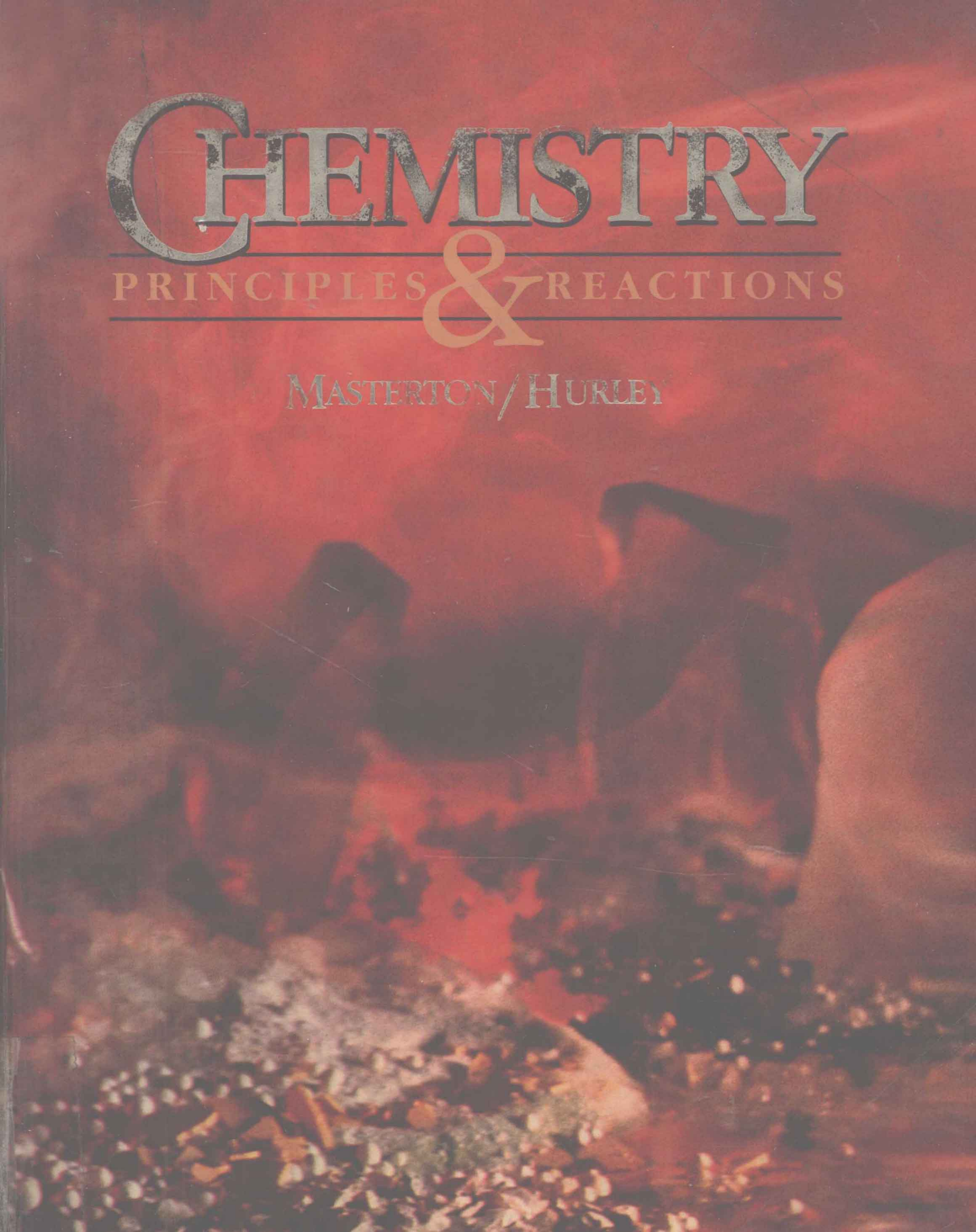
# CHEMISTRY
## PRINCIPLES & REACTIONS

MASTERTON / HURLEY



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## Principles & Reactions

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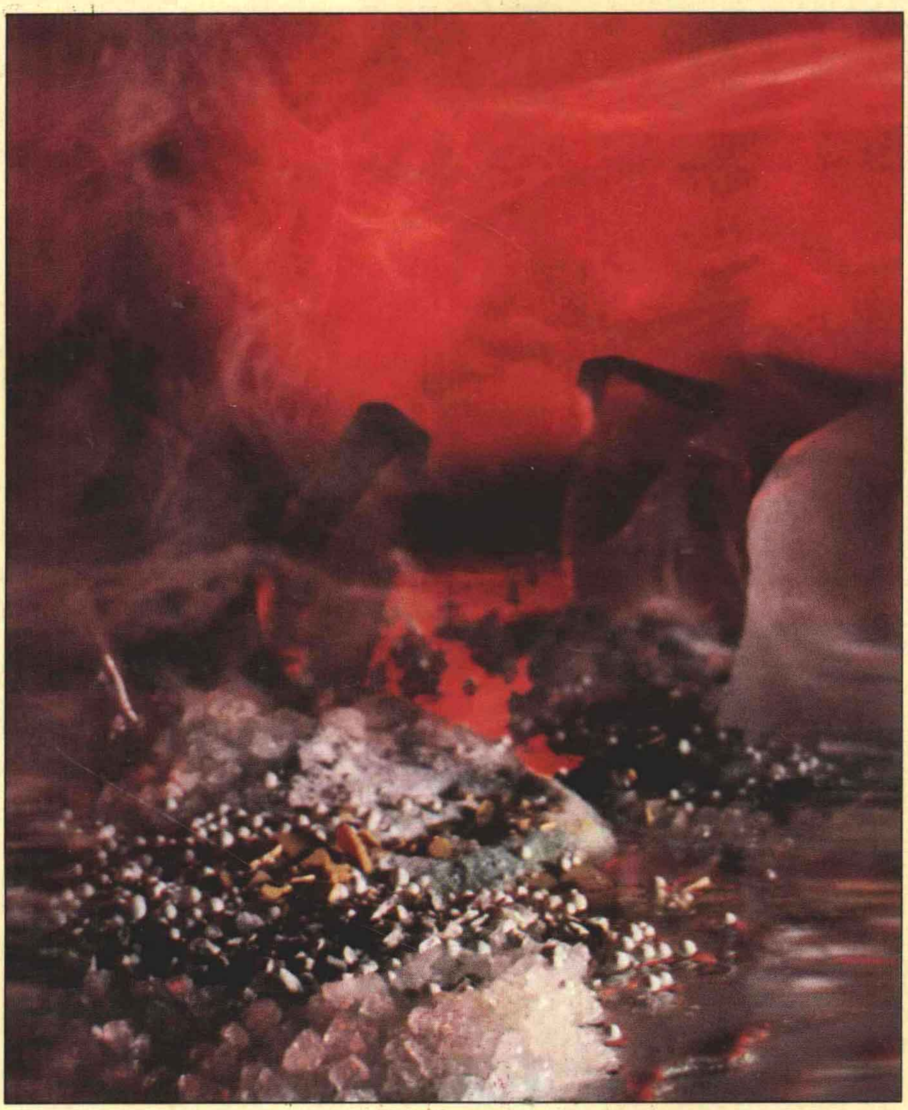


# DEDICATION

***To Loris and Jim***

*For their understanding when entropy was high*
*and their encouragement when energy was low.*

# PREFACE

It is difficult for authors to praise the virtues of their own book. We could tell you it is so inspiring that students will be turned on to chemistry with no effort on your part, but we doubt you would believe that. We could tell you that the text is so clearly written that your students will learn chemistry with little or no effort on their part; certainly you wouldn't believe that. We can tell you that our two goals in writing this book have been to make it as clear and as interesting as possible. We hope you will believe that, because it is true.

As the title, "Chemistry: Principles and Reactions" implies, this text blends theory with practice and calculations with descriptive chemistry. Three major topics are emphasized in the first half of the book. These are,

**Stoichiometry** Molarity is introduced in Chapter 2, immediately following the mole concept. Chapter 3 deals with formulas and mass relations in reactions. It also includes sections on the formulas and names of ionic and simple molecular compounds. Our objective is to establish a firm foundation for the chemical principles to follow.

**Atomic and Molecular Structure** Chapter 5 describes the electronic structures of atoms and ions. The Periodic Table, introduced in

Chapter 1, is analyzed in some detail in Chapter 6. That chapter concludes with a discussion of the chemistry of the main-group metals (the alkalis, alkaline earths, and aluminum). Two chapters are devoted to covalent bonding: Chapter 8 emphasizes Lewis structures and Chapter 9 the VSEPR model of molecular structure.

**States of Matter** The gas laws are covered in Chapter 4; liquids and solids are deferred to in Chapter 10, following chemical bonding. Chapter 11 emphasizes the physical properties of aqueous solutions, laying a foundation for later discussions of solution chemistry.

The second half of the book emphasizes two general areas:

**Chemical Equilibrium** Chapter 13 applies equilibrium principles to gaseous systems; $K_p$ is treated as well as $K_c$. Solution equilibria are first discussed in Chapter 14, where $K_w$, $K_a$, and $K_b$ are introduced. In Chapter 15, these equilibrium constants are applied to explain the characteristics of buffers and acid-base titrations. The chapter concludes with a discussion of the solubility product constant, $K_{sp}$. Formation constants for complex ions are included in Chapter 16 (coordination chemistry). Once the principles of equilibrium have been introduced, they are referred to repeatedly in subsequent chapters.

**Descriptive Chemistry** Two chapters (16 and 22) are devoted to the transition metals, two (23 and 24) to the nonmetals, and two more (26 and 27) to an introduction to organic chemistry and biochemistry. We have tried to avoid the dreary recitation of facts that has put a generation of students and their instructors to sleep. Instead of endlessly plodding through the chemistry of one element after another, we have organized descriptive chemistry around chemical principles. Perhaps the best example of this approach is seen in Chapter 22. There the chemistry of the transition metals is tied to the types of reactions undergone, first by the metals themselves, then by transition metal cations, and finally by their oxyanions (e.g., $CrO_4^{2-}$ and $MnO_4^-$).

Thermodynamics is divided between two chapters. Thermochemistry, $\Delta H$, and the First Law are presented in Chapter 7, after stoichiometry and the gas laws. This chapter serves as a quantitative interlude between qualitative discussions of atomic structure (Chapter 5 and 6) and chemical bonding (Chapters 8 and 9); it directly precedes the discussion of bond energies in Chapter 8. The more subtle aspects of thermodynamics, $\Delta G$, $\Delta S$, and the Second Law, are deferred to Chapter 20, immediately preceding the treatment of electrochemistry in Chapter 21.

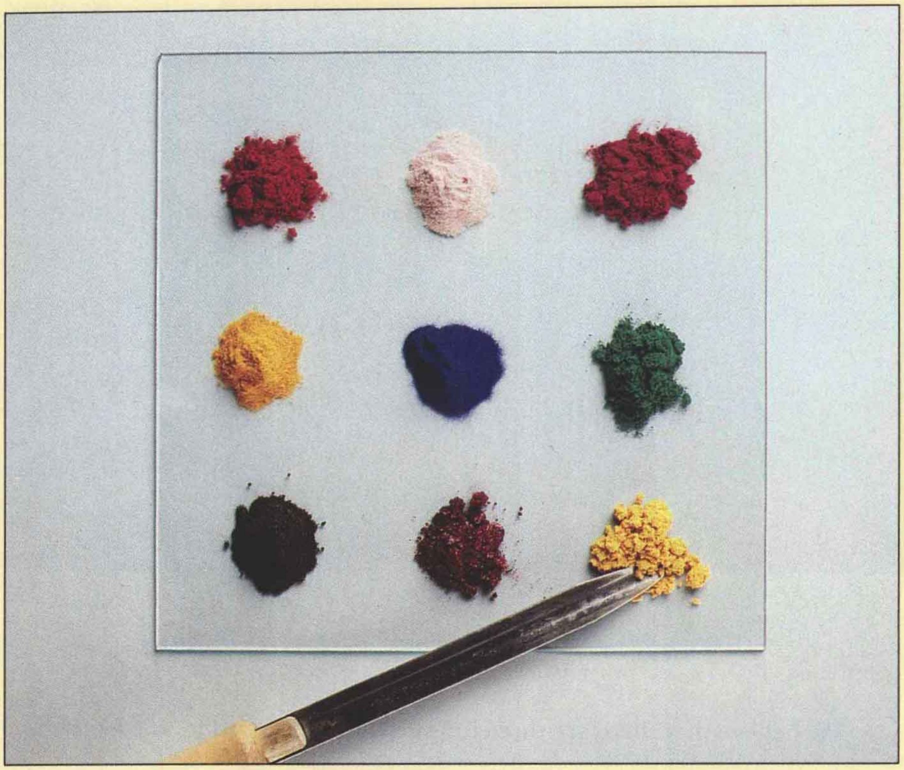
We believe that there are three unique chapters found in this text:

**Reactions in Aqueous Solution** (Chapter 12) This covers the writing and balancing of net ionic equations for precipitation, acid-base, and redox reactions. It also deals with the stoichiometry of these reactions and their application to volumetric analysis. Too often, this important material gets lost in discussions of more esoteric topics.

**Qualitative Analysis** (Chapter 17) This deals with group separations in cation analysis and spot tests for a variety of anions. This material has an obvious application to the general chemistry laboratory. Beyond that, it offers a splendid opportunity to review the principles of solution chemistry presented in previous chapters.

**Chemistry of the Atmosphere** (Chapter 19) Included here are such topics as nitrogen fixation, weather modification and the greenhouse effect, depletion of the ozone layer, and the ravages of acid rain. Throughout, the principles of chemical kinetics (Chapter 18) and equilibrium are applied. We hope you will find time to cover this material, because we believe it is both interesting and relevant.

More information about content can be found in the introductory discussions at the beginning of each chapter. Alternatively, you may wish to read the chapter summaries that are included in Appendix 5. Many pedagogical features of the text are described in the section addressed "To the Student," which follows this preface. We call your attention in particular to the Summary Problems and the Perspectives, two innovations in this text.



## ANCILLARY PACKAGE

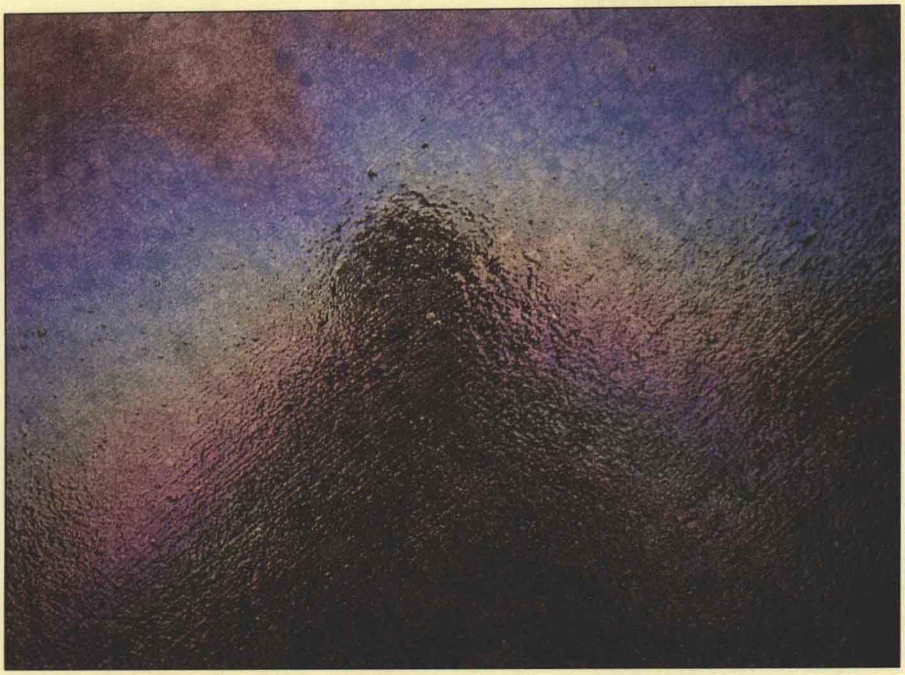
A complete resource package has been prepared to enhance the student's learning and the professor's teaching of *Chemistry: Principles and Reactions*.

**Lecture Outline** by Ronald O. Ragsdale (University of Utah). It helps students to organize the class lectures and frees them of extensive note taking.

**Student Solutions Manual** by John E. Bauman (University of Missouri, Columbia). It contains detailed solutions to half of the end-of-chapter problems and all the challenging problems.

**Study Guide/Workbook** by Cecile N. Hurley. It contains worked examples and problem-solving techniques to help the student's understanding of general chemistry. It also has fill-in-the-blanks, exercises, and self-tests to help the student gauge his mastery of the chapter.

**Instructor's Manual** by William L. Masterton. Included are basic skills, lecture outlines, classroom demonstrations, quizzes, and solutions to half of the end-of-chapter questions.



**Chemical Principles in the Laboratory, 5th edition** by Emil J. Slowinski, Wayne C. Wolsey, and William L. Masterton. A revision of the best-selling general chemistry laboratory manual. It includes 43 experiments, each with a pre-lab study assignment. An instructor's manual is also available.

**Overhead Transparencies** One-hundred four-color figures from the text.

**Computerized Test Bank** by Gordon Eggleton (Southeastern Oklahoma State University). A multiple-choice test bank with over 1000 test items for IBM PC or compatibles.

**Printed Test Bank** Tests generated from the computerized test bank.

**Audio-Tape Lessons** by B. Shakhashiri, R. Schreiner, and P. A. Meyer (all of University of Wisconsin, Madison). Enables students to study and learn chemistry at their own pace. Students listen to the instructions on the tape and follow the examples in the workbook.

**Tutorial Software** Wilkie Computerized Chemistry, for Apple and IBM. COMPress, for Apple II+ and Apple IIe.

## ACKNOWLEDGMENTS

We wish to express our deepest appreciation to two individuals who contributed a great deal to this text although their names do not appear on it. Emil Slowinski worked with us from the beginning, reviewing our material with candor and, above all, compassion. Beyond that, he wrote the marginal notes in his own inimitable style. Ruven Smith supervised and set up all the photography; somehow he managed to turn an onerous task into a delightful experience.

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Finally, we express our appreciation to all the people at Saunders who helped us with this book. In particular, we are grateful to Becca Gruliow, Charlotte Hyland, and Kate Pachuta for their thoughtfulness, good humor, and insightful suggestions. Special thanks go to Sandi Kiselica and John Vondeling, who deflected with equanimity the protestations showered upon them by two strong-willed authors.

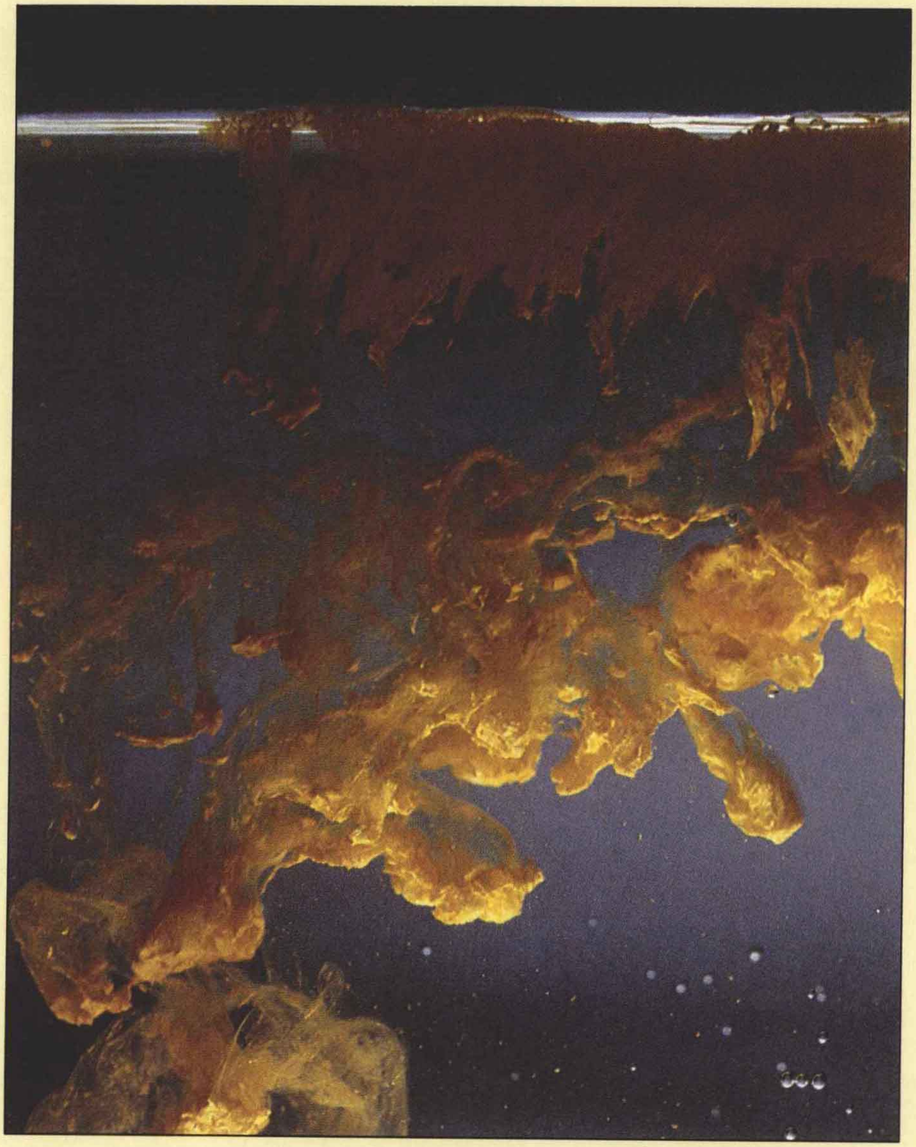
***William L. Masterton***
***Cecile N. Hurley***

# TO THE STUDENT

Over the next several months, you will probably receive a lot of advice from your instructor, teaching assistant, and fellow students about how to study chemistry. We hesitate to add our advice; experience as teachers and parents has taught us that students tend to do surprisingly well without it. We would, however, like to acquaint you with some of the learning tools in this text. They are briefly described and illustrated in the sample pages that follow.

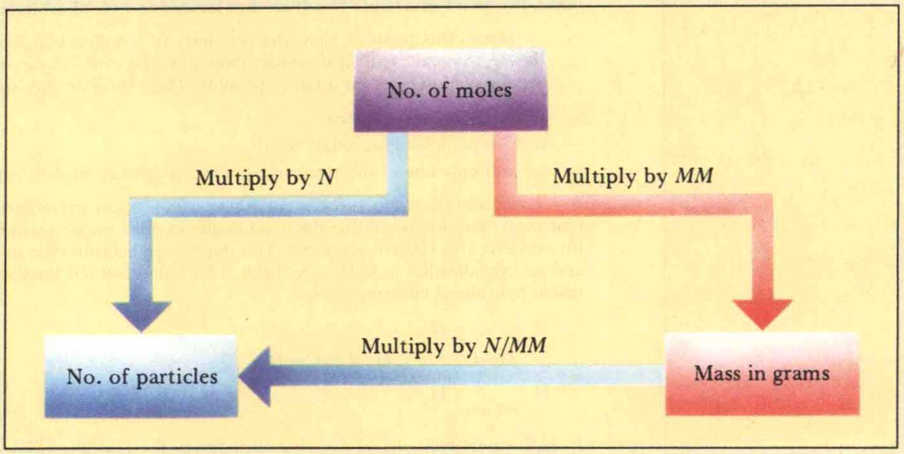
**Chapter-Opening Photographs** These illustrate, in a somewhat abstract way, chemical reactions of one type or another. Each photograph is accompanied by a chemical equation and a description of the reaction involved. All reactions shown are discussed in this text.

Included with the photograph at the beginning of each chapter is a poem or quotation. Be sure to read the one associated with Chapter 27, even if that chapter is not assigned.



**Flow Charts**

Scattered throughout the book are several diagrams that suggest a general approach to solving a specific type of problem. This particular flow chart describes conversions between moles, grams, and number of particles. In using a flow chart, you should not attempt to memorize the various steps. Instead you should try to understand the process involved; once you do that, the sequence of steps will seem to be a logical one.




■ **EXAMPLE 2.9**

The bottle labeled "concentrated hydrochloric acid" in the lab contains 12.0 mol of the compound HCl per liter of solution, that is, M = 12.0 mol/L.

a. How many moles of HCl are there in 25.0 mL of this solution?

b. What volume of concentrated hydrochloric acid must be taken to contain 1.00 mol HCl?

**Solution**

The molarity of the HCl relates the number of moles of HCl to the number of liters of solution. Since there are 12.0 mol HCl per liter, we can say that

$$12.0 \text{ mol} \simeq 1 \text{ L solution}$$

This relation gives us the conversion factors we need to go from liters of solution to moles or vice versa.

a. We first convert 25.0 mL to liters:

$$\text{number liters solution} = 25.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.0250 \text{ L}$$

Now we convert to moles of HCl:

$$\text{no. moles HCl} = 0.0250 \text{ L} \times \frac{12.0 \text{ mol HCl}}{1 \text{ L}} = 0.300 \text{ mol HCl}$$

b. To find the volume in liters, we start with the number of moles of HCl and use the conversion factor 1 L/12.0 mol HCl:

$$\text{number liters solution} = 1.00 \text{ mol HCl} \times \frac{1 \text{ L}}{12.0 \text{ mol HCl}}$$

$$= 0.0833 \text{ L} \quad (83.3 \text{ mL})$$

**Exercise**

How many grams of HCl (molar mass = 36.46 g/mol) are there in 0.100 L of this solution? Answer: 43.8 g.

**Examples and Exercises**

In a typical chapter, you will find 10 or more examples, each designed to illustrate a particular principle. These have answers, screened in yellow to save you the trouble of highlighting them. More important, the step-wise solutions are worked out in some detail. Following each example is an exercise, for which only the answer is given. Try the exercise; if you do not get the right answer, the chances are you did not completely understand the principle illustrated. In that case, try again, getting help if you need it.

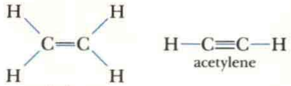
In Section 9.1, we pointed out that insofar as geometry is concerned, a multiple bond acts as if it were a single bond. In other words, the "extra" electron pairs in a double or triple bond have no effect upon the geometry of the molecule. This behavior is explained in terms of hybridization.

**The extra electron pairs in a multiple bond (one pair in a double bond, two pairs in a triple bond) are not located in hybrid orbitals.**

From this point of view, the geometry of a molecule is fixed by the electron pairs in hybrid orbitals about a central atom. These orbitals are directed to be as far apart as possible. The hybrid orbitals contain

— all unshared electron pairs.
— electron pairs forming single bonds.
— one and only one of the electron pairs in a double or triple bond.

To illustrate this rule, consider the ethylene ($C_2H_4$) and acetylene ($C_2H_2$) molecules. You will recall that the bond angles in these molecules are 120° for ethylene and 180° for acetylene. This implies $sp^2$ hybridization in $C_2H_4$ and sp hybridization in $C_2H_2$ (see Table 9.3). Using colored lines to represent hybridized electron pairs,


ethylene acetylene

$C_2H_4$—3 electron pairs in hybrid, so it is $sp^2$
$C_2H_2$—2 electron pairs in hybrid, so it is sp

In both cases, only one of the electron pairs in the multiple bond is hybridized.

**Marginal Notes**

Sprinkled throughout the text are a number of short notes that have been placed in the margin. Many of these are of the "now, hear this" variety; a few make points that we forgot to emphasize in the body of the text. Some, probably fewer than we think, are humorous.

**Summary Problems**

At the end of each chapter is a several-part problem covering all or nearly all of the main ideas in the chapter. You can test your understanding of the chapter by working this problem; you may wish to do this as part of your preparation for intraterm exams. A major advantage of a summary problem is that it ties together many different concepts, showing how they correlate with one another.

**SUMMARY PROBLEM**

Consider the thermochemical equation:

$$C_2H_6(g) + \tfrac{7}{2} O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l); \qquad \Delta H = -1559.7\ kJ$$

**a.** Calculate $\Delta H$ for the thermochemical equations:

$$2\ C_2H_6(g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(l)$$

$$2\ CO_2(g) + 3\ H_2O(l) \rightarrow C_2H_6(g) + \tfrac{7}{2} O_2(g)$$

**b.** The heat of vaporization of $H_2O(l)$ is +44.0 kJ/mol. Calculate $\Delta H$ for the equation:

$$C_2H_6(g) + \tfrac{7}{2} O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$$

**c.** The heats of formation of $CO_2(g)$ and $H_2O(l)$ are −393.5 and −285.8 kJ/mol, respectively. Calculate $\Delta H_f^0$ of $C_2H_6(g)$.

**d.** How much heat is evolved when 1.00 g of $C_2H_6(g)$ is burned to give $CO_2(g)$ and $H_2O(l)$ in an open container?

**e.** When 1.00 g of $C_2H_6$ is burned in a bomb calorimeter, the temperature rises from 22.00°C to 33.13°C. In a separate experiment, it is found that absorption of 10.0 kJ of heat raises the temperature of the calorimeter by 2.15°C. Calculate $C_{calorimeter}$ and $q_{reaction}$.

**f.** Calculate $\Delta E$ at 25°C for the equation:

$$C_2H_6(g) + \tfrac{7}{2} O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$$

**Answers**

**a.** −3119.4 kJ; +1559.7 kJ **b.** −1427.7 kJ **c.** −84.7 kJ
**d.** 51.9 kJ **e.** 4.65 kJ/°C, −51.8 kJ **f.** −1553.5 kJ

## QUESTIONS AND PROBLEMS

The questions and problems listed here are typical of those at the end of each chapter. Some involve discussion and most require calculations, writing equations, or other quantitative work. The topic emphasized in each question or problem is indicated in the heading, such as "Symbols and Formulas" or "Significant Figures." Those in the "Unclassified" category may involve more than one concept, including, perhaps, topics from a preceding chapter. "Challenge Problems," listed at the end of the set, require extra skill and/or effort.

The "classified" questions and problems (Problems 1–50 in this set) are arranged in matched pairs, one below the other, and illustrate the same concept. For example, Questions 1 and 2 below are nearly identical in nature; the same is true of Questions 3 and 4, and so on. Problems numbered in color are answered in Appendix 4.

### Symbols and Formulas

**1.** Give the color, state of matter at room temperature, and symbol of the following elements. Use Tables 1.4 and 1.5.
a. bromine  b. iron

2. Use Tables 1.4 and 1.5 to write the name and symbol for the element that is
a. a green-yellow gas at 25°C and 1 atm.
b. a red solid at 25°C and 1 atm.

**3.** Give the symbols for
a. potassium  b. cadmium  c. gold
d. antimony  e. rubidium

4. Name the elements whose symbols are
a. Mn  b. Na  c. As  d. W  e. P

**5.** How many elements are there in the following groups?
a. Group 2  b. Group 3  c. Group 8
d. the subgroup headed by Cr

6. How many elements are there in the following periods?
a. Period 1  b. Period 2  c. Period 3
d. Period 4  e. Period 5

### Measurements

**7.** Classify each of the following as units of mass, volume, length, density, energy, or pressure.
a. mg  b. mL  c. $cm^3$  d. mm
e. $kg/m^3$  f. mm Hg  g. kJ

8. Classify each of the following units as units of mass, volume, length, density, energy, or pressure.
a. nm  b. kg  c. J  d. $m^3$
e. $g/cm^3$  f. atm  g. kcal

**9.** Select the smaller member of each pair.

10. Select the smaller member of each pair.
a. 27.12 g or 27.12 kg
b. 35 $cm^3$ or 0.035 $m^3$
c. 2.87 g/L or 2.87 $g/cm^3$
d. 525 mm or $5.25 \times 10^{-3}$ km

**11.** Most laboratory experiments are done at 25°C. Express this in
a. °F  b. K

12. A child has a temperature of 104°F. What is his temperature in
a. °C  b. K

**13.** Carbon dioxide, $CO_2$, at room temperature (70°F) is a gas. It can be frozen at −69.7°F and 5 atm pressure to solid carbon dioxide, popularly known as dry ice. What is the freezing point of carbon dioxide in °C?

14. Superconductors use liquid nitrogen as a coolant. Liquid nitrogen boils at −195.8°C. What is its boiling point in
a. °F  b. K

### Significant Figures

**15.** How many significant figures are there in each of the following?
a. 1.92 mm  b. 0.032100 g
c. $6.022 \times 10^{23}$ atoms  d. 460.00 L
e. 0.00036 $cm^3$  f. $2 \times 10^9$ nm

16. How many significant figures are there in each of the following?
a. 23.437 m  b. 0.002017 g  c. $30.0 \times 10^{20}$ nm
d. 50.010 L  e. 2.30790 atm  f. 350 miles

**17.** A student prepares a salt solution by dissolving 85.638 g of sodium chloride (NaCl) in enough water to form 237 $cm^3$ of solution. Calculate the number of grams of salt per cubic centimeter of solution.

18. Calculate the volume of a sodium atom, which has a radius of 0.186 nm. Assume the atom is spherical. The volume of a sphere is given by the expression $V = 4\pi r^3/3$.

**19.** Calculate the following to the correct number of significant figures.
a. $x = \dfrac{1.27\ g}{5.296\ cm^3}$  b. $x = \dfrac{12.235\ g}{1.01\ L}$
c. $x = 12.2\ g + 0.38\ g$  d. $x = \dfrac{17.3\ g + 2.785\ g}{30.20\ cm^3}$

20. How many significant figures are there in the values of $x$ obtained from
a. $x = \dfrac{34.0300\ g}{12.09\ cm^3}$
b. $x = 39.647\ g - 39.297\ g$

### End-of-Chapter Problems

Most of these are "classified," that is, grouped by type under a particular heading, such as symbols and formulas and significant figures. These classified problems are in matched pairs. The second member of each pair illustrates the same principle as the first; it is numbered in color and answered in Appendix 4. Your instructor may assign unanswered problems as homework. After these problems have been discussed, you should work the corresponding answered problems to make sure you know what's going on. Each chapter also contains a smaller number of "unclassified" and "challenge" problems. These are not paired; all of them are answered in Appendix 4.