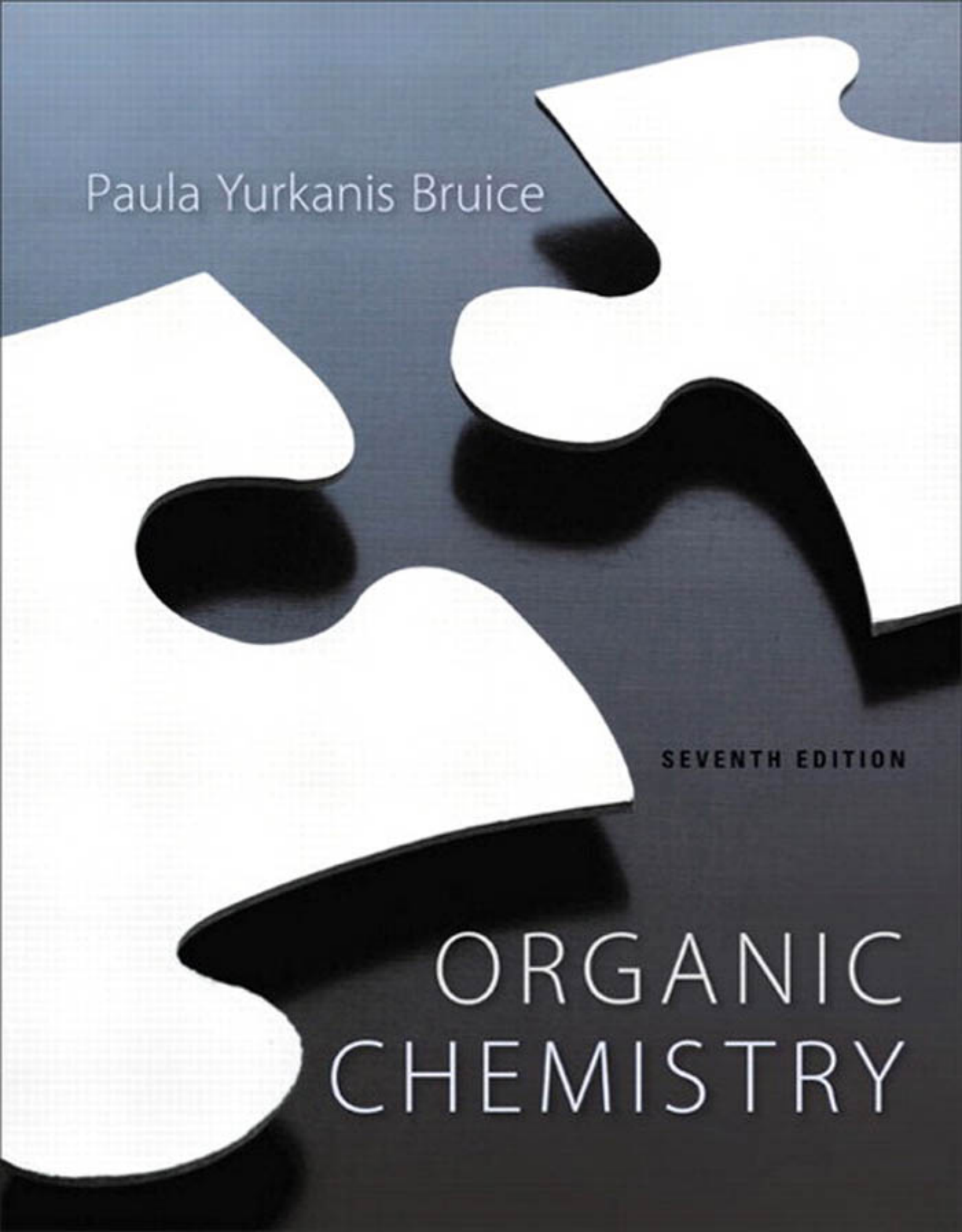
Paula Yurkanis Bruice
SEVENTH EDITION
ORGANIC CHEMISTRY

To the Student

Welcome to the fascinating world of organic chemistry. You are about to embark on an exciting journey. This book has been written with students like you in mind—those who are encountering the subject for the first time. The book's central goal is to make this journey through organic chemistry both stimulating and enjoyable by helping you understand central principles and asking you to apply them as you progress through the pages. You will be reminded about these principles at frequent intervals in references back to sections you have already mastered.

You should start by familiarizing yourself with the book. Inside the back cover is information you may want to refer to often during the course. The list of Some Important Things to Remember and the Reaction Summary at each chapter's end provide helpful checklists of the concepts you should understand after studying the chapter. The Glossary at the end of the book can also be a useful study aid, as can the Appendices, which consolidate useful categories of information. The molecular models and electrostatic potential maps that you will find throughout the book are provided to give you an appreciation of what molecules look like in three dimensions and to show how charge is distributed within a molecule. Think of the margin notes as the author's opportunity to inject personal reminders of ideas and facts that are important to remember. Be sure to read them.

Work all the problems *within* each chapter. These are drill problems that you will find at the end of each section that allow you to check whether you have mastered the skills and concepts the particular section is teaching before you go on to the next section. Some of these problems are solved for you in the text. Short answers to some of the others—those marked with a diamond—are provided at the end of the book. Do not overlook the "Problem-Solving Strategies" that are also sprinkled throughout the text; they provide practical suggestions on the best way to approach important types of problems.

In addition to the *within-chapter* problems, work as many *end-of-chapter* problems as you can. The more problems you work, the more comfortable you will be with the subject matter and the better prepared you will be for the material in subsequent chapters. Do not let any problem frustrate you. If you cannot figure out the answer in a reasonable amount of time, turn to the *Study Guide and Solutions Manual* to learn how you should have approached the problem. Later on, go back and try to work the problem on your own again. Be sure to visit www.MasteringChemistry.com, where you can explore study tools including Exercise Sets, an Interactive Molecular Gallery, Biographical Sketches of historically important chemists, and where you can access content on many important topics.

The most important advice to remember (and follow) in studying organic chemistry is DO NOT FALL BEHIND! The individual steps to learning organic chemistry are quite simple; each by itself is relatively easy to master. But they are numerous, and the subject can quickly become overwhelming if you do not keep up.

Before many of the theories and mechanisms were figured out, organic chemistry was a discipline that could be mastered only through memorization. Fortunately, that is no longer true. You will find many unifying ideas that allow you to use what you have learned in one situation to predict what will happen in other situations. So, as you read the book and study your notes, always making sure that you understand *why* each chemical event or behavior happens. For example, when the reasons behind reactivity are understood, most reactions can be predicted. Approaching the course with the misconception that to succeed you must memorize hundreds of unrelated reactions could be your downfall. There is simply too much material to memorize. Understanding and reasoning, not memorization, provide the necessary foundation on which to lay subsequent learning. Nevertheless, from time to time some memorization will be required: some fundamental rules will have to be memorized, and you will need to learn the common names of a number of organic compounds. But that should not be a problem; after all, your friends have common names that you have been able to learn and remember.

Students who study organic chemistry to gain entrance into medical school sometimes wonder why medical schools pay so much attention to this topic. The importance of organic chemistry is not in the subject matter alone, however. Mastering organic chemistry requires a thorough understanding of certain fundamental principles and the ability to use those fundamentals to analyze, classify, and predict. The study of medicine makes similar demands: a physician uses an understanding of certain fundamental principles to analyze, classify, and diagnose.

Good luck in your study. I hope you will enjoy studying organic chemistry and learn to appreciate the logic of this fascinating discipline. If you have any comments about the book or any suggestions for improving it, I would love to hear from you. Remember, positive comments are the most fun, but negative comments are the most useful.

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Organic Chemistry

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Organic Chemistry

SEVENTH EDITION

Paula Yurkanis Bruice

UNIVERSITY OF CALIFORNIA
SANTA BARBARA

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To Meghan, Kenton, and Alec
with love and immense respect
and to Tom, my best friend

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Contents

New material on how to draw Lewis structures and how to predict bond angles and the orbitals used in bonding.

New chapter on Acid/Base Chemistry reinforces fundamental concepts.

New tutorial on Acid/Base Chemistry provides students with opportunities to self assess and develop foundational skills needed for future topics in organic chemistry.

Enhanced by MasteringChemistry®

- Acids and Bases: Equilibrium Basics
- Acids and Bases: Factors Influencing Acid Strength
- Acids and Bases: pH Influence on Acid and Base Structure

Increased content on noncovalent interactions in chemical and biological systems.

Enhanced by MasteringChemistry®
- Using Molecular Models: Basics of Model Building
- Using Molecular Models: Interpret Chiral Models
- Using Molecular Models: Interpret Cyclic Models

The coverage of stereoisomers now precedes the coverage of the reactions of alkenes.

Two new tutorials reinforce student understanding and visualization of structure.

Enhanced by MasteringChemistry®
- Interconverting Structural Representations: Interpreting Fischer Projections
- Interconverting Structural Representations: Fischer Projections with Multiple Stereocenters
- Interconverting Structural Representations: Interpreting Newman Projections

Introduces a new feature, "Organizing What We Know," which highlights how all organic compounds can be divided into families and all members of a family react in the *same way*. Furthermore, each family can be put into one of four groups and all the families in a group react in *similar ways*.

New tutorial gives students practice drawing curved arrows.

Enhanced by MasteringChemistry®

- An Exercise in Drawing Curved Arrows: Basics of Pushing Electrons
- An Exercise in Drawing Curved Arrows: Predicting Electron Movement
- An Exercise in Drawing Curved Arrows: Interpreting Electron Movement

Alkoxymercuration was removed since it is now rarely used because of toxicity concerns. Ozonolysis has been added as has using 9-BBN for hydroboration and MCPBA for epoxidation.

Discussion of reactivity has been reorganized and clarified. The mechanism for keto-enol interconversion has been added.

Discussion of aromaticity has been added to allow this concept to be carried throughout the text starting at an earlier point.

New tutorial gives students practice drawing resonance contributors.

Enhanced by MasteringChemistry®
- Drawing Resonance Contributors: Moving π Electrons
- Drawing Resonance Contributors: Predicting Contributor Structure
- Drawing Resonance Contributors: Substituted Benzene Compounds

Rewritten to incorporate the new finding that secondary alkyl halides do not undergo S_N1 reactions.

Rewritten to incorporate the new finding that secondary alkyl halides do not undergo E1 reactions.

Hypochlorous acid introduced as an alternative to toxic-chromuium-containing compounds.

Discussion of palladium-catalyzed coupling reactions and their mechanisms has been expanded. Solved problems and problem-solving strategies were added to facilitate understanding.

There are now 50 additional spectroscopy problems in the *Study Guide and Solutions Manual.*

Acid anhydrides are carboxylic acid derivatives but they don't look like carboxylic acids. Anhydrides, therefore, were moved to the end of the chapter to allow students to focus on the similarities between carboxylic acids, acyl chlorides, esters, and amides. Acid anhydrides are now better placed since they come just before phosphoric acid anhydrides.

Enhanced discussion of reduction reactions. Added a discussion of chemoselective reactions.

Streamlined the discussion of both the reactions of enolate ions and crossed aldol additions and condensations. Added new examples of retrosynthetic analysis.

The reactions of aromatic heterocycles now follows the reactions of other aromatic compounds.

A new discussion on diseases caused by protein misfolding.

Revised to emphasize the connection between the organic reactions that occur in test tubes with the organic reactions that occur in cells.

Added the mechanism for the conversion of succinate to fumarate.

New coverage of organic reactions that occur in gluconeogenesis and discussions of thermodynamic control and the regulation of metabolic pathways. Revised to emphasize the connection between the organic reactions that occur in test tubes with those that occur in cells. New section on terpene biosynthesis.

New section on antiviral drugs and the chemical reasons for their antiviral activity. Recently published information about the function of segments of DNA that were thought to contain no information.

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Preface

TO THE INSTRUCTOR

The guiding principle behind this book is to present organic chemistry as an exciting and vitally important science. To counter the impression that the study of organic chemistry consists primarily of memorizing a diverse collection of molecules and reactions, this book is organized around shared features and unifying concepts, and it emphasizes principles that can be applied again and again. I want students to learn how to apply what they have learned to new settings, reasoning their way to a solution rather than memorizing a multitude of facts. I also want them to see that organic chemistry is a fascinating discipline that is integral to biology as well as to their daily lives.

NEW TO THIS EDITION

In planning the changes to this edition, our focus was on two questions:

1. What is the best way to help students learn and study organic chemistry?
2. How can we prepare students for the new MCAT while still meeting the needs of students majoring in chemistry and chemical engineering?

HELPING STUDENTS LEARN AND STUDY ORGANIC CHEMISTRY.

As each student generation evolves and becomes increasingly diverse, we are challenged as teachers to support the unique ways students acquire knowledge, study, practice, and master a subject. In order to support contemporary students who are often visual learners, with preferences for interactivity and small 'bites' of information, I have revisited this edition with the goal of helping students organize the vast amount of information that comprises organic chemistry. **Through significant changes to the organization, a new and modern design, and new pedagogical tools, the Seventh Edition helps students focus on fundamental concepts and skills, make connections from one topic to the next, and review the material visually through the guidance of an annotated art program and new tutorial spreads.** Details about the many changes to this text are outlined below:

A New Feature, "Organizing What We Know About Organic Chemistry", lets students see where they have been and where they are going as they proceed through the course, encouraging them to keep in mind the fundamental reason behind the reactions of all organic compounds: *electrophiles react with nucleophiles.*

When students see the first reaction (other than an acid-base reaction) of an organic compound, they are told that all organic compounds can be divided into families and all members of a family react in the *same way*. And to make things even easier—each family can be put into one of four groups and all the families in a group react in *similar ways*.

The book then proceeds with each of the four groups (Group I: compounds with carbon-carbon double and triple bonds; Group II: compounds with an electronegative group attached to an sp^3 carbon; Group III: carbonyl compounds; and Group IV: aromatic compounds). When the chemistry of all the members of a particular group has been covered, students see a summary of the characteristic reactions of that group (see pages 381, 524, 894, and 1010) that they can compare with the summary of the characteristic reactions of the groups studied previously.

New Tutorials spreads following relevant chapters give students extra practice so they can better master important topics: acid-base chemistry, interconverting chemical structures, building molecular models, drawing curved arrows, drawing contributing resonance structures, drawing curved arrows in radical systems, synthesis and retrosynthetic

analysis. MasteringChemistry includes additional online tutorials on each of these topics that can be assigned as homework or for test preparation.

New Modern Design and Streamlined narrative allow students to navigate through content and study more efficiently with the text. With **three fewer chapters than the previous edition,** an updated organization and presentation allows for a more efficient path through the content and ultimately the course.

An **Enhanced Art program** with new annotations provides key information to students so that they can review important parts of the chapter with the support of the visual program. New margin notes throughout the book succinctly repeat key points and help students review important material at a glance.

Cutting Edge Content—The chapters on nucleophilic substitution and elimination have been rewritten to incorporate the new finding that secondary alkyl halides do not undergo S_N1/E1 reactions. You will be surprised at how much easier the addition of this one new fact makes this topic. I feel badly that students have been tortured for so long by misinformation!

The discussion of palladium-catalyzed coupling reactions and their mechanisms has been expanded while Solved problems and problem-solving strategies were added to facilitate understanding.

Many of the sections on bioorganic chemistry were rewritten to emphasize the connection between the organic reactions that occur in the laboratory and those that occur in cells.

Many new interest boxes have been added to intrigue students and reinforce their appreciation for how organic chemistry relates to biological systems. Some examples: Why Did Nature Choose Phosphates?, What Drug Enforcement Dogs are Really Detecting, Synthetic Alkynes are Used to Treat Parkinson's Disease, Influenza Pandemics.

ORGANIZATIONAL CHANGES

Stereoisomers are now covered (Chapter 4) before the students see any reactions. Therefore, the Reactions of Alkenes (Chapter 6) now covers both the reactions of alkenes and the stereochemistry of those reactions. This reorganization also allows the compounds in Group I (alkenes, alkynes, and dienes) to be covered sequentially.

The concepts of electronic effects and aromaticity have been moved up (Chapter 8) to allow them to be carried though the text starting at an earlier point.

The reactions of benzene and substituted benzenes now come after carbonyl chemistry. This allows the two chapters that discuss compounds in Group IV (aromatic compounds) to be adjacent. Coverage of oxidation-reduction reactions, lipids, and drug discovery and design have been integrated into early chapters where appropriate.

PROBLEM SOLVING SUPPORT

Fifty new spectroscopy problems—in addition to the many spectroscopy problems in the text—have been added to the *Study Guide/Solutions Manual.*The spectroscopy chapters (Chapters 14 and 15) are written so they can be covered at any time during the course, For those who prefer to teach spectroscopy at the beginning of the course—or in a separate laboratory course—there is a table of functional groups at the beginning of Chapter 14.

Because many students enjoy the challenge of designing multistep syntheses and find them to be a good test of their understanding of reactivity, **many new examples of retrosynthetic analysis** have been added. There are also **new solved problems and problem-solving strategies on multistep synthesis.**

This edition has more than **200 new problems,** both in-chapter and end-of-chapter. They include new solved problems, new problem-solving strategies, and new problems incorporating information from more than one chapter. I keep a list of questions my students have when they come to office hours. Many of the new problems were created as a result of these questions.

PREPARING STUDENTS FOR MCAT[2015] WHILE STILL MEETING THE NEEDS OF STUDENTS MAJORING IN CHEMISTRY AND CHEMICAL ENGINEERING.

I do not think we should dismantle our current organic chemistry courses in response to the upcoming changes in the MCAT. I do not think we should teach only those reactions that occur in living systems, nor do I think we should stop teaching synthesis. Synthesis is a good way for students to see if they really understand organic reactions, and most students enjoy the challenge of designing multistep syntheses.

I have long believed that students who take organic chemistry also should be exposed to bioorganic chemistry—the organic chemistry that occurs in biological systems. Bioorganic chemistry is the *bridge* between organic chemistry and biochemistry, and generally is not taught in organic chemistry courses or in biochemistry courses.

Many of the changes in this edition were done to provide students with the "bioorganic bridge," while maintaining the rigor of the traditional organic course.

Information on the chemistry of living systems has been integrated into all the chapters. **As examples, noncovalent interactions in biological systems has been added to Chapter 3, the discussion of catalysis in Chapter 4 now includes a discussion of enzymatic catalysis, the mechanism for the oxidation of fats and oils by oxygen has been added to Chapter 13, and waxes, membranes and phospholipids are now part of Chapter 16.**

The six chapters (chapters 21-26) that focus primarily on the organic chemistry of living systems have been rewritten to emphasize the connection between the organic reactions that occur in the laboratory and those that occur in cells. Each organic reaction that occurs in a cell is explicitly compared to the organic reaction with which the student is already familiar.

Many new interest boxes have been added that relate organic chemistry to biology and medicine. Some examples: Breast Cancer and Aromatase Inhibitors, Searching for Drugs: An Antihistamine, a Nonsedating Antihistamine, and a Drug for Ulcers; Diseases Caused by a Misfolded Protein; How Tamiflu Works; Three Different Antibiotics Act by a Common Mechanism.

The reactions of aromatic compounds (Chapter 19 and 20) now come after carbonyl chemistry. If something needs to be deleted from the course to find room to teach the organic chemistry that occurs in cells, some of the material in these chapters might be omitted. Electronic effects (now introduced in Chapter 8) are important, but these could be revisited by showing how they affect pK_a values substituted benzoic acids, phenols and anilinium ions rather than how they affect the reactivity of a benzene ring (Section 19.16). The electrophilic aromatic substitution reactions of benzene and the nucleophilic substitution reactions of pyridine are important, but the rest of the material in these chapters could be omitted as it will not be important to material that appears in subsequent chapters.

MCAT[2015]

Now that it has been announced that the MCAT will start testing almost exclusively on the organic chemistry of living systems, it is even more important that we provide our students with the "bioorganic bridge"—the material that provides the bridge between organic chemistry and biochemistry. (Some books define bioorganic chemistry as the synthesis by chemists of organic compounds found in nature, which is a very different definition.) **Students should see that the organic reactions that chemists carry out in the laboratory are in many ways just the same as those performed by nature inside a cell. In other words, bioorganic reactions can be thought of as organic reactions that take place in tiny flasks called cells.**

For example, the first step in glycolysis is an S_N2 reaction, the second step is identical to the enediol rearrangement that students learned when they studied carbohydrate chemistry, the third step is another S_N2 reaction, and the fourth step is a reverse aldol addition,

and so on. The first step in the citric acid cycle is an aldol addition followed by thioester hydrolysis, the second step is an E2 dehydration followed by the conjugate addition of water, and third step is oxidation of a secondary alcohol followed by decarboxylation of a 3-oxocarboxylate ion, and so on.

We teach students about halide and sulfonate leaving groups. Adding phosphate and pyrophosphate leaving groups takes little additional time, but introduces the students to valuable information if they are going on to study biochemistry. Students who are studying organic chemistry learn about tautomerization and imine hydrolysis, and students studying biochemistry learn that DNA has thymine bases in place of the uracil bases in RNA. But how many of these students are ever told that the reason for the difference in the bases in DNA and RNA is because of tautomerization and imine hydrolysis?

Bioorganic chemistry is found throughout the text to show students that organic chemistry and biochemistry are not separate entities but are closely related on a continuum of knowledge. Once students learn how, for example, electron delocalization, leaving-group propensity, electrophilicity, and nucleophilicity affect the reactions of simple organic compounds, they can appreciate how these same factors influence the reactions of organic compounds in living systems. I have found that the economy of presentation achieved in the first twenty chapters of the text (see The Functional Group. . . on the following page) makes it possible to devote time to the "bioorganic bridge."

In Chapters 1–20, the bioorganic material is limited mostly to "interest boxes" and to the last sections of the chapters. Thus, the material is available to the curious student without requiring the instructor to introduce bioorganic topics into the course. For example, after the stereochemistry of organic reactions is presented, the stereochemistry of enzyme-catalyzed reactions is discussed; after alkyl halides are discussed, a biological methylation reaction is examined and the reason for the use of different methylating agents by chemists and cells is explained; after the methods chemists use to activate carboxylic acids are presented (by giving them halide or anhydride leaving groups), the methods cells use to activate these same acids are explained (by giving them phosphoanhydride or thiol leaving groups); after condensation reactions are discussed, the mechanisms of some biological condensation reactions are shown.

In addition, six chapters in the last part of the book (Chapters 21–26) focus on the organic chemistry of living systems. These chapters have the unique distinction of containing more chemistry than is typically found in the corresponding parts of a biochemistry text. Chapter 23 (Catalysis in Organic Reactions and in Enzymatic Reactions), for example, explains the various modes of catalysis employed in organic reactions and then shows that they are identical to the modes of catalysis found in reactions catalyzed by enzymes. All of this is presented in a way that allows students to understand the lightning-fast rates of enzymatic reactions. Chapter 24 (The Organic Chemistry of the Coenzymes, Compounds Derived from Vitamins) emphasizes the role of vitamin B_1 in electron delocalization, vitamin K as a strong base, vitamin B_{12} as a radical initiator, biotin as a compound that transfers a carboxyl group by means of a nucleophilic addition–elimination reaction, and describes how the many different reactions of vitamin B_6 have common mechanisms. Chapter 25 (The Organic Chemistry of Metabolic Pathways • Terpene Biosynthesis) explains the chemical function of ATP and shows the students that the reactions encountered in metabolism are just additional examples of reactions that they already have mastered. In Chapter 26 (The Chemistry of the Nucleic Acids), students learn that 2′-OH group on the ribose molecules in RNA catalyzes its hydrolysis and that is why DNA, which has to stay in tact for the life of the cell, does not have 2′-OH groups. Students also see that the synthesis of proteins in cells is just another example of a nucleophilic-addition elimination reaction. Thus, these chapters do not replicate what will be covered in a biochemistry course; they provide a bridge between the two disciplines, allowing students to see how the organic chemistry that they have learned is repeated in the biological world.

AN EARLY AND CONSISTENT EMPHASIS ON ORGANIC SYNTHESIS

Students are introduced to synthetic chemistry and retrosynthetic analysis early in the book (Chapters 6 and 7, respectively), so they can start designing multistep syntheses early in the course. Nine special sections on synthesis design, each with a different focus, are introduced at appropriate intervals. There is a new tutorial on synthesis and retrosynthetic analysis that includes some examples of complicated multistep syntheses from the literature.

PROBLEMS, SOLVED PROBLEMS, AND PROBLEM-SOLVING STRATEGIES

The book contains more than 2000 problems, many with multiple parts. The answers (and explanations, when needed) to all the problems are in the accompanying *Study Guide and Solutions Manual*, which I authored to ensure consistency in language with the text. The problems within each chapter are primarily drill problems. They appear at the end of each section, so they allow students to test themselves on material just covered before moving on to the next section. Selected problems are accompanied by worked-out solutions to provide insight into problem-solving techniques. Short answers provided at the end of the book for problems marked with a diamond give students immediate feedback concerning their mastery of a skill or concept. The many Problem-Solving Strategies in the book teach students how to approach various kinds of problems. Each Problem-Solving Strategy is followed by an exercise giving the student an opportunity to use the problem-solving strategy just learned.

The end-of-chapter problems vary in difficulty. They begin with drill problems that integrate material from the entire chapter, requiring the student to think in terms of all the material in the chapter rather than focusing on individual sections. The problems become more challenging as the student proceeds, often reinforcing concepts from prior chapters. The net result for the student is a progressive building of both problem-solving ability and confidence. (I have chosen not to label problems as particularly challenging so as not to intimidate the students before they try to solve the problem.)

Preview the Text

4

Isomers: The Arrangement of Atoms in Space

mirror image

Chapter Openers have all new photos and introductions that allow students to immediately see the relevancy of the chapter content ahead.

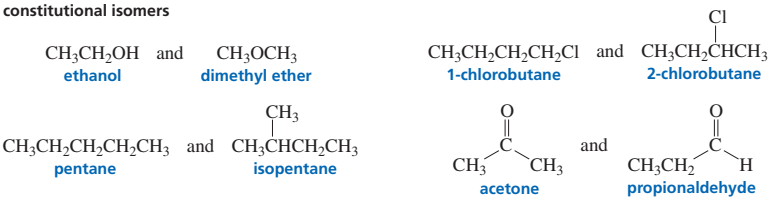
In this chapter we will see why interchanging two groups bonded to a carbon can have a profound effect on the physiological properties of a compound. For example, interchanging a hydrogen and a methyl group converts the active ingredient in Vicks vapor inhaler to methamphetamine, the street drug known as speed. The same change converts the active ingredient in Aleve, a common drug for pain, to a compound that is highly toxic to the liver.

We will now turn our attention to **isomers**—compounds with the same molecular formula but different structures. Isomers fall into two main classes: *constitutional isomers* and *stereoisomers*.

Constitutional isomers differ in the way their atoms are connected (see Problem 17 on page 18). For example, ethanol and dimethyl ether are constitutional isomers because they both have molecular formula C_2H_6O, but their atoms are connected differently (the oxygen in ethanol is bonded to a carbon and to a hydrogen, whereas the oxygen in dimethyl ether is bonded to two carbons).

A new, streamlined narrative allows students to navigate the content more easily and study more effectively.

constitutional isomers



Unlike constitutional isomers, the atoms in stereoisomers are connected in the same way. **Stereoisomers** (also called **configurational isomers**) differ in the way their atoms are arranged in space. Like constitutional isomers, stereoisomers can be separated

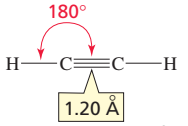
…nd and two π bonds. Because the two unhy-…endicular to each other, they create regions of …in front of and back of the internuclear axis of …

…otential map for ethyne—the negative charge …d the egg-shaped molecule.

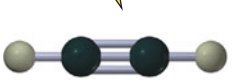
A triple bond consists of one σ bond and two π bonds.

Molecular models and electrostatic potential maps give students an appreciation of what molecules look like in three dimensions and show how charge is distributed within a molecule.

Marginal notes encapsulate key points that students should remember.

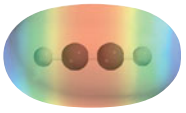


a triple bond consists of one σ bond and two π bonds



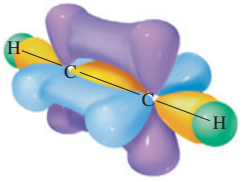
ball-and-stick model of ethyne

space-filling model of ethyne



electrostatic potential map for ethyne

The two carbon atoms in a triple bond are held together by six electrons, so a triple bond is stronger (231 kcal/mol or 967 kJ/mol) and shorter (1.20 Å) than a double bond (174 kcal/mol or 728 kJ/mol, and 1.33 Å).



▲ Figure 1.17
The triple bond has an electron dense region above and below and in front of and in back of the internuclear axis of the molecule.

PROBLEM 28

Put a number in each of the blanks:

a. ___ *s* orbital and ___ *p* orbitals form ____ sp^3 orbitals.
b. ___ *s* orbital and ___ *p* orbitals form ____ sp^2 orbitals.
c. ___ *s* orbital and ___ *p* orbitals form ____ *sp* orbitals.

PROBLEM 29 Solved

For each of the given species:

a. Draw its Lewis structure.
b. Describe the orbitals used by each carbo… bond angles.

1. H_2CO **2.** CCl_4

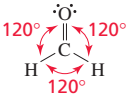
Problems throughout each section and chapter allow students to check whether they have mastered the skills and concepts the particular section is teaching before they move on. Every section in the text works like a mini-tutorial for the students, with key content, supportive art and notes, and problems to allow them to test their understanding.

Solution to 29a1 Our first attempt at … hydrogens on the outside of the molecule) sh… the needed number of bonds.

H—C—O—H

If we place a double bond between carbon and oxygen and move the H from O to C (which still keeps the Hs on the outside of the molecule) then all the atoms end up with the correct number of bonds. Lone-pair electrons are used to give oxygen a filled outer shell. When we check to see if any atom needs to be assigned a formal charge, we find that none of them does.

Solution to 29b1 Because carbon forms a double bond, we know that it uses sp^2 orbitals (as it does in ethene) to bond to the two hydrogens and the oxygen. It uses its "left-over" *p* orbital to form the second bond to oxygen. Because carbon is sp^2 hybridized, the bond angles are approximately 120°.



PROBLEM-SOLVING STRATEGY

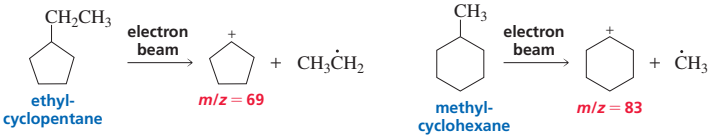
Using Mass Spectra to Determine Structures

The mass spectra of two very stable cycloalkanes both show a molecular ion peak at $m/z = 98$. One spectrum shows a base peak at $m/z = 69$ whereas the other shows a base peak at $m/z = 83$. Identify the cycloalkanes.

First, let's determine the molecular formula of the compounds from the m/z value of their molecular ions. Dividing 98 by 13 results in 7 with 7 left over. Thus, each of the molecular formulas is C_7H_{14}.

Now let's see what fragment is lost to give the base peak. A base peak of 69 means the loss of an ethyl radical $(98 - 69 = 29)$, whereas a base peak of 83 means the loss of a methyl radical $(98 - 83 = 15)$.

Because the two cycloalkanes are known to be very stable, we can assume they do not have three- or four-membered rings. A seven-carbon cycloalkane with a base peak signifying the loss of an ethyl radical must be ethylcyclopentane. A seven-carbon cycloalkane with a base peak signifying the loss of a methyl radical must be methylcyclohexane.

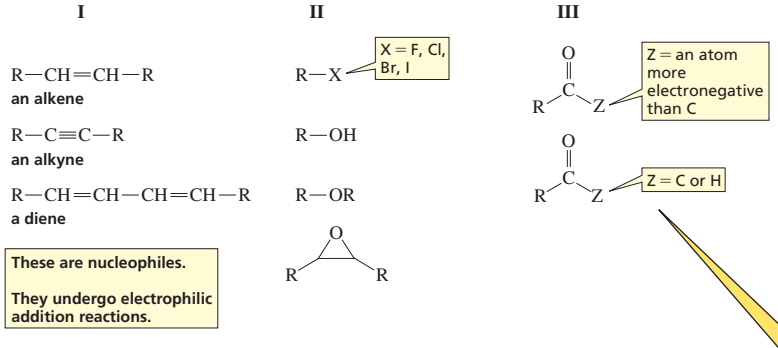


Now use the strategy you have just learned to solve Problem 8.

Problem-Solving Strategies are followed by an exercise that gives students an opportunity to use the problem-solving skill just learned. Students learn how to approach a variety of problems, organize their thoughts, and improve their problem-solving abilities.

8.21 ORGANIZING WHAT WE KNOW ABOUT THE REACTIONS OF ORGANIC COMPOUNDS

When you were first introduced to the reactions of organic compounds in Section 5.6, you saw that organic compounds can be classified into families and that all the members of a family react in the same way. You also saw that each family can be put into one of four groups, and that all the families in a group react in similar ways. Let's revisit the first group.



All the families in the first group are nucleophiles, because of their electron-rich carbon–carbon double or triple bonds. And because double and triple bonds have relatively weak π bonds, the families in this group undergo addition reactions. Since the first species that reacts with a nucleophile is an electrophile, the reactions that the families in this group undergo are more precisely called *electrophilic addition reactions.*

- Alkenes have one π bond so they undergo one electrophilic addition reaction.
- Alkynes have two π bonds so they can undergo two electrophilic addition reactions. However, if the first addition reaction forms an enol, the enol immediately rearranges to a ketone (or to an aldehyde), so a second addition reaction cannot occur.
- If the double bonds of a diene are isolated, they react just like alkenes. If, however, the double bonds are conjugated, they undergo both 1,2- and 1,4-addition reactions, because the carbocation intermediate has delocalized electrons.

In Chapter 9, we will move on to the families in the second group.

Organizing What We Know sections have been added throughout the text to show readers that organic compounds can be classified into families, that all members of a family react the same way, and that the families can be organized into four groups.

The art program throughout contains new annotations and supportive marginal notes to help students visualize organic chemistry while giving them study tools for when they revisit the chapter content.

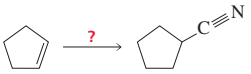
DESIGNING A SYNTHESIS II

Expanded "Designing a Synthesis" features help students learn to design a multistep synthesis. Each of these emphasizes a different tool in the synthetic chemist's toolbox.

10.11 APPROACHING THE PROBLEM

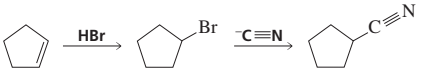
When you are asked to design a synthesis, one way to approach the task is to think about the starting material you have been given and ask yourself if there is an obvious series of reactions beginning with the starting material that can get you on the road to the **target molecule** (the desired product). Sometimes this is the best way to approach a *simple* synthesis. The following examples will give you practice employing this strategy.

Example 1. Using the given starting material, how could you prepare the target molecule?



Adding HBr to the alkene would form a compound with a leaving group that can be replaced by a nucleophile. Because $^{-}C{\equiv}N$ is a relatively weak base (the pK_a of $HC{\equiv}N$ is 9.1), the desired substitution reaction will be favored over the competing elimination reaction.

synthesis

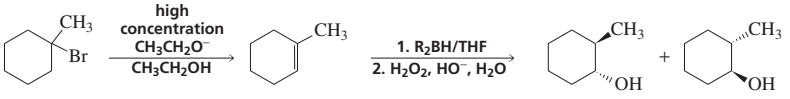


target molecule

Example 2. Starting with 1-bromo-1-methylcyclohexane, how could you prepare *trans*-2-methylcyclohexanol?

Elimination of HBr from the reactant will form an alkene that can add water *via* an electrophilic addition reaction. The elimination reaction should be carried out under E2 conditions because the tertiary alkyl halide will undergo only elimination, so there will be no competing substitution product. Hydroboration-oxidation will put the OH on the right carbon. Because R_2BH will add preferentially to the less sterically hindered side of the double bond and the overall hydroboration–oxidation reaction results in the syn addition of water, the target molecule (as well as its enantiomer) is obtained.

synthesis



target molecule

As you saw in Section 7.12, working backward can be a useful way to design a synthesis, particularly when the starting material does not clearly indicate how to proceed as in Example 3.

Look at the target molecule and ask yourself how it could be prepared. Once you have an answer, look at the precursor you have identified for the target molecule and ask yourself how the precursor could be prepared. Keep working backward one step at a time, until you get to the given starting material. Recall that this technique is called *retrosynthetic analysis*.

Interest boxes connect chemistry to real life and often provide any needed additional instruction. These boxes have been divided into four different categories (Chemical, Medical, Biological, and General). The listing of these categories can be found in the front endpapers.

Which Are More Harmful, Natural Pesticides or Synthetic Pesticides?

Learning to synthesize new compounds is an important part of organic chemistry. Long before chemists learned to synthesize compounds that would protect plants from predators, plants were doing the job themselves. Plants have every incentive to synthesize pesticides. When you cannot run, you need to find another way to protect yourself. But which pesticides are more harmful, those synthesized by chemists or those synthesized by plants? Unfortunately, we do not know because while federal laws require all human-made pesticides to be tested for any adverse effects, they do not require plant-made pesticides to be tested. Besides, risk evaluations of chemicals are usually done on rats, and something that is harmful to a rat may or may not be harmful to a human. Furthermore, when rats are tested, they are exposed to much higher concentrations of the chemical than would be experienced by a human, and some chemicals are harmful only at high doses. For example, we all need sodium chloride for survival, but high concentrations are poisonous; and, although we associate alfalfa sprouts with healthy eating, monkeys fed very large amounts of alfalfa sprouts have been found to develop an immune system disorder.

New Feature: Some Important Things to Remember are end-of-chapter summaries that review the major concepts of the chapter to emphasize key points.

SOME IMPORTANT THINGS TO REMEMBER

- **Alkenes** undergo **electrophilic addition reactions.** These reactions start with the addition of an *electrophile* to the sp^2 carbon bonded to the most hydrogens and end with the addition of a nucleophile to the other sp^2 carbon.
- A curved arrow always points from the electron donor to the electron acceptor.
- The addition of hydrogen halides and the acid-catalyzed addition of water and alcohols form **carbocation intermediates.**
- **Tertiary carbocations** are more stable than **secondary carbocations,** which are more stable than **primary carbocations.**
- The more stable carbocation is formed more rapidly.
- The **Hammond postulate** states that a transition state is more similar in structure to the species to which it is closer in energy.
- **Regioselectivity** is the preferential formation of one **constitutional isomer** over another.
- A carbocation will rearrange if it becomes more stable as a result of the rearrangement.
- **Carbocation rearrangements** occur by **1,2-hydride shifts** and **1,2-methyl shifts.**
- If a reaction does not form a carbocation intermediate, a carbocation rearrangement cannot occur.
- The addition of Br_2 or Cl_2 forms an intermediate with a three-membered ring that reacts with nucleophiles.
- **Ozonolysis** forms an intermediate with a five-membered ring.
- **Hydroboration, epoxidation,** and **catalytic hydrogenation** do not form an intermediate.
- An **oxidation** reaction decreases the number of C—H bonds and/or increases the number of C—O, C—N, or C—X bonds (where X = a halogen).
- A **reduction** reaction increases the number of C—H bonds and/or decreases the number of C—O, C—N, or C—X bonds.

TUTORIAL

Enhanced by MasteringChemistry®

USING MOLECULAR MODELS

Build the models suggested as you proceed through the chapter.

1. Build a model of each of the enantiomers of 2-bromobutane (see page
- **a.** Try to superimpose them.
- **b.** Turn them so you can see that they are mirror images.
- **c.** Which one is (*R*)-2-bromobutane?

2. Build models of the stereoisomers of 3-chloro-2-butanol that are labeled **1** a
the top of page 165.
- **a.** Where are the Cl and OH substituents (relative to each other) in the Fisc
(Recall that in a Fischer projection, the horizontal lines represent bonds
the plane of the paper toward the viewer, whereas the vertical lines repre
point back from the plane of the paper away from the viewer.)
- **b.** Where are the Cl and OH substituents (relative to each other) in the mos
conformer (considering rotation about the C-2—C-3 bond)?

3. **a.** Build models of the stereoisomers of 2,3-dibromobutane labeled **1** and **2** shown on the top of page 169.
- **b.** Build models of their mirror images.
- **c.** Show that the stereoisomer labeled **1** is superimposable on its mirror image, but the stereoisomer labeled **2** is not.

4. Build a model of each of the four stereoisomers of 2,3-dibromopentane. Why does 2,3-dibromopentane have four stereoisomers, whereas 2,3-dibromobutane has only three?

5. Build a model of (*S*)-2-pentanol.

6. Build a model of (2*S*,3*S*)-3-bromo-2-butanol. Rotate the model so its conformation is displayed as a Fischer projection. Compare this structure with that shown on page 174.

7. Build a model of each of the compounds shown in Problem 44 on page 176. Name the compounds.

8. **a.** Build a model of *cis*-1-bromo-4-chlorocyclohexane. Build its mirror image. Are they superimposable?
- **b.** Build a model of *cis*-1-bromo-2-chlorocyclohexane. Build its mirror image. Are they superimposable?

9. Build models of *cis*-1,2-dichlorocyclohexene and *trans*-1,2-dichlorocyclohexene. Build their mirror images. Show that the mirror images of the cis stereoisomers are superimposable but the mirror images of the trans stereoisomers are not superimposable.

10. Build models of the molecules shown in Problems 84a and 84c on page 186. What is the configuration of the asymmetric center in each of the molecules?

Do the *last two* problems after you study Chapter 6.

11. Build two models of *trans*-2-pentene. To each model, add Br_2 to opposite sides of the double bond, adding Br^+ to the top of the double bond in one model and adding it to the bottom of the double bond in the other model, thereby forming the enantiomers shown on page 283. Rotate the models so they represent Fischer projections. Are they erythro or threo enantiomers? Compare your answer with that given on page 283.

12. See the box titled "Cyclic Alkenes" on page 280. Build models of the following compounds. Can any of them not be built?
- **a.** *cis*-cyclooctene
- **b.** *trans*-cyclooctene
- **c.** *cis*-cyclohexene
- **d.** *trans*-cyclohexene

New Tutorials cover critical content areas including acid–base chemistry and retrosynthetic analysis. These print tutorials are paired with MasteringChemistry online tutorials and can be used as additional problem sets that can be assigned as homework or test preparation.

MasteringChemistry®
for Organic Chemistry

MasteringChemistry tutorials guide you through the toughest topics in chemistry with self-paced tutorials that provide individualized coaching. These assignable, in-depth tutorials are designed to coach you with hints and feedback specific to your individual misconceptions. For additional practice on Molecular Models, go to MasteringChemistry where the following tutorials are available:

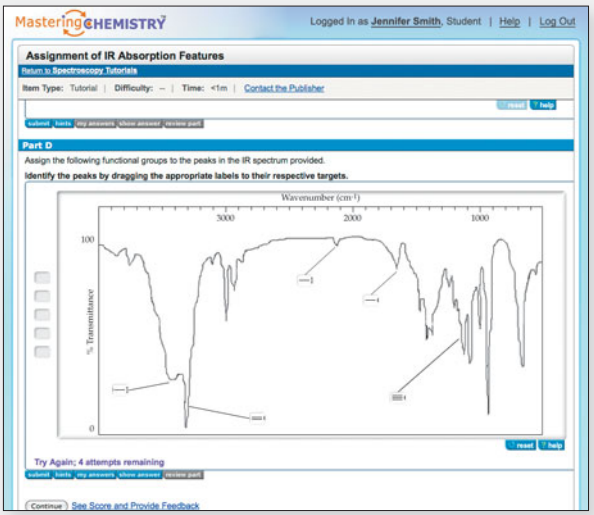
- Using Molecular Models: Basics of Model Building
- Using Molecular Models: Interpret Chiral Models
- Using Molecular Models: Interpret Cyclic Models

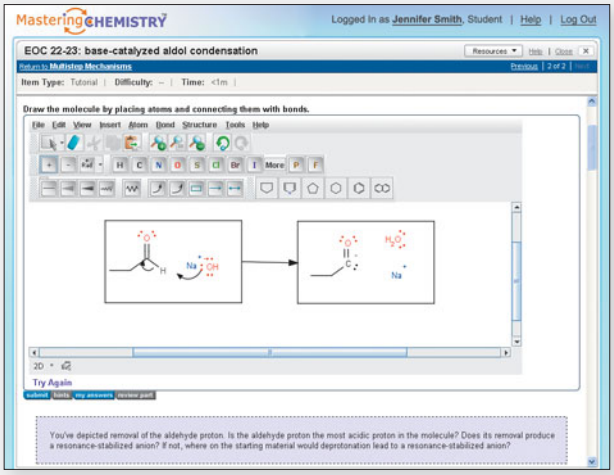
MasteringChemistry® for Organic Chemistry

NEW for this edition! MasteringChemistry® leads students through the process of solving problems while promoting their understanding of chemical concepts. This assessment and tutorial program supplies quantifiable metrics and enables professors to compare their class performance against the national average on specific questions or topics. At a glance, professors can see class distribution of grades, time spent, most difficult problems, most difficult steps, and even the most common answer.

Student Tutorial

MasteringChemistry® tutorials guide students through the toughest topics in organic chemistry with **self-paced tutorials that provide individualized coaching**. These assignable, in depth tutorials are designed to coach students with hints and feedback specific to their individual misconceptions.



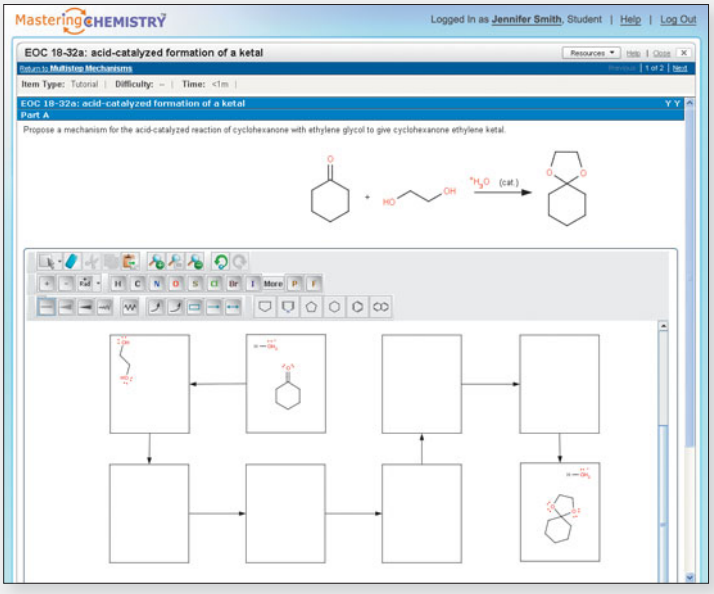


Molecular Drawing Tool

MasteringChemistry's new molecular drawing tool accommodates the diversity of structures and reaction mechanisms inherent to organic chemistry while providing students with error-specific feedback. A comprehensive tutorial on drawing with MarvinSketch within Mastering helps students get up and running quickly on their homework. The drawing tool supports Lewis structures, skeletal structures, and complex mechanisms/arrow pushing and evaluates multiple aspects of the student-created structures in order to provide the most precise feedback possible.

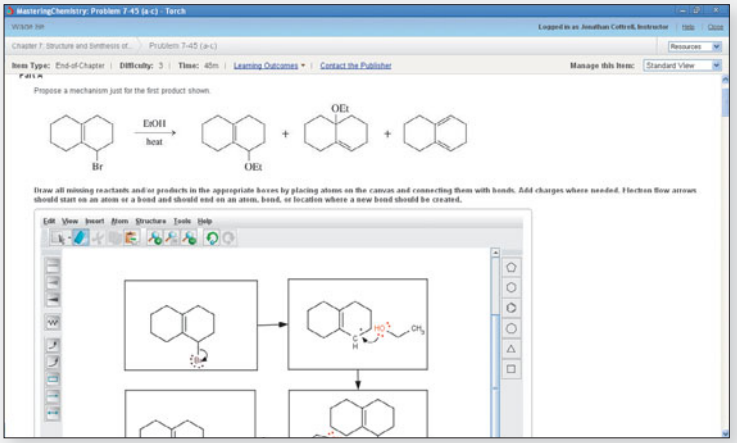
MasteringChemistry® allows students to draw reaction mechanisms. Ranging in difficulty levels, the new mechanism problems provide students with detailed, immediate feedback after each step of their mechanism or, if assigned, feedback after completion of an entire mechanism as to where they made their first mistake. Professors maintain control over the grade value of each mechanistic step and can limit student attempts as well as assign a more challenging mechanistic problem for credit alone. Every individual student attempt is recorded within the gradebook and can be accessed by professors as they work with students to identify their misconceptions.

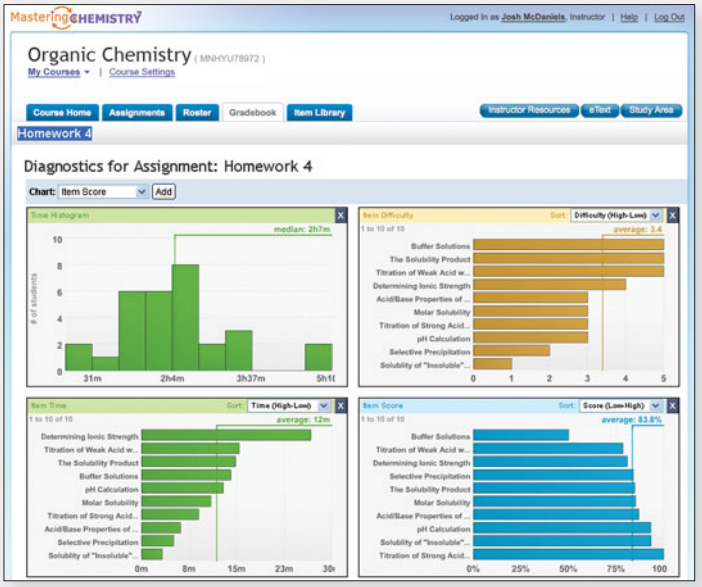
New PreBuilt assignments, compiled by organic chemistry professors, are now available to help make the class start up more effecient.



End of Chapter Problems

Almost all of the Problems from the Seventh Edition of Bruice are available within MasteringChemistry® and can be automatically graded and assigned for homework or practice. A robust, additional problem set associated with each chapter in Bruice can also be assigned to encourage students to apply their knowledge to new problems and provide an excellent source for quiz questions.



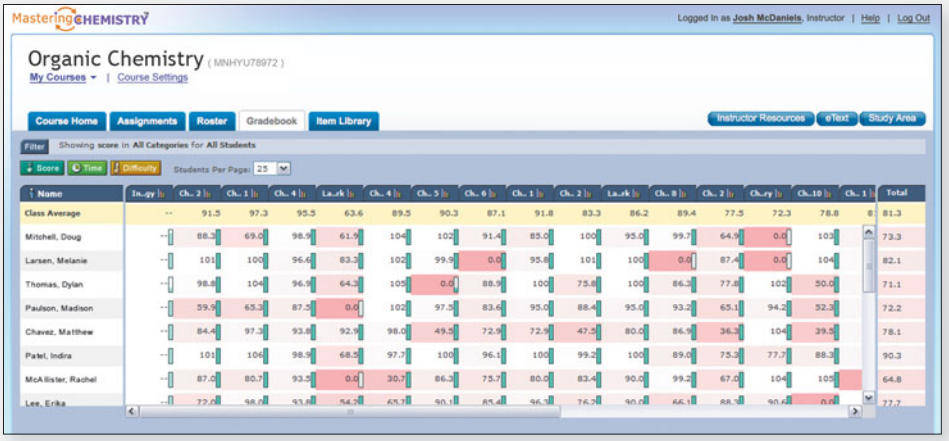


Gradebook

Every assignment is automatically graded. At a glance, shades of red highlight vulnerable students and challenging assignments.

Gradebook Diagnostics

Gradebook Diagnostics provide unique insight into class and student performance. With a single click, charts summarize the most difficult problems, vulnerable students, grade distribution, and score improvement over the duration of the course.



RESOURCES IN PRINT AND ONLINE

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ACKNOWLEDGMENTS

It gives me great pleasure to acknowledge the dedicated efforts of many good friends who made this book a reality—Ed Skibo of Arizona State University, Ron Magid of the University of Tennessee, and Ron Starkey of the University of Wisconsin–Green Bay. Particular thanks go to Jordan Fantini and Malcolm Forbes who checked every inch of the book for accuracy; David Yerzley, M.D., for his assistance with the section on MRI; Warren Hehre of Wavefunction, Inc., and Alan Shusterman of Reed College for their advice on the electrostatic potential maps that appear in the book; and Jeremy Davis who created the art that appears on page 150. I am also very grateful to my students, who pointed out sections that needed clarification, worked the problems and suggested new ones, and searched for errors.

The following reviewers have played an enormously important role in the development of this book.

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To make this textbook as user friendly as possible, I would appreciate any comments that will help me achieve this goal in future editions. If you find sections that could be clarified or expanded, or examples that could be added, please let me know. Finally, this edition has been painstakingly combed for typographical errors. Any that remain are my responsibility; if you find any, please send me a quick e-mail so they can be corrected in future printings of this edition.

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About the Author

Paula Bruice with Zeus, Bacchus, and Abigail

Paula Yurkanis Bruice was raised primarily in Massachusetts. After graduating from the Girls' Latin School in Boston, she earned an A.B. from Mount Holyoke College and a Ph.D. in chemistry from the University of Virginia. She then received an NIH postdoctoral fellowship for study in the Department of Biochemistry at the University of Virginia Medical School and held a postdoctoral appointment in the Department of Pharmacology at the Yale School of Medicine.

Paula has been a member of the faculty at the University of California, Santa Barbara since 1972, where she has received the Associated Students Teacher of the Year Award, the Academic Senate Distinguished Teaching Award, two Mortar Board Professor of the Year Awards, and the UCSB Alumni Association Teaching Award. Her research interests center on the mechanism and catalysis of organic reactions, particularly those of biological significance. Paula has a daughter and a son who are physicians and a son who is a lawyer. Her main hobbies are reading mystery and suspense novels and enjoying her pets (three dogs, two cats, and two parrots).

Organic Chemistry

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PART ONE

An Introduction to the Study of Organic Chemistry

The first three chapters of this text cover a variety of topics that you need to be familiar with in order to start a study of the reactions and synthesis of organic compounds.

CHAPTER 1 Remembering General Chemistry: Electronic Structure and Bonding

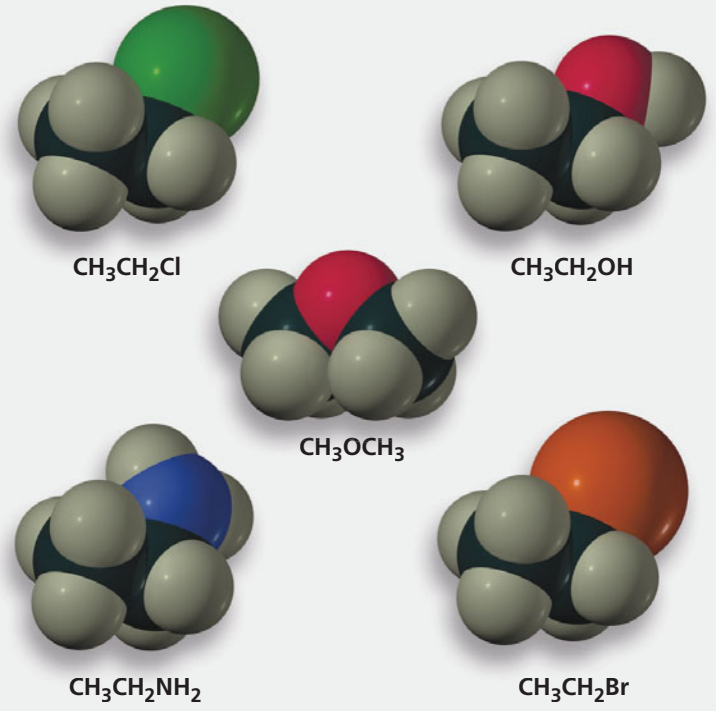
Chapter 1 reviews the topics from general chemistry that will be important to your study of organic chemistry. The chapter starts with a description of the structure of atoms and then proceeds to a description of the structure of molecules. Molecular orbital theory is introduced.

CHAPTER 2 Acids and Bases: Central to Understanding Organic Chemistry

Chapter 2 discusses acid–base chemistry, a topic that is central to understanding many organic reactions. You will see how the structure of a molecule affects its acidity and how the acidity of a solution affects molecular structure.

CHAPTER 3 An Introduction to Organic Compounds: Nomenclature, Physical Properties, and Representation of Structure

To discuss organic compounds, you must be able to name them and to visualize their structures when you read or hear their names. In **Chapter 3,** you will learn how to name five different families of organic compounds. This will give you a good understanding of the basic rules for naming compounds. Because the compounds examined in the chapter are the reactants or the products of many of the reactions presented in the first third of the book, you will have numerous opportunities to review the nomenclature of these compounds as you proceed through these chapters. Chapter 3 also compares and contrasts the structures and physical properties of these compounds, which makes learning about them a little easier than if the structure and physical properties of each family were presented separately. Because organic chemistry is a study of compounds that contain carbon, the last part of Chapter 3 discusses the spatial arrangement of the atoms in both chains and rings of carbon atoms.

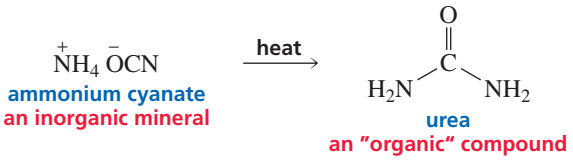


1 Remembering General Chemistry: Electronic Structure and Bonding

To stay alive, early humans must have been able to distinguish between the different kinds of materials in their world. "You can live on roots and berries," they might have said, "but you can't eat dirt. You can stay warm by burning tree branches, but you can't burn rocks."

By the early eighteenth century, scientists thought they had grasped the nature of that difference, and in 1807 Jöns Jakob Berzelius gave names to the two kinds of materials. Compounds derived from living organisms were believed to contain an immeasurable vital force—the essence of life. These he called "organic." Compounds derived from minerals—those lacking the vital force—were "inorganic."

Because chemists could not create life in the laboratory, they assumed they could not create compounds that had a vital force. Since this was their mind-set, you can imagine how surprised chemists were in 1828 when Friedrich Wöhler produced urea—a compound known to be excreted by mammals—by heating ammonium cyanate, an inorganic mineral.



ammonium cyanate
an inorganic mineral

urea
an "organic" compound

NOTE TO THE STUDENT

Biographies of the scientists mentioned in this book can be found on the book's Website.

For the first time, an "organic" compound had been obtained from something other than a living organism and certainly without the aid of any kind of vital force. Chemists, therefore, needed a new definition for "organic compounds." **Organic compounds** are now defined as *compounds that contain carbon.*

Organic compounds are compounds that contain carbon.

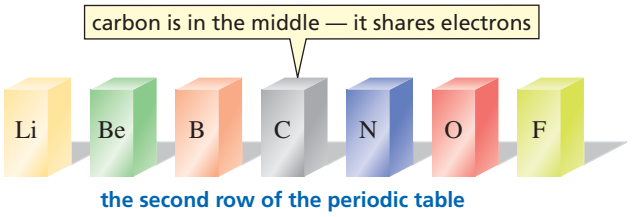
Why is an entire branch of chemistry devoted to the study of carbon-containing compounds? We study organic chemistry because just about all of the molecules that make life possible and that make us who we are—proteins, enzymes, vitamins, lipids, carbohydrates, DNA, RNA—are organic compounds. Thus the chemical reactions that take

place in living systems, including our own bodies, are reactions of organic compounds. Most of the compounds found in nature—those that we rely on for all of our food, for some of our clothing (cotton, wool, silk), and for energy (natural gas, petroleum)—are organic as well.

Organic compounds are not limited, however, to those found in nature. Chemists have learned to synthesize millions of organic compounds never found in nature, including synthetic fabrics, plastics, synthetic rubber, and even things like compact discs and Super Glue. And most importantly, almost all of our commonly prescribed drugs are synthetic organic compounds.

Some synthetic organic compounds prevent shortages of naturally occurring products. For example, it has been estimated that if synthetic materials—nylon, polyester, Lycra—were not available for clothing, then all of the arable land in the United States would have to be used for the production of cotton and wool just to provide enough material to clothe us. Other synthetic organic compounds provide us with materials we would not have—Teflon, Plexiglas, Kevlar—if we had only naturally occurring organic compounds. Currently, there are about 16 million known organic compounds, and many more are possible that we cannot even imagine today.

What makes carbon so special? Why are there so many carbon-containing compounds? The answer lies in carbon's position in the periodic table. Carbon is in the center of the second row of elements. We will see that the atoms to the left of carbon have a tendency to give up electrons, whereas the atoms to the right have a tendency to accept electrons (Section 1.3).



Because carbon is in the middle, it neither readily gives up nor readily accepts electrons. Instead, it shares electrons. Carbon can share electrons with several different kinds of atoms, and it can share electrons with other carbon atoms. Consequently, carbon is able to form millions of stable compounds with a wide range of chemical properties simply by sharing electrons.

Natural Organic Compounds Versus Synthetic Organic Compounds

It is a popular belief that natural substances—those made in nature—are superior to synthetic ones—those made in the laboratory. Yet when a chemist synthesizes a compound, such as penicillin or morphine, the compound is exactly the same in all respects as the compound synthesized in nature. Sometimes chemists can even improve on nature. For example, chemists have synthesized analogues of penicillin that do not produce the allergic responses that a significant fraction of the population experiences from naturally produced penicillin, or that do not have the bacterial resistance of the naturally produced antibiotic (Section 16.15). Chemists have also synthesized analogues of morphine—compounds with structures similar to but not identical to that of morphine—that have pain-killing effects like morphine but, unlike morphine, are not habit forming.

A field of poppies growing in Afghanistan. Most commercial morphine is obtained from opium, the juice extracted from this species of poppy. Morphine is the starting material for the synthesis of heroin. One of the side products formed in the synthesis has an extremely pungent odor; dogs used by drug enforcement agencies are trained to recognize this odor (Section 16.20). Nearly three-quarters of the world's supply of heroin comes from the poppy fields of Afghanistan.

When we study organic chemistry, we learn how organic compounds react. Organic compounds consist of atoms held together by bonds. When an organic compound reacts, some of these bonds break and some new bonds form. *Bonds form when two atoms share electrons, and bonds break when two atoms no longer share electrons.*

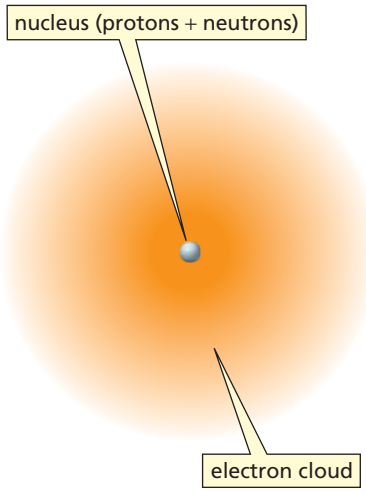
How readily a bond forms and how easily it breaks depend on the particular electrons that are shared, which depend, in turn, on the atoms to which the electrons belong. So, if we are going to start our study of organic chemistry at the beginning, we must start with an understanding of the structure of an atom—what electrons an atom has and where they are located.

1.1 THE STRUCTURE OF AN ATOM

An atom consists of a tiny dense nucleus surrounded by electrons that are spread throughout a relatively large volume of space around the nucleus called an electron cloud. The nucleus contains **positively charged protons** and **uncharged neutrons,** so it is positively charged. The **electrons** are **negatively charged.** The amount of positive charge on a proton equals the amount of negative charge on an electron. Therefore, the number of protons and the number of electrons in an uncharged atom must be the same.

The nucleus contains positively charged protons and uncharged neutrons.

The electrons are negatively charged.



an atom

Electrons move continuously. Like anything that moves, electrons have kinetic energy, and this energy is what counteracts the attractive force of the positively charged protons that would otherwise pull the negatively charged electrons into the nucleus.

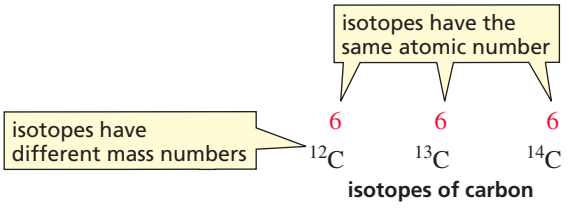
Protons and neutrons have approximately the same mass and are about 1800 times more massive than an electron. Most of the *mass* of an atom, therefore, is in its nucleus. Most of the *volume* of an atom, however, is occupied by its electrons, and this is where our focus will be because it is the electrons that form chemical bonds.

The **atomic number** of an atom is the number of protons in its nucleus. The atomic number is unique to a particular element. For example, the atomic number of carbon is 6, which means that all uncharged carbon atoms have six protons and six electrons. Atoms can gain electrons and thereby become negatively charged, or they can lose electrons and become positively charged, but the number of protons in an atom of a particular element never changes.

Although *all carbon atoms have the same atomic number,* they do not all have the same mass number because they do not all have the same number of neutrons. The **mass number** of an atom is the sum of its protons and neutrons. For example, 98.89% of all carbon atoms have six neutrons—giving them a mass number of 12—and 1.11% have seven neutrons—giving them a mass number of 13. These two different kinds of carbon atoms (^{12}C and ^{13}C) are called **isotopes.**

atomic number = the number of protons in the nucleus

mass number = the number of protons + the number of neutrons



isotopes of carbon

Carbon also contains a trace amount of ^{14}C, which has six protons and eight neutrons. This isotope of carbon is radioactive, decaying with a half-life of 5730 years. (The *half-life* is the time it takes for one-half of the nuclei to decay.) As long as a plant or animal is alive, it takes in as much ^{14}C as it excretes or exhales. When it dies, however, it no longer takes in ^{14}C, so the ^{14}C in the organism slowly decreases. Therefore, the age of a substance derived from a living organism can be determined by its ^{14}C content.

atomic weight = the average mass of the atoms in the element

molecular weight = the sum of the atomic weights of all the atoms in the molecule

The **atomic weight** of an element is the average mass of its atoms. Because an *atomic mass unit (amu)* is defined as exactly 1/12 of the mass of ^{12}C, the atomic mass of ^{12}C is 12.0000 amu; the atomic mass of ^{13}C is 13.0034 amu. Therefore, the atomic weight of carbon is 12.011 amu because $(0.9889 \times 12.0000) + (0.0111 \times 13.0034) = 12.011$.

PROBLEM 1♦

Oxygen has three isotopes, ^{16}O, ^{17}O, and ^{18}O. The atomic number of oxygen is 8. How many protons and neutrons does each of the isotopes have?

PROBLEM 2♦

Chlorine has two isotopes, ^{35}Cl and ^{37}Cl; 75.77% of chlorine is ^{35}Cl and 24.23% is ^{37}Cl. The atomic mass of ^{35}Cl is 34.969 amu and the atomic mass of ^{37}Cl is 36.966 amu. What is the atomic weight of chlorine?

1.2 HOW THE ELECTRONS IN AN ATOM ARE DISTRIBUTED

The bronze sculpture of Albert Einstein, on the grounds of the National Academy of Sciences in Washington, D.C., measures 21 feet from the top of the head to the tip of the feet and weighs 7000 pounds. In his left hand, Einstein holds the mathematical equations that represent his three most important contributions to science: the photoelectric effect, the equivalency of energy and matter, and the theory of relativity. At his feet is a map of the sky.

For a long time, electrons were perceived to be particles—infinitesimal "planets" that orbit the nucleus of an atom. In 1924, however, a French physicist named Louis de Broglie showed that electrons also have wavelike properties. He did this by combining a formula developed by Albert Einstein that relates mass and energy with a formula developed by Max Planck that relates frequency and energy. The realization that electrons have wavelike properties spurred physicists to propose a mathematical concept known as quantum mechanics.

Quantum mechanics uses the same mathematical equations that describe the wave motion of a guitar string to characterize the motion of an electron around a nucleus. The version of quantum mechanics most useful to chemists was proposed by Erwin Schrödinger in 1926.

According to Schrödinger, the electrons in an atom can be thought of as occupying a set of concentric shells that surround the nucleus. The first shell is the one closest to the nucleus. The second shell lies farther from the nucleus. The third and higher numbered shells lie even farther out.

Each shell contains subshells known as **atomic orbitals.** *Each atomic orbital has a characteristic shape and energy and occupies a characteristic volume of space.*

The first shell consists only of an *s* atomic orbital; the second shell consists of *s* and *p* atomic orbitals; the third shell consists of *s*, *p*, and *d* atomic orbitals; and the fourth and higher shells consist of *s, p, d*, and *f* atomic orbitals (Table 1.1).

Table 1.1 Distribution of Electrons in the First Four Shells That Surround the Nucleus

	First shell	Second shell	Third shell	Fourth shell
Atomic orbitals	*s*	*s, p*	*s, p, d*	*s, p, d, f*
Number of atomic orbitals	1	1, 3	1, 3, 5	1, 3, 5, 7
Maximum number of electrons	2	8	18	32

Degenerate orbitals are orbitals that have the same energy.

Each shell contains one *s* orbital. Each second and higher shell—in addition to its *s* orbital—contains three *degenerate p* orbitals. **Degenerate orbitals** are orbitals that have the same energy. The third and higher shells—in addition to their *s* and *p* orbitals—contain five degenerate *d* orbitals, and the fourth and higher shells also contain seven degenerate *f* orbitals.

Because a maximum of two electrons can coexist in an atomic orbital (see the Pauli exclusion principle on page 6), the first shell, with only one atomic orbital, can contain no more than two electrons (Table 1.1). The second shell, with four atomic orbitals—one *s* and three *p*—can have a total of eight electrons. Eighteen electrons can occupy the nine atomic orbitals—one *s*, three *p*, and five *d*—of the third shell, and 32 electrons can occupy the 16 atomic orbitals of the fourth shell. In studying organic chemistry, we will be concerned primarily with atoms that have electrons only in the first and second shells.

The **ground-state electronic configuration** of an atom describes the orbitals occupied by the atom's electrons when they are all in the available orbitals with the lowest energy. If energy is applied to an atom in the ground state, one or more electrons can jump into a higher-energy orbital. The atom then would be in an excited state and have an **excited-state electronic configuration.**

The ground-state electronic configurations of the smallest atoms are shown in Table 1.2. (Each arrow—whether pointing up or down—represents one electron.)

Table 1.2 The Electronic Configurations of the Smallest Atoms

Atom	Name of element	Atomic number	1*s*	2*s*	2p_x	2p_y	2p_z	3*s*
H	Hydrogen	1	↑					
He	Helium	2	↑↓					
Li	Lithium	3	↑↓	↑				
Be	Beryllium	4	↑↓	↑↓				
B	Boron	5	↑↓	↑↓	↑			
C	Carbon	6	↑↓	↑↓	↑	↑		
N	Nitrogen	7	↑↓	↑↓	↑	↑	↑	
O	Oxygen	8	↑↓	↑↓	↑↓	↑	↑	
F	Fluorine	9	↑↓	↑↓	↑↓	↑↓	↑	
Ne	Neon	10	↑↓	↑↓	↑↓	↑↓	↑↓	
Na	Sodium	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑

The following three rules specify which orbitals an atom's electrons occupy:

1. The **aufbau principle** (*aufbau* is German for "building up") tells us the first thing we need to know to be able to assign electrons to the various atomic orbitals. According to this principle:

   An electron always goes into the available orbital with the lowest energy.

   It is important to remember that the closer the atomic orbital is to the nucleus, the lower is its energy.

Because a 1*s* orbital is closer to the nucleus, it is lower in energy than a 2*s* orbital, which is lower in energy—and closer to the nucleus—than a 3*s* orbital. When comparing atomic orbitals in the same shell, we see that an *s* orbital is lower in energy than a *p* orbital, and a *p* orbital is lower in energy than a *d* orbital.

Relative energies of atomic orbitals:

lowest energy → $1s < 2s < 2p < 3s < 3p < 3d$ ← highest energy

2. The **Pauli exclusion principle** states that

   a. **no more than two electrons can occupy each atomic orbital, and**
   b. **the two electrons must be of opposite spin.**

It is called an exclusion principle because it limits the number of electrons that can occupy any particular shell. (Notice in Table 1.2 that spin in one direction is designated by ↑, and spin in the opposite direction by ↓.)

From these first two rules, we can assign electrons to atomic orbitals for atoms that contain one, two, three, four, or five electrons. The single electron of a hydrogen atom occupies a 1*s* orbital, the second electron of a helium atom fills the 1*s* orbital, the third electron of a lithium atom occupies a 2*s* orbital, the fourth electron of a beryllium atom fills the 2*s* orbital, and the fifth electron of a boron atom occupies

one of the 2*p* orbitals. (The subscripts *x, y*, and *z* distinguish the three 2*p* orbitals.) Because the three *p* orbitals are degenerate, the electron can be put into any one of them. Before we can discuss atoms containing six or more electrons, we need to define Hund's rule.

3. **Hund's rule** states that

   when there are two or more atomic orbitals with the same energy, an electron will occupy an empty orbital before it will pair up with another electron.

   In this way, electron repulsion is minimized.

The sixth electron of a carbon atom, therefore, goes into an empty 2*p* orbital, rather than pairing up with the electron already occupying a 2*p* orbital (see Table 1.2). There is one more empty 2*p* orbital, so that is where nitrogen's seventh electron goes. The eighth electron of an oxygen atom pairs up with an electron occupying a 2*p* orbital rather than going into the higher-energy 3*s* orbital.

The locations of the electrons in the remaining elements can be assigned using these three rules.

Core electrons are electrons in inner shells.

Valence electrons are electrons in the outermost shell.

The electrons in inner shells (those below the outermost shell) are called **core electrons.** Core electrons do not participate in chemical bonding. The electrons in the outermost shell are called **valence electrons.**

Carbon has two core electrons and four valence electrons (Table 1.2). Lithium and sodium each have one valence electron. If you examine the periodic table inside the back cover of this book, you will see that lithium and sodium are in the same column. Elements in the same column of the periodic table have the same number of valence electrons. Because the number of valence electrons is the major factor determining an element's chemical properties, elements in the same column of the periodic table have similar chemical properties. Thus, the chemical behavior of an element depends on its electronic configuration.

The chemical behavior of an element depends on its electronic configuration.

PROBLEM 3♦

How many valence electrons do the following atoms have?

a. boron **b.** nitrogen **c.** oxygen **d.** fluorine

PROBLEM 4♦

a. Write electronic configurations for chlorine (atomic number 17), bromine (atomic number 35), and iodine (atomic number 53).

b. How many valence electrons do chlorine, bromine, and iodine have?

PROBLEM 5

Look at the relative positions of each pair of atoms listed here in the periodic table. How many core electrons does each have? How many valence electrons does each have?

a. carbon and silicon
b. oxygen and sulfur
c. nitrogen and phosphorus
d. magnesium and calcium

1.3 IONIC AND COVALENT BONDS

Now that you know about the electronic configuration of atoms, let's now look at why atoms come together to form bonds. In explaining why atoms form bonds, G. N. Lewis proposed that

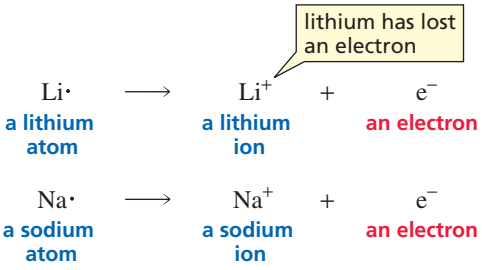
an atom is most stable if its outer shell is either filled or contains eight electrons, and it has no electrons of higher energy.

According to Lewis's theory, an atom will give up, accept, or share electrons in order to achieve a filled outer shell or an outer shell that contains eight electrons. This theory has come to be called the **octet rule** (even though hydrogen needs only two electrons to achieve a filled outer shell).

Lithium (Li) has a single electron in its 2*s* orbital. If it loses this electron, the lithium atom ends up with a filled outer shell—a stable configuration. Lithium, therefore, loses an electron relatively easily. Sodium (Na) has a single electron in its 3*s* orbital, so it too loses an electron easily.

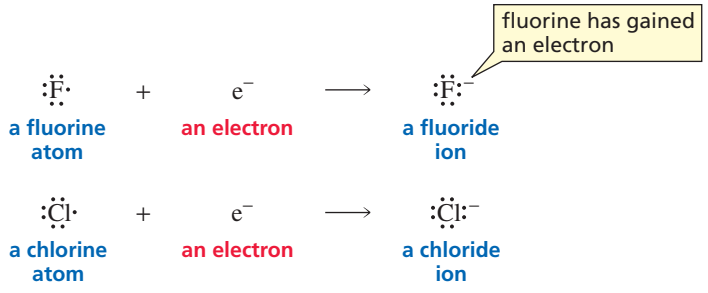
Each of the elements in the first column of the periodic table readily loses an electron because each has a single electron in its outermost shell.

When we draw the electrons around an atom, as in the following equations, core electrons are not shown; only valence electrons are shown because only valence electrons are used in bonding. Each valence electron is shown as a dot. When the single valence electron of lithium or sodium is removed, the species that is formed is called an ion because it carries a charge.

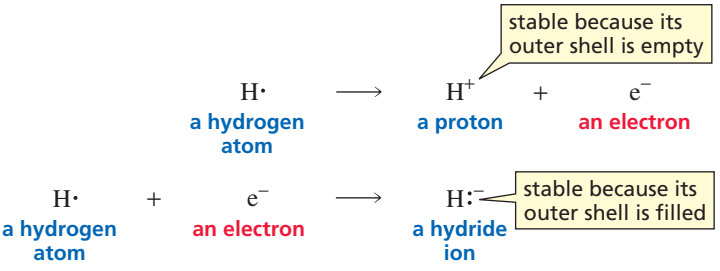


Fluorine has seven valence electrons (Table 1.2). Consequently, it readily acquires an electron in order to have an outer shell of eight electrons, thereby forming F^-, a fluoride ion. Elements in the same column as fluorine (such as chlorine, bromine, and iodine) also need only one electron to have an outer shell of eight, so they, too, readily acquire an electron.

Elements (such as fluorine and chlorine) that readily acquire an electron are said to be electronegative.



A hydrogen atom has one valence electron. Therefore, it can achieve a completely empty shell by losing an electron or a filled outer shell by gaining an electron.



Loss of its sole electron results in a positively charged **hydrogen ion.** A positively charged hydrogen ion is called a **proton** because when a hydrogen atom loses its valence electron, only the hydrogen nucleus—which consists of a single proton—remains. When a

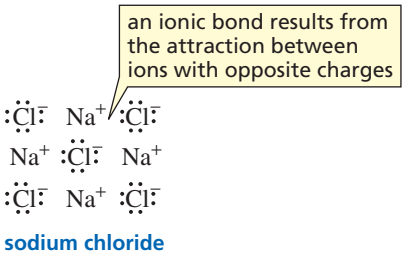
hydrogen atom gains an electron, a negatively charged hydrogen ion—called a **hydride ion**—is formed.

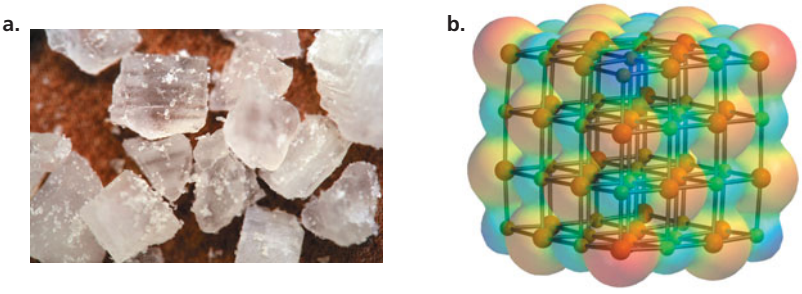
PROBLEM 6♦

a. Find potassium (K) in the periodic table and predict how many valence electrons it has.
b. What orbital does the unpaired electron occupy?

Ionic Bonds Are Formed by the Attraction Between Ions of Opposite Charge

We have just seen that sodium gives up an electron easily and chlorine readily acquires an electron, both in order to achieve a filled outer shell. Therefore, when sodium metal and chlorine gas are mixed, each sodium atom transfers an electron to a chlorine atom, and crystalline sodium chloride (table salt) is the result. The positively charged sodium ions and negatively charged chloride ions are held together by the attraction of opposite charges (Figure 1.1).





An ionic bond results from the attraction between ions of opposite charge.

▲ Figure 1.1

(a) Crystalline sodium chloride.

(b) The electron-rich chloride ions are red, and the electron-poor sodium ions are blue. Each chloride ion is surrounded by six sodium ions, and each sodium ion is surrounded by six chloride ions. Ignore the sticks holding the balls together; they are there only to keep the model from falling apart.

A **bond** is an attractive force between two ions or between two atoms. Attractive forces between opposite charges are called **electrostatic attractions.** A bond formed as a result of the electrostatic attraction between ions of opposite charge is called an **ionic bond.**

Sodium chloride is an example of an ionic compound. **Ionic compounds** are formed when an element on the left side of the periodic table *transfers* one or more electrons to an element on the right side of the periodic table.

Covalent Bonds Are Formed by Sharing a Pair of Electrons

Instead of giving up or acquiring electrons to achieve a filled outer shell, an atom can achieve a filled outer shell by sharing a pair of electrons. For example, two fluorine atoms can each attain a filled second shell by sharing their unpaired valence electrons.

Salar de Uyuni in Bolivia—the largest deposit of natural lithium in the world.

Lithium salts are used clinically. Lithium chloride (Li^+Cl^-) is an antidepressant, lithium bromide (Li^+Br^-) is a sedative, and lithium carbonate ($Li_2{}^+CO_3{}^{2-}$) is used to stabilize mood swings in people who suffer from bipolar disorder. Scientists do not yet know why lithium salts have these therapeutic effects.