



ORGANIC CHEMISTRY

EIGHTH EDITION

L. G. WADE JR.

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L. G. WADE, JR.

WHITMAN COLLEGE

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About the Author

L. G. "Skip" Wade decided to become a chemistry major during his sophomore year at Rice University, while taking organic chemistry from Professor Ronald M. Magid. After receiving his B.A. from Rice in 1969, Wade went on to Harvard University, where he did research with Professor James D. White. While at Harvard, he served as the Head Teaching Fellow for the organic laboratories and was strongly influenced by the teaching methods of two master educators, Professors Leonard K. Nash and Frank H. Westheimer.

After completing his Ph.D. at Harvard in 1974, Dr. Wade joined the chemistry faculty at Colorado State University. Over the course of fifteen years at Colorado State, Dr. Wade taught organic chemistry to thousands of students working toward careers in all areas of biology, chemistry, human medicine, veterinary medicine, and environmental studies. He also authored research papers in organic synthesis and in chemical education, as well as eleven books reviewing current research in organic synthesis. Since 1989, Dr. Wade has been a chemistry professor at Whitman College, where he teaches organic chemistry and pursues research interests in organic synthesis and forensic chemistry. Dr. Wade received the A. E. Lange Award for Distinguished Science Teaching at Whitman in 1993.

Dr. Wade's interest in forensic science has led him to testify as an expert witness in court cases involving drugs and firearms, and he has worked as a police firearms instructor, drug consultant, and boating safety officer. He also enjoys repairing and restoring old violins and bows, which he has done professionally for many years.



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New to this Edition

- 1** Cutting-edge coverage of organometallic reactions and reagents includes the palladium-catalyzed **Suzuki and Heck reactions** that were recognized by the 2010 Nobel Prize in Chemistry. **New discussions of carbon-carbon bond formation**, including organometallic reagents in addition to reducing agents like DIBAL-H, are presented in a manner that introductory students can understand.
- 2** **Modern methods of oxidizing alcohols like Dess-Martin and Swern oxidations** are explained by a unifying mechanism that covers the major methods to oxidize alcohols to aldehydes and ketones (Chapter 11).
- 3** **Additional coverage on silyl ethers** addresses their use as protecting groups for alcohols and carbohydrates.
- 4** **A new section on colored compounds** is added in Chapter 15, including natural and synthetic dyes, and also a **new section on biochemical and clinical applications of UV-visible spectroscopy**.
- 5** **Chapter Goals (Learning Outcomes) added to each chapter align with the Essential Problem-Solving Skills** at the end of each chapter as well as the Study Problems in the text and in MasteringChemistry.
- 6** **Nomenclature has been updated selectively** to reflect the latest IUPAC naming convention standards.
- 7** **A new visual format throughout ensures consistency in the art**, helping students make visual connections between concepts and enhancing their accurate understanding of the figures.
- 8** **Approximately 100 new problems have been added**, both within the chapters and in the Study Problems at the ends of the chapters.
- 9** **New sections and notes of interest to biology majors and premedical students have been added throughout**, including a new section on clinical analysis, as well as numerous applications relating to cancer and toxicology, green chemistry, biochemistry, and medicine.

Preface

To the Student

As you begin your study of organic chemistry, you might feel overwhelmed by the number of compounds, names, reactions, and mechanisms that confront you. You might even wonder whether you can learn all this material in a single year. The most important function of a textbook is to organize the material to show that most of organic chemistry consists of a few basic principles and many extensions and applications of these principles. Relatively little memorization is required if you grasp the major concepts and develop flexibility in applying those concepts. Frankly, I have a poor memory, and I hate memorizing lists of information. I don't remember the specifics of most of the reactions and mechanisms in this book, but I can work them out by remembering a few basic principles, such as "alcohol dehydrations usually go by E1 mechanisms."

Still, you'll have to learn some facts and fundamental principles to serve as the working "vocabulary" of each chapter. As a student, I learned this the hard way when I made a D on my second organic chemistry exam. I thought organic would be like general chemistry, where I could memorize a couple of equations and fake my way through the exams. For example, in the ideal gas chapter, I would memorize $PV = nRT$, and I was good to go. When I tried the same approach in organic, I got a D. We learn by making mistakes, and I learned a lot in organic chemistry.

In writing this book, I've tried to point out a small number of important facts and principles that should be learned to prepare for solving problems. For example, of the hundreds of reaction mechanisms shown in this book, about 20 are the fundamental mechanistic steps that combine into the longer, more complicated mechanisms. I've highlighted these fundamental mechanisms in *Key Mechanism* boxes to alert you to their importance. Spectroscopy is another area where a student might feel pressured to memorize hundreds of facts, such as NMR chemical shifts and infrared vibration frequencies. I couldn't do that, so I've always gotten by with knowing about a dozen NMR chemical shifts and about a dozen IR vibration frequencies, and knowing how they are affected by other influences. I've listed those important infrared frequencies in Table 12-2 and the important NMR chemical shifts in Table 13-3.

Don't try to memorize your way through this course. It doesn't work; you have to know what's going on so you can apply the material. Also, don't think (like I did) that you can get by without memorizing *anything*. Read the chapter, listen carefully to the lectures, and *work the problems*. The problems will tell you whether or not you know the material. If you can do the problems, you should do well on the exams. If you can't do the problems, you probably won't be able to do the exams, either. If you keep having to look up an item to do the problems, that item is a good one to learn.

Here are some hints I give my students at the beginning of the course:

1. Read the material in the book before the lecture (expect 13–15 pages per lecture). Knowing what to expect and what is in the book, you can take fewer notes and spend more time listening and understanding the lecture.
2. After the lecture, review your notes and the book, and do the in-chapter problems. Also, read the material for the next lecture.
3. If you are confused about something, visit your instructor during office hours immediately, before you fall behind. Bring your attempted solutions to problems with you to show the instructor where you are having trouble.
4. To study for an exam, begin by reviewing each chapter and your notes, then concentrate on the end-of-chapter problems. Also use old exams for practice, if available. Many students find that working in a study group and posing problems for each other is particularly helpful.

Remember the two “golden rules” of organic chemistry.

1. ***Don't Get Behind!*** The course moves too fast, and it's hard to catch up.
2. ***Work Lots of Problems.*** Everyone needs the practice, and the problems show where you need more work.

I am always interested to hear from students using this book. If you have any suggestions about how the book might be made better, or if you've found an error, please let me know (L. G. Wade, Whitman College, Walla Walla, WA 99362; E-mail wadelg@whitman.edu). I take students' suggestions seriously, and hundreds of them now appear in this book. For example, Whitman student Brian Lian suggested Figure 21-9, and University of Minnesota student (and race-car driver) Jim Coleman gave me the facts on the use of methanol at Indianapolis.

Good luck with your study of organic chemistry. I'm certain you will enjoy this course, especially if you let yourself relax and develop an interest in how organic compounds influence our lives. My goal in writing this book has been to make the process a little easier: to build the concepts logically on top of each other, so they flow naturally from one to the next. The hints and suggestions for problem solving have helped my students in the past, and I hope some of them will help you to learn and use the material. Even if your memory is worse than mine (highly unlikely), you should be able to do well in organic chemistry. I hope this will be a good learning experience for all of us.

To the Instructor

In writing the first edition of this text, my goal was to produce a modern, readable text that uses the most effective techniques of presentation and review. I wanted a book that presents organic chemistry at the level needed for chemistry and biochemistry majors, but one that presents and explains the material in ways that facilitate success for all the many different kinds of students who take the course. Subsequent editions have extended and refined these goals, with substantial rewriting and reorganizing and with many new features. This eighth edition incorporates even more refinements than the seventh edition with revisions in the organization, writing, and graphics.

NEW TO THIS EDITION

In order to help students navigate the material and study more effectively, **summarized Chapter Goals** have been added to the start of each chapter to reflect the major focus and breadth of the chapter content. **Revised Essential Problem-Solving Skills** at the end of each chapter reinforce the **Chapter Goals** and provide students with a guide to major take-away skills they need from each chapter. **New problem references with the Essential Problem-Solving Skills** enable students to identify which in-chapter and end-of-chapter problems will help them master each of the skills. **Updated Applications**, including cases relating to cancer and toxicology, green chemistry, biochemistry, and medicine, now have descriptive titles to help students understand the relevance of an example to what they are learning in the text. Contemporary content has been updated throughout, including the palladium catalyzed Suzuki and Heck reactions, biochemical and clinical applications of UV-visible spectroscopy, a brief introduction to graphene, and the use of silyl ethers as a protecting group for alcohols ensuring that this edition is the most up-to-date organic chemistry resource possible. A **revised visual program** helps students make visual and accurate connections between concepts and from one figure to the next.

KEY FEATURES

Up-to-Date Treatment: In addition to the classical reactions, this book covers many techniques and reactions that have more recently gained wide use among practicing chemists. Molecular-orbital theory is included early and used to explain electronic effects in conjugated and aromatic systems, pericyclic reactions, and ultraviolet spectroscopy. Carbon-13 NMR spectroscopy is treated as the routine tool it has become in most research laboratories, and the DEPT technique is included in this edition. Many of the newer

synthetic techniques are also included, such as Suzuki coupling and the Heck reaction, asymmetric hydrogenation and epoxidation, reductions using DIBAL-H, olefin metathesis, silyl ether protecting groups, and oxidations using chromium-free reagents such as the Swern and Dess–Martin oxidations.

Reaction Mechanisms: Reaction mechanisms are important in all areas of organic chemistry, but they are difficult for many students. Students fall into the trap of memorizing a mechanism while not understanding why it proceeds as it does. This book stresses the principles used to predict mechanisms. Problem-solving sections develop basic techniques for approaching mechanism problems, and they work to minimize rote memorization. These techniques emphasize deciding whether the reaction is acidic, basic, or free radical in nature, then breaking it down into Lewis acid–base interactions and using “electron pushing arrows” to illustrate these individual steps. Important mechanisms are highlighted by placing them in the *Mechanism* and *Key Mechanism* boxes.

Introduction to Mechanisms Using Free-Radical Halogenation: The advantages and disadvantages of using free-radical halogenation to introduce reaction mechanisms have been debated for many years. The principal objection to free-radical halogenation is that it is not a useful synthetic reaction. But useful reactions such as nucleophilic substitution and additions to alkenes are complicated by participation of the solvent and other effects. Gas-phase free-radical halogenation allows a clearer treatment of kinetics and thermodynamics, as long as its disadvantages as a synthetic reaction are discussed and students are aware of the limitations.

Organic Synthesis: Organic synthesis is stressed throughout this book, with progressive discussions of the process involved in developing a synthesis. *Retrosynthetic analysis* is emphasized, and the student learns to work backward from the target compound and forward from the starting materials to find a common intermediate.

Typical yields have been provided for many synthetic reactions, although I hope students will not misuse these numbers. Too often students consider the yield of a reaction to be a fixed characteristic just as the melting point of a compound is fixed. In practice, many factors affect product yields, and literature values for apparently similar reactions often differ by a factor of 2 or more. The yields given in this book are *typical* yields that a good student with excellent technique might obtain.

Spectroscopy: Spectroscopy is one of the most important tools of the organic chemist. This book develops the theory for each type of spectroscopy and then discusses the characteristic spectral features. The most useful and dependable characteristics are summarized into a small number of rules of thumb that allow the student to interpret most spectra without looking up or memorizing large tables of data. For reference use, extensive tables of NMR and IR data are provided as appendices.

This approach is particularly effective with IR and NMR spectroscopy, and with mass spectrometry. Practical rules are given to help students see what information is available in the spectrum and what spectral characteristics usually correspond to what structural features. Sample problems and Study Problems located throughout the text show how the clues from various spectra are combined to propose a structure. The emphasis is on helping students develop an intuitive feel for using spectroscopy to solve structural problems. A comprehensive list of the spectroscopy problems found in each chapter is available online at www.pearsonhighered.com.

Nomenclature: The most recent IUPAC nomenclature is stressed throughout the book, but common nomenclature is also discussed and used to develop students' familiarity. Teaching only the IUPAC nomenclature might be justifiable in theory, but such an approach would handicap students in their further study and use of the literature. Much of the literature of chemistry, biology, and medicine uses common names such as methyl ethyl ketone, isovaleric acid, methyl *tert*-butyl ether, γ -aminobutyric acid, and ϵ -caprolactam. This book emphasizes why systematic nomenclature is often preferred, yet it encourages familiarity with common names as well.

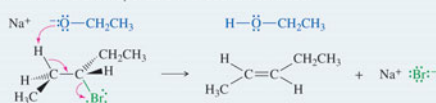
Key Mechanism Boxes

KEY MECHANISM 6-10 The E2 Reaction

The concerted E2 reaction takes place in a single step. A strong base abstracts a proton on a carbon next to the leaving group, and the leaving group leaves. The product is an alkene.



EXAMPLE: E2 elimination of 3-bromopentane with sodium ethoxide.



The order of reactivity for alkyl halides in E2 reactions is $3^\circ > 2^\circ > 1^\circ$.

PROBLEM 6-36

Under second-order conditions (strong base/nucleophile), S_N2 and E2 reactions may occur simultaneously and compete with each other. Show what products might be expected from the reaction of 2-bromo-3-methylbutane (a moderately hindered 2° alkyl halide) with sodium ethoxide.

20 Key Mechanism Boxes are the fundamental mechanistic principles that recur throughout the course. They are the mechanisms that compose most of the longer, more complex mechanisms. Each Key Mechanism Box reinforces student understanding with steps and explanations that describe the the reaction mechanism (how the reaction occurs), a specific example of the mechanism for reinforcement, and a concluding problem or question so students can assess their understanding.

Mechanism Boxes

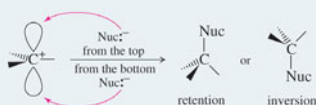
MECHANISM 6-5 Racemization in the S_N1 Reaction

The S_N1 reaction involves ionization to a flat carbocation, which can be attacked from either side.

Step 1: Ionization of a tetrahedral carbon gives a flat carbocation.



Step 2: A nucleophile may attack either side of the carbocation.



These two products may be different if the carbon atom is stereogenic.

150 Mechanism Boxes help students understand how reactions occur by focusing on the individual steps of each reaction. The Mechanism Boxes are shaded in blue so students can locate them easily as they thumb through the chapter.

Multi-Part Problems

SOLVED PROBLEM 5-5

Calculate the e.e. and the specific rotation of a mixture containing 6.0 g of (+)-butan-2-ol and 4.0 g of (-)-butan-2-ol.

SOLUTION

In this mixture, there is a 2.0 g excess of the (+) isomer and a total of 10.0 g, for an e.e. of 20%. We can envision this mixture as 80% racemic [4.0 g (+) and 4.0 g (-)] and 20% pure (+).

$$\text{o.p.} = \text{e.e.} = \frac{6.0 - 4.0}{6.0 + 4.0} = \frac{2.0}{10.0} = 20\%$$

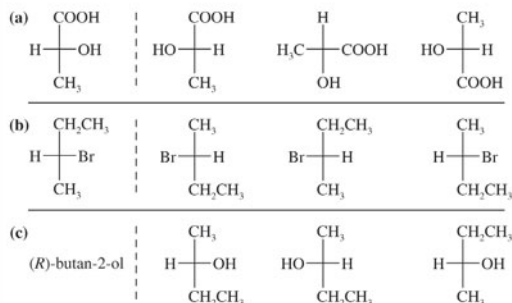
The specific rotation of enantiomerically pure (+)-butan-2-ol is $+13.5^\circ$. The rotation of this mixture is

$$\begin{aligned} \text{observed rotation} &= (\text{rotation of pure enantiomer}) \times (\text{o.p.}) \\ &= (+13.5^\circ) \times (20\%) = +2.7^\circ \end{aligned}$$

Over 1400 (mostly multi-part) problems provide immediate review and reinforcement as students learn the material and make sure they understand each section well enough before moving on to the next.

PROBLEM 5-16

For each set of examples, make a model of the first structure, and indicate the relationship of each of the other structures to the first structure. Examples of relationships: same compound, enantiomer, structural isomer.



Problem Solving Strategies

Problem-Solving Strategies help students break down the multitude of complex problems into simpler pieces and help students establish thoughtful methods for approaching complicated problems—like those that require proposing mechanisms and developing multi-step synthesis.

PROBLEM-SOLVING STRATEGY

Proposing Reaction Mechanisms

At this point, we have seen examples of three major classes of reaction mechanisms:

- Those involving strong bases and strong nucleophiles
- Those involving strong acids and strong electrophiles
- Those involving free radicals

Many students have difficulty proposing mechanisms. We can use some general principles to approach this process, however, by breaking it down into a series of logical steps. Using a systematic approach, we can usually come up with a mechanism that is at least possible and that explains the products, without requiring any unusual steps. Appendix 3A contains more complete methods for approaching mechanism problems.

First, Classify the Reaction

Before you begin to propose a mechanism, you must determine what kind of reaction you are dealing with. Examine what you know about the reactants and the reaction conditions:

A free-radical initiator such as chlorine, bromine, or a peroxide (with heat or light) suggests that a free-radical chain reaction is most likely. Free-radical reactions were discussed in detail in Chapter 4.

Strong acids or strong electrophiles (or a reactant that can dissociate to give a strong electrophile) suggest mechanisms such as the S_N1 , $E1$, alcohol dehydration, etc. that involve carbocations and other strongly acidic intermediates.

Strong bases or strong nucleophiles suggest mechanisms such as the S_N2 or $E2$, involving attack by the strong base or nucleophile on a substrate.

Problem Solving Hints

Problem Solving Hints appear in the margins and remind students of facts or principles that may be useful for solving common types of problems. They are the tips the author gives his own students to help them work problems and reviews for exams.

Problem-solving Hint

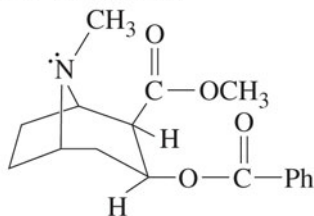
Every object has a mirror image. Is its mirror image the same or different? Different: The object is chiral. Same: The object is achiral.

Application Boxes

Application Boxes throughout demonstrate the relevance of Organic Chemistry to students' lives and areas of interest including contemporary topics such as Biochemistry, Drugs, Environment, Medicine, Fuels, and Green Chemistry.

Application Drugs

Bicyclic molecules are found in many natural product structures. Cocaine is a derivative of bicyclo[3.2.1]octane in which nitrogen replaces the carbon at the one-carbon bridge.



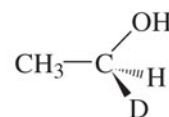
cocaine
in coca leaves

Application: Fuels

Tetraethyl lead (TEL), formula $(CH_3CH_2)_4Pb$, was once added to gasoline to increase the octane rating and lubricate the valves. In the 1970s lead was banned from automotive gasoline because it inactivates catalytic converters and introduces lead into the environment. TEL is still used in 100LL, which is low-lead 100-octane aviation fuel for piston aircraft engines. No suitable replacement fuel has yet been certified for the old engines.

Application: Biochemistry

Scientists frequently use the isotopes of hydrogen to assign the configuration of the products of biological reactions. Ethanol, made chiral by the presence of a deuterium (D or 2H), is one of the early examples.



(*S*)-1-deuterioethanol

Chapter Goals and Essential Problem Solving Skills

GOALS FOR CHAPTER 4

- | | |
|---|--|
| <ol style="list-style-type: none"> 1 Propose mechanisms and explain the steps for simple reactions such as free-radical halogenation. 2 Draw a reaction-energy diagram, and use it to identify the factors controlling the thermodynamics and kinetics of a reaction. | <ol style="list-style-type: none"> 3 Use the mechanism, thermodynamics, and kinetics of a reaction to predict which of several possible products is the major product. 4 Identify reactive intermediates and explain their properties. |
|---|--|

ESSENTIAL PROBLEM-SOLVING SKILLS IN CHAPTER 4

Each skill is followed by problem numbers exemplifying that particular skill.

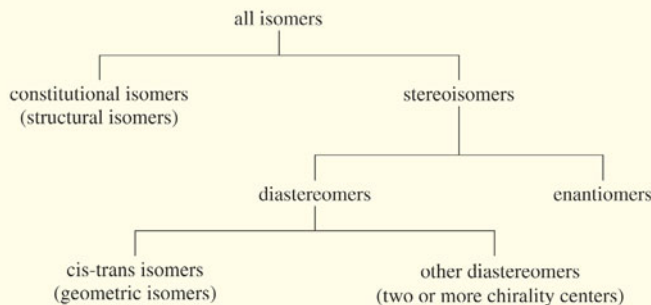
- | | |
|--|--|
| <ol style="list-style-type: none"> 1 Propose a detailed mechanism for the free-radical halogenation of an alkane. 2 Predict the major halogenation products based on the stability of the intermediates and the selectivity of the halogenation. 3 Draw a reaction-energy diagram for a mechanism, and point out the corresponding transition states, activation energies, intermediates, and rate-limiting steps. 4 Use bond-dissociation enthalpies to calculate the enthalpy change for each step of a reaction, and the overall enthalpy change for the reaction. 5 Calculate free-energy changes from equilibrium constants, and calculate the position of an equilibrium from the free-energy changes. 6 Determine the kinetic order of a reaction based on its rate equation. 7 Use the Hammond postulate to predict whether a transition state will be reactant-like or product-like, and explain how this distinction affects the selectivity of a reaction. 8 Draw and describe the structures of carbocations, carbanions, free radicals, and carbenes and the structural features that stabilize them. Explain which are electrophilic and which are nucleophilic. | <p>Problems 4-43, 45, 50, and 55</p> <p>Problems 4-42, 46, 47, and 48</p> <p>Problems 4-35, 36, and 37</p> <p>Problems 4-40, 50, 53, 54, 55, and 57</p> <p>Problems 4-52 and 57</p> <p>Problems 4-34 and 38</p> <p>Problems 4-49 and 56</p> <p>Problems 4-39, 41, 44, 45, 46, and 51</p> |
|--|--|

Enhanced pedagogical tools including Chapter Goals and Essential Problem Solving Skills help students navigate the material and assess their understanding and proficiency throughout each chapter. Professors can use these features at-a-glance to assign homework related to specific skills (also available in MasteringChemistry) while students can study more effectively by solving problems directly tied to chapter goals.

Summary

Summary Feature: The Summaries, located in key locations throughout the chapters highlight important information using charts and graphs when possible.

SUMMARY Types of Isomers



Isomers are different compounds with the same molecular formula.

Constitutional isomers are isomers that differ in the order in which atoms are bonded together. Constitutional isomers are sometimes called **structural isomers** because they have different connections among their atoms.

Stereoisomers are isomers that differ only in the orientation of the atoms in space.

Enantiomers are mirror-image isomers.

Diastereomers are stereoisomers that are not mirror images of each other.

Cis-trans isomers (geometric isomers) are diastereomers that differ in their cis-trans arrangement on a ring or double bond.

Resources in Print and Online

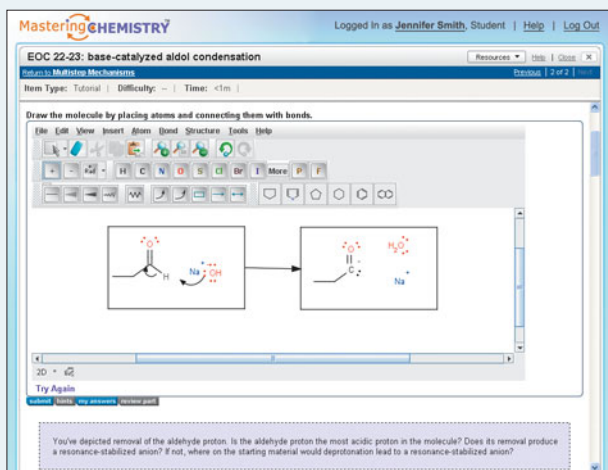
Supplement	Available in Print?	Available Online?	Instructor or Student Supplement	Description
MasteringChemistry®		✓	Instructor and Student Supplement	MasteringChemistry from Pearson has been designed and refined with a single purpose in mind: to help educators create that moment of understanding with their students. The Mastering platform delivers engaging, dynamic learning opportunities—focused on your course objectives and responsive to each student's progress—that are proven to help students absorb course material and understand difficult concepts. By complementing your teaching with our engaging technology and content, you can be confident your students will arrive at that moment—the moment of true understanding. (Available at www.masteringchemistry.com)
Solutions Manual by Jan William Simek	✓		Instructor and Student Supplement	This Solutions Manual provides detailed solutions to all in-chapter as well as the end-of-chapter exercises in the text.
IRDVD	✓	✓	Instructor Supplement	This resource provides an integrated collection of resources to help instructors make efficient and effective use of their time. This DVD features all artwork from the text, including figures and tables in PDF format for high-resolution printing, as well as four pre-built PowerPoint™ presentations. The first presentation contains the images embedded within PowerPoint slides. The second includes a complete lecture outline that is modifiable by the user. The final two presentations contain worked “in chapter” sample exercises and questions to be used with classroom iClicker systems. This DVD also contains movies, animations, and electronic files of the Instructor's Resource Manual, as well as the Test bank.
Testbank	✓	✓	Instructor Supplement	This testbank contains over 3000 multiple-choice, true/false and matching questions. It is available in print format, in the TestGen program, in word format and in included in the item library of MasteringChemistry..
Organic Molecular Kit (Darling)	✓		Instructor and Student Supplement	Darling Models™ contain various pieces used to build atoms, bonds, and molecules. This model kit allows you to build molecules and see the three-dimensional aspects of organic chemistry that can only be imagined in a two-dimensional drawing.
Prentice Hall Molecular Model Kit for Organic Chemistry	✓		Instructor and Student Supplement	The Prentice Hall molecular model set allows you to build space-filling and ball-and-stick models of organic molecules. The components are precision-tooled from quality plastics, are virtually indestructible, and come in a sturdy plastic case for easy storage. Provides a useful Instruction Book—with photos, diagrams, and concise discussions of chemical principles.

Extend Learning Beyond the Classroom

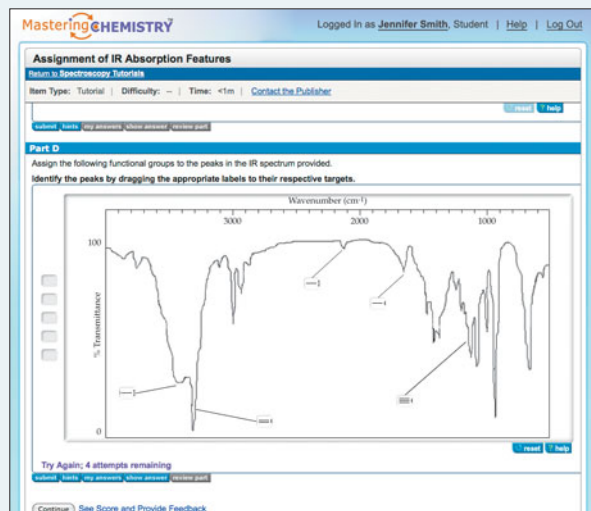
NEW for this edition! MasteringChemistry® leads students through the process of solving problems while promoting their understanding of chemical concepts. This assessment and tutorial program supplies quantifiable metrics and enables professors to compare their class performance against the national 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.

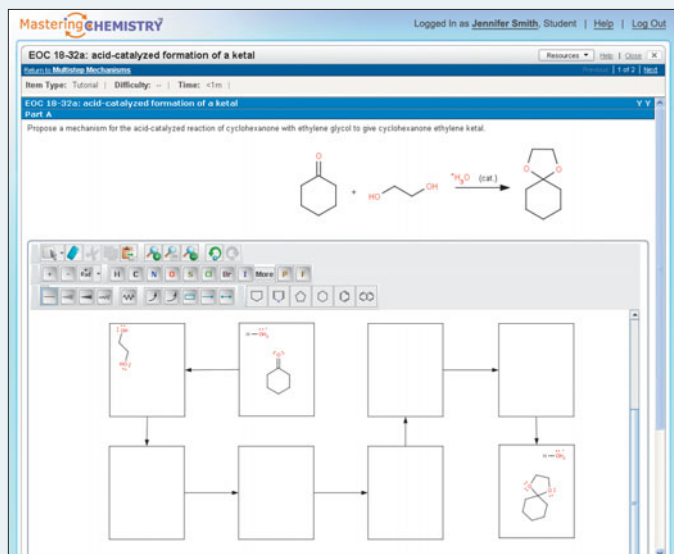


MasteringChemistry allows students to draw reaction mechanisms in a step-wise manner. Ranging in difficulty levels, the new mechanism problem types provide students with detailed, immediate feedback after each step of their mechanism or, if assigned, feedback after completion of an entire multipart mechanism 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.



Molecular Drawing Tool

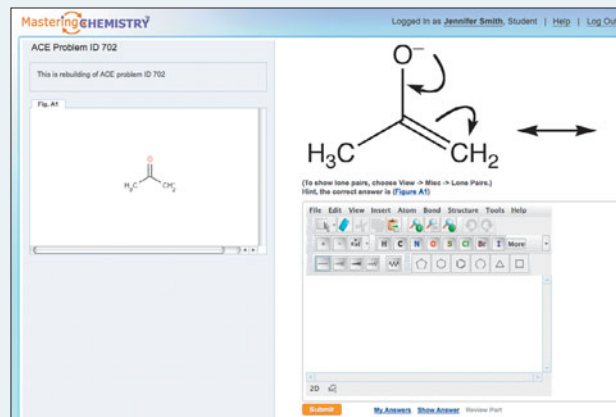
MasteringChemistry's new molecular drawing tool accommodates the diversity of structures and reaction mechanisms inherent to organic chemistry while providing students with error-specific feedback. A comprehensive tutorial on drawing with MarvinSketch within Mastering helps students get up and running 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®

End of Chapter Problems

Almost all Study Problems from the Eighth Edition of Wade 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 Wade 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.



MasteringCHEMISTRY
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Organic Chemistry (MNHYU7872)
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Filter: Showing score in All Categories for All Students

Score Time Difficulty Students Per Page 25

Name	Study 1	Ch. 2	Ch. 3	Ch. 4	Lab 1	Ch. 4	Ch. 5	Ch. 6	Ch. 7	Ch. 8	Ch. 9	Lab 2	Ch. 9	Ch. 10	Ch. 11	Total
Class Average	--	91.5	97.3	95.5	63.6	89.5	90.3	87.1	91.8	83.3	86.2	89.4	77.5	72.3	78.8	81.3
Mitchel, Doug	--	88.3	69.0	98.0	61.9	100	102	91.4	85.0	100	95.4	99.7	64.9	0.0	100	73.3
Larsen, Melanie	--	101	100	96.0	83.3	100	99.9	0.0	95.8	101	100	0.0	87.4	0.0	100	82.1
Thomas, Dylan	--	98.4	104	96.0	64.3	100	0.0	88.9	100	75.9	100	86.3	77.8	100	50.0	71.1
Faulson, Madison	--	59.9	65.5	87.5	0.0	100	97.5	83.6	90.0	88.4	95.0	93.2	65.1	94.5	52.5	72.2
Chavez, Matthew	--	84.4	97.2	93.8	92.9	98.0	49.5	72.9	72.9	47.5	80.0	86.9	36.3	100	39.5	78.1
Patel, Indira	--	101	104	98.0	68.3	97.7	100	94.1	100	99.5	100	89.0	73.5	77.0	88.3	90.3
McWister, Rachel	--	87.0	80.7	93.5	0.0	30.3	86.3	75.7	80.0	83.4	90.0	99.2	67.0	100	100	64.8
Lee, Erica	--	77.0	58.0	91.8	54.3	65.7	90.1	85.4	94.3	74.3	90.9	66.1	88.3	40.8	0.0	77.7

Chapter-by-Chapter Changes

Every chapter begins with Chapter Goals and ends with Essential Problem-Solving Skills, including references to particular end-of-chapter problems that reinforce each skill. New problems, Problem-Solving Hints, Essential Terms, and Applications have been added to almost every chapter. All IUPAC names have been updated to current IUPAC recommendations.

Chapter 1

- The section on acidity has been revised to include inductive effects of substituents on the acidity of carboxylic acids, in addition to resonance effects and electronegativity.

Chapter 2

- The section on solubility has been expanded to emphasize the role of hydrogen bonding and molecular size in the role of water solubility of organic molecules.

Chapter 3

- New problems show the student how to interconvert and name structural formulas and Newman projections.

Chapter 5

- The different types of chemical notation used to indicate the three-dimensional spatial arrangement of bonds around carbon have been presented.

Chapter 8

- Dihydroxylation has been updated to emphasize catalytic methods.

Chapter 9

- New problems emphasizing synthesis and identification of unknown structures have been added.

Chapter 11

- Newer methods of alcohol oxidation (Swern, Dess–Martin) are introduced as environmentally preferable to the older chromium methods, including a description of a general, unifying mechanism of alcohol oxidation to aldehydes and ketones. TEMPO is shown as an oxidation catalyst to enhance hypochlorite oxidation.

Chapter 12

- An Application on the MALDI technique for mass spectral analysis of biological molecules has been added.

Chapter 14

- A new section covers the formation and cleavage of silyl ethers, and their strategy and use as protecting groups on alcohols. This new material introduces the concept of

protecting groups earlier than acetals in Chapter 18. Problems using silyl ether chemistry reinforce the concept.

- Sharpless Asymmetric Epoxidation (Nobel Prize 2001) is presented in a problem.

Chapter 15

- A new section, Colored Organic Compounds, has been added to explain how the HOMO-LUMO concept of highly conjugated molecules leads to absorption in the visible region, and how that applies to natural products, dyes, pH indicators, and food colors.
- A new section, UV-Visible Analysis in Biology and Medicine, has been added to introduce UV analysis in biochemistry, and to show the structural features of biological molecules that are responsible for UV absorption. An example of a reagent used in a clinical analyzer that undergoes a color change when changed by alkaline phosphatase demonstrates how organic chemical principles are used directly in medical technology.

Chapter 16

- A new description of graphene (Nobel Prize 2010 in Physics) has been added in the section on Fullerenes (Nobel Prize 1996) and nanotubes.

Chapter 17

- A new section, Aromatic Substitutions Using Organometallic Reagents, has been added. In addition to expanding the discussion of organocuprate reagents, new discussions of the Heck reaction and Suzuki coupling (Nobel Prize 2010) are introduced, including methods of preparing boronic acids and esters for the Suzuki reaction. Several problems illustrating these reactions in synthesis are included.

Chapter 18

- The chemistry of 1,3-dithianes has been deleted.
- The use of DIBAL-H to reduce nitriles to aldehydes has been added, as has the low-temperature reduction of esters with DIBAL-H to produce aldehydes. Several problems have been added that include these reactions in synthesis.

Chapter 19

- The use of amine salts as phase-transfer catalysts has been deleted.
- Hofmann rearrangement of amides has been deleted.

Chapter 21

- Newly added reactions are DIBAL-H reduction of esters, and dialkylcuprate reaction with acid chlorides to produce ketones.

Chapter 23

- The use of silyl ethers of carbohydrates to alter the solubility properties is incorporated in problems.
- The Fischer proof of glucose has been condensed to an extended problem.

Chapter 26

- Ring-opening metathesis polymerization (ROMP) has been demonstrated in a problem.

Acknowledgments

I am pleased to thank the many talented people who helped with this revision. More than anyone else, Jan William Simek, author of the Solutions Manual, has consistently provided me with excellent advice and sound judgment through several editions of this book. In this edition, Jan provided input on all of the chapter revisions, and helped to write and edit all of the new sections. He also co-authored most of the new problems and all of the Answers to Selected Problems. Particular thanks are also due to Developmental Editor John Murdzek, who made thousands of useful suggestions throughout the writing and revision process, and who helped to shape this new edition.

I would like to thank the reviewers for their valuable insight and commentary. Although I did not adopt all their suggestions, most of them were helpful and contributed to the quality of the final product.

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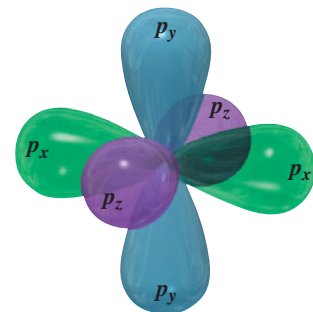
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David Son	Southern Methodist University
Joseph B. Wachter	Michigan State University

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I've enjoyed working on this new edition, and I hope that it is an improved fine-tuning of the seventh edition. I've tried to make this book as error-free as possible, but I'm sure some errors have slipped by. If you find errors, or have suggestions about how the book might be made better, please let me know (L. G. Wade, Whitman College, Walla Walla, WA 99362; e-mail: wadelg@whitman.edu). Errors can be fixed quickly in the next printing. I've already started a file of possible changes and improvements for the next edition, and I hope many of the current users will contribute suggestions to this file. I hope this book makes your job easier and helps more of your students to succeed. That's the most important reason why I wrote it.

L. G. Wade, Jr.
Walla Walla, Washington

1 Introduction and Review



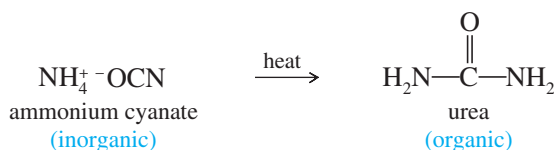
GOALS FOR CHAPTER 1

- 1 Review concepts from general chemistry that are essential for success in organic chemistry, such as the electronic structure of the atom, Lewis structures and the octet rule, types of bonding, electronegativity, and formal charges.
- 2 Predict patterns of covalent and ionic bonding involving C, H, O, N, and the halogens. Identify resonance-stabilized structures and compare the relative importance of their resonance forms.
- 3 Draw and interpret the types of structural formulas commonly used in organic chemistry, including condensed structural formulas and line-angle formulas.
- 4 Identify acids, bases, electrophiles, and nucleophiles. Compare their strengths and predict their reactions based on structure and bonding, as well as K_a and pK_a values.

The modern definition of organic chemistry is *the chemistry of carbon compounds*. What is so special about carbon that a whole branch of chemistry is devoted to its compounds? Unlike most other elements, carbon forms strong bonds to other carbon atoms and to a wide variety of other elements. Chains and rings of carbon atoms can be built up to form an endless variety of molecules. It is this diversity of carbon compounds that provides the basis for life on Earth. Living creatures are composed largely of complex organic compounds that serve structural, chemical, or genetic functions.

The term **organic** literally means “derived from living organisms.” Originally, the science of organic chemistry was the study of compounds extracted from living organisms and their natural products. Compounds such as sugar, urea, starch, waxes, and plant oils were considered “organic,” and people accepted **Vitalism**, the belief that natural products needed a “vital force” to create them. Organic chemistry, then, was the study of compounds having the vital force. Inorganic chemistry was the study of gases, rocks, and minerals, and the compounds that could be made from them.

In the nineteenth century, experiments showed that organic compounds could be synthesized from inorganic compounds. In 1828, the German chemist Friedrich Wöhler converted ammonium cyanate, made from ammonia and cyanic acid, to urea simply by heating it in the absence of oxygen.



1-1 The Origins of Organic Chemistry



The AbioCor self-contained artificial heart, which was first implanted into a patient on July 3, 2001. The outer shell is polycarbonate, and the valves and inner bladder are polyurethane.

Urea had always come from living organisms and was presumed to contain the vital force, yet ammonium cyanate is inorganic and thus lacks the vital force. Some chemists claimed that a trace of vital force from Wöhler's hands must have contaminated the reaction, but most recognized the possibility of synthesizing organic compounds from inorganics. Many other syntheses were carried out, and the vital force theory was eventually discarded.

Since Vitalism was disproved in the early nineteenth century, you'd think it would be extinct by now. And you'd be wrong! Vitalism lives on today in the minds of those who believe that "natural" (plant-derived) vitamins, flavor compounds, etc. are somehow different and more healthful than the identical "artificial" (synthesized) compounds.

As chemists, we know that plant-derived compounds and the synthesized compounds are identical. Assuming they are pure, the only way to tell them apart is through ^{14}C dating: Compounds synthesized from petrochemicals have a lower content of radioactive ^{14}C and appear old because their ^{14}C has decayed over time. Plant-derived compounds are recently synthesized from CO_2 in the air. They have a higher content of radioactive ^{14}C . Some large chemical suppliers provide isotope-ratio analyses to show that their "naturals" have high ^{14}C content and are plant-derived. Such a sophisticated analysis lends a high-tech flavor to this twenty-first-century form of Vitalism.

Even though organic compounds do not need a vital force, they are still distinguished from inorganic compounds. The distinctive feature of organic compounds is that they *all* contain one or more carbon atoms. Still, not all carbon compounds are organic; substances such as diamond, graphite, carbon dioxide, ammonium cyanate, and sodium carbonate are derived from minerals and have typical inorganic properties. Most of the millions of carbon compounds are classified as organic, however.

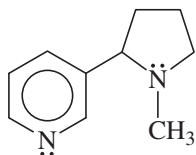
We humans are composed largely of organic molecules, and we are nourished by the organic compounds in our food. The proteins in our skin, the lipids in our cell membranes, the glycogen in our livers, and the DNA in the nuclei of our cells are all organic compounds. Our bodies are also regulated and defended by complex organic compounds.

Application: Biochemistry

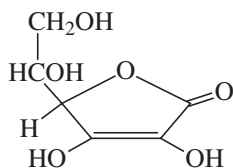
One of nicotine's effects is to increase the concentration of dopamine, a chemical in the brain's reward system. Release of this chemical makes smokers feel good and reinforces the need to smoke.



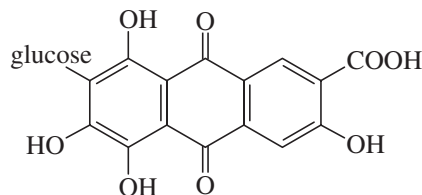
nicotine



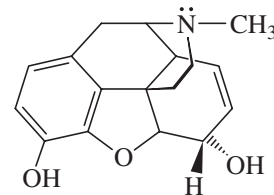
vitamin C



carmine



morphine



Four examples of organic compounds in living organisms. Tobacco contains nicotine, an addictive alkaloid. Rose hips contain vitamin C, essential for preventing scurvy. The red dye carmine comes from cochineal insects, shown on a prickly pear cactus. Opium poppies contain morphine, a pain-relieving, addictive alkaloid.

Chemists have learned to synthesize or simulate many of these complex molecules. The synthetic products serve as drugs, medicines, plastics, pesticides, paints, and fibers. Many of the most important advances in medicine are actually advances in organic chemistry. New synthetic drugs are developed to combat disease, and new polymers are molded to replace failing organs. Organic chemistry has gone full circle. It began as the study of compounds derived from “organs,” and now it gives us the drugs and materials we need to save or replace those organs.

Application: Drug Research

One of the reasons chemists synthesize derivatives of complex organic compounds like morphine is to discover new drugs that retain the good properties (potent painrelieving) but not the bad properties (highly addictive).

Before we begin our study of organic chemistry, we must review some basic principles. These concepts of atomic and molecular structure are crucial to your understanding of the structure and bonding of organic compounds.

1-2A Structure of the Atom

Atoms are made up of protons, neutrons, and electrons. Protons are positively charged and are found together with (uncharged) neutrons in the nucleus. Electrons, which have a negative charge that is equal in magnitude to the positive charge on the proton, occupy the space surrounding the nucleus (Figure 1-1). Protons and neutrons have similar masses, about 1800 times the mass of an electron. Almost all the atom’s mass is in the nucleus, but it is the electrons that take part in chemical bonding and reactions.

Each element is distinguished by the number of protons in the nucleus (the atomic number). The number of neutrons is usually similar to the number of protons, although the number of neutrons may vary. Atoms with the same number of protons but different numbers of neutrons are called **isotopes**. For example, the most common kind of carbon atom has six protons and six neutrons in its nucleus. Its mass number (the sum of the protons and neutrons) is 12, and we write its symbol as ^{12}C . About 1% of carbon atoms have seven neutrons; the mass number is 13, written ^{13}C . A very small fraction of carbon atoms have eight neutrons and a mass number of 14. The ^{14}C isotope is radioactive, with a half-life (the time it takes for half of the nuclei to decay) of 5730 years. The predictable decay of ^{14}C is used to determine the age of organic materials up to about 50,000 years old.

1-2B Electronic Structure of the Atom

An element’s chemical properties are determined by the number of protons in the nucleus and the corresponding number of electrons around the nucleus. The electrons form bonds and determine the structure of the resulting molecules. Because they are small and light, electrons show properties of both particles and waves; in many ways, the electrons in atoms and molecules behave more like waves than like particles.

Electrons that are bound to nuclei are found in **orbitals**. Orbitals are mathematical descriptions that chemists use to explain and predict the properties of atoms and molecules. The *Heisenberg uncertainty principle* states that we can never determine exactly where the electron is; nevertheless, we can determine the **electron density**, the probability of finding the electron in a particular part of the orbital. An orbital, then, is an allowed energy state for an electron, with an associated probability function that defines the distribution of electron density in space.

Atomic orbitals are grouped into different “shells” at different distances from the nucleus. Each shell is identified by a principal quantum number n , with $n = 1$ for the lowest-energy shell closest to the nucleus. As n increases, the shells are farther from the nucleus, higher in energy, and can hold more electrons. Most of the common elements in organic compounds are found in the first two rows of the periodic table, indicating that their electrons are found in the first two electron shells. The first shell ($n = 1$) can hold two electrons, and the second shell ($n = 2$) can hold eight.

The first electron shell contains just the $1s$ orbital. All s orbitals are spherically symmetrical, meaning that they are nondirectional. The electron density is only a function of the distance from the nucleus. The electron density of the $1s$ orbital is graphed

1-2 Principles of Atomic Structure

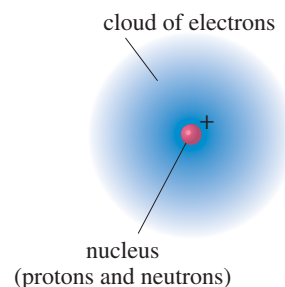


FIGURE 1-1 Basic atomic structure. An atom has a dense, positively charged nucleus surrounded by a cloud of electrons.

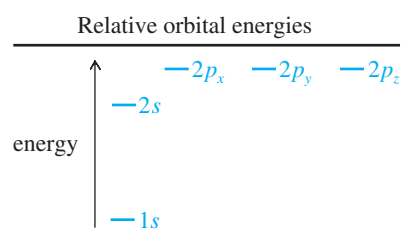
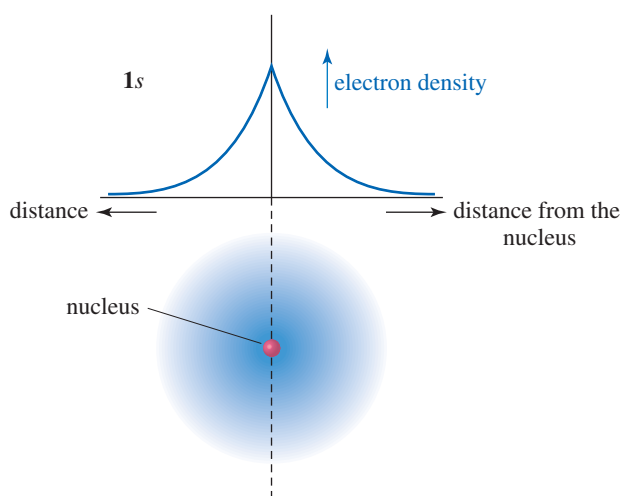


FIGURE 1-2

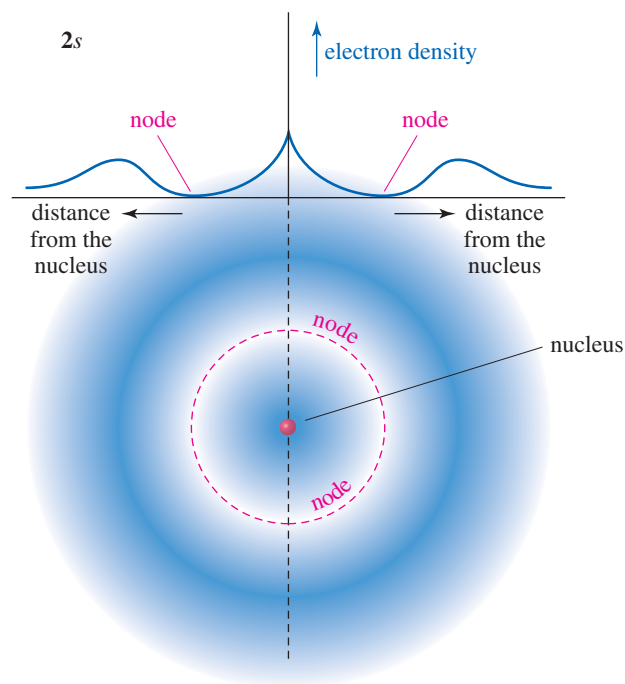
Graph and diagram of the $1s$ atomic orbital. The electron density is highest at the nucleus and drops off exponentially with increasing distance from the nucleus in any direction.



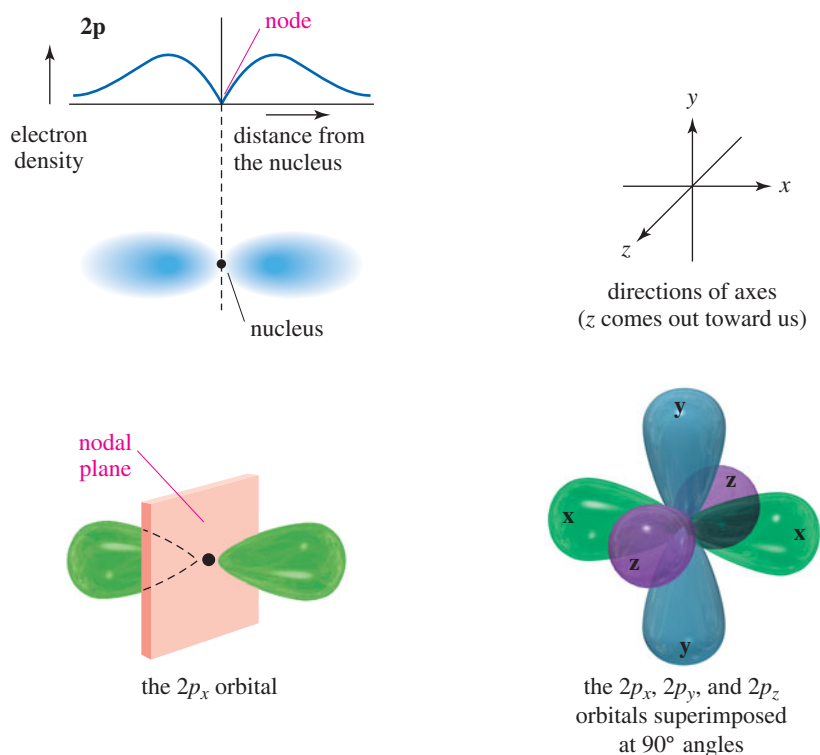
in Figure 1-2. Notice how the electron density is highest *at* the nucleus and falls off exponentially with increasing distance from the nucleus. The $1s$ orbital might be imagined as a cotton boll, with the cottonseed at the middle representing the nucleus. The density of the cotton is highest nearest the seed, and it becomes less dense at greater distances from this “nucleus.”

The second electron shell consists of the $2s$ and $2p$ orbitals. The $2s$ orbital is spherically symmetrical like the $1s$ orbital, but its electron density is not a simple exponential function. The $2s$ orbital has a smaller amount of electron density close to the nucleus. Most of the electron density is farther away, beyond a region of zero electron density called a **node**. Because most of the $2s$ electron density is farther from the nucleus than that of the $1s$, the $2s$ orbital is higher in energy. Figure 1-3 shows a graph of the $2s$ orbital.

In addition to the $2s$ orbital, the second shell also contains three $2p$ atomic orbitals, one oriented in each of the three spatial directions. These orbitals are called the $2p_x$, the $2p_y$, and the $2p_z$, according to their direction along the x , y , or z axis. The $2p$ orbitals

**FIGURE 1-3**

Graph and diagram of the $2s$ atomic orbital. The $2s$ orbital has a small region of high electron density close to the nucleus, but most of the electron density is farther from the nucleus, beyond a node, or region of zero electron density.

**FIGURE 1-4**

The $2p$ orbitals. Three $2p$ orbitals are oriented at right angles to each other. Each is labeled according to its orientation along the x , y , or z axis.

are slightly higher in energy than the $2s$, because the average location of the electron in a $2p$ orbital is farther from the nucleus. Each p orbital consists of two lobes, one on either side of the nucleus, with a **nodal plane** at the nucleus. The nodal plane is a flat (planar) region of space, including the nucleus, with zero electron density. The three $2p$ orbitals differ only in their spatial orientation, so they have identical energies. Orbitals with identical energies are called **degenerate orbitals**. Figure 1-4 shows the shapes of the three degenerate $2p$ atomic orbitals.

The *Pauli exclusion principle* tells us that each orbital can hold a maximum of two electrons, provided that their spins are paired. The first shell (one $1s$ orbital) can accommodate two electrons. The second shell (one $2s$ orbital and three $2p$ orbitals) can accommodate eight electrons, and the third shell (one $3s$ orbital, three $3p$ orbitals, and five $3d$ orbitals) can accommodate 18 electrons.

1-2C Electronic Configurations of Atoms

Aufbau means “building up” in German, and the *aufbau principle* tells us how to build up the electronic configuration of an atom’s ground (most stable) state. Starting with the lowest-energy orbital, we fill the orbitals in order until we have added the proper number of electrons. Table 1-1 shows the ground-state electronic configurations of the elements in the first two rows of the periodic table.

Two additional concepts are illustrated in Table 1-1. The **valence electrons** are those electrons that are in the outermost shell. Carbon has four valence electrons, nitrogen has five, and oxygen has six. Helium has a filled first shell with two valence electrons, and neon has a filled second shell with eight valence electrons (ten electrons total). In general (for the representative elements), the column or group number of the periodic table corresponds to the number of valence electrons (Figure 1-5). Hydrogen and lithium have one valence electron, and they are both in the first column (group 1A) of the periodic table. Carbon has four valence electrons, and it is in group 4A of the periodic table.

Application: Drugs

Lithium carbonate, a salt of lithium, is a mood-stabilizing agent used to treat the psychiatric disorder known as mania. Mania is characterized by behaviors such as elated mood, feelings of greatness, racing thoughts, and an inability to sleep. We don’t know how lithium carbonate helps to stabilize these patients’ moods.

TABLE 1-1 Electronic Configurations of the Elements of the First and Second Rows

Element	Configuration	Valence Electrons
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^2 2s^1$	1
Be	$1s^2 2s^2$	2
B	$1s^2 2s^2 2p_x^1$	3
C	$1s^2 2s^2 2p_x^1 2p_y^1$	4
N	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	5
O	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	6
F	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	7
Ne	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	8

FIGURE 1-5

First three rows of the periodic table. The organization of the periodic table results from the filling of atomic orbitals in order of increasing energy. For these representative elements, the number of the column corresponds to the number of valence electrons.

Partial periodic table

1A							noble gases 8A
H	2A	3A	4A	5A	6A	7A	He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

Notice in Table 1-1 that carbon's third and fourth valence electrons are not paired; they occupy separate orbitals. Although the Pauli exclusion principle says that two electrons can occupy the same orbital, the electrons repel each other, and pairing requires additional energy. **Hund's rule** states that when there are two or more orbitals of the same energy, electrons will go into *different* orbitals rather than pair up in the same orbital. The first $2p$ electron (boron) goes into one $2p$ orbital, the second $2p$ electron (carbon) goes into a different orbital, and the third $2p$ electron (nitrogen) occupies the last $2p$ orbital. The fourth, fifth, and sixth $2p$ electrons must pair up with the first three electrons.

PROBLEM 1-1

- (a) Nitrogen has relatively stable isotopes (half-life greater than 1 second) of mass numbers 13, 14, 15, 16, and 17. (All except ^{14}N and ^{15}N are radioactive.) Calculate how many protons and neutrons are in each of these isotopes of nitrogen.
- (b) Write the electronic configurations of the third-row elements shown in the partial periodic table in Figure 1-5.

1-3

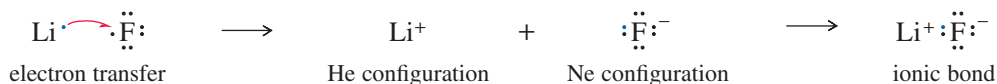
Bond Formation: The Octet Rule

In 1915, G. N. Lewis proposed several new theories describing how atoms bond together to form molecules. One of these theories states that a filled shell of electrons is especially stable, and *atoms transfer or share electrons in such a way as to attain a filled shell of electrons*. A filled shell of electrons is simply the electron configuration of a noble gas, such as He, Ne, or Ar. This principle has come to be called the **octet rule**

because a filled shell implies eight valence electrons for the elements in the second row of the periodic table. Elements in the third and higher rows (such as Al, Si, P, S, Cl, and above) can have an “expanded octet” of more than eight electrons because they have low-lying *d* orbitals available.

1-3A Ionic Bonding

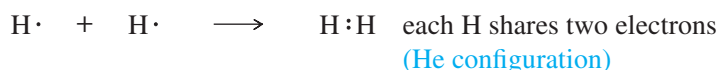
There are two ways that atoms can interact to attain noble-gas configurations. Sometimes atoms attain noble-gas configurations by transferring electrons from one atom to another. For example, lithium has one electron more than the helium configuration, and fluorine has one electron less than the neon configuration. Lithium easily loses its valence electron, and fluorine easily gains one:



A transfer of one electron gives each of these two elements a noble-gas configuration. The resulting ions have opposite charges, and they attract each other to form an **ionic bond**. Ionic bonding usually results in the formation of a large crystal lattice rather than individual molecules. Ionic bonding is common in inorganic compounds but relatively uncommon in organic compounds.

1-3B Covalent Bonding

Covalent bonding, in which electrons are shared rather than transferred, is the most common type of bonding in organic compounds. Hydrogen, for example, needs a second electron to achieve the noble-gas configuration of helium. If two hydrogen atoms come together and form a bond, they “share” their two electrons, and each atom has two electrons in its valence shell.



We will study covalent bonding in more detail in Chapter 2.

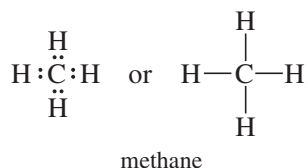
Problem-solving Hint

When we speak of a molecule having “all octets satisfied,” we mean that all the second-row elements have octets. Hydrogen atoms have just two electrons (the He configuration) in their filled valence shell.

1-4 Lewis Structures

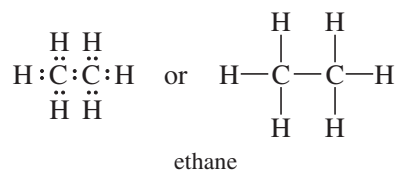
One way to symbolize the bonding in a covalent molecule is to use **Lewis structures**. In a Lewis structure, each valence electron is symbolized by a dot. A bonding pair of electrons is symbolized by a pair of dots or by a dash (—). We try to arrange all the atoms so they have their appropriate noble-gas configurations: two electrons for hydrogen, and octets for the second-row elements.

Consider the Lewis structure of methane (CH_4).



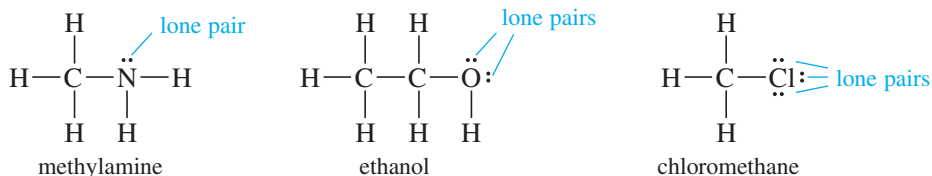
Carbon contributes four valence electrons, and each hydrogen contributes one, to give a total of eight electrons. All eight electrons surround carbon to give it an octet, and each hydrogen atom shares two of the electrons with the carbon atom.

The Lewis structure for ethane (C_2H_6) is more complex.



Once again, we have computed the total number of valence electrons (14) and distributed them so that each carbon atom is surrounded by 8 and each hydrogen by 2. The only possible structure for ethane is the one shown, with the two carbon atoms sharing a pair of electrons and each hydrogen atom sharing a pair with one of the carbons. The ethane structure shows the most important characteristic of carbon—its ability to form strong carbon–carbon bonds.

Nonbonding electrons are valence-shell electrons that are *not* shared between two atoms. A pair of nonbonding electrons is often called a **lone pair**. Oxygen atoms, nitrogen atoms, and the halogens (F, Cl, Br, I) usually have nonbonding electrons in their stable compounds. These lone pairs of nonbonding electrons help to determine the reactivity of their parent compounds. The following Lewis structures show one lone pair of electrons on the nitrogen atom of methylamine and two lone pairs on the oxygen atom of ethanol. Halogen atoms usually have three lone pairs, as shown in the structure of chloromethane.



A correct Lewis structure should show any lone pairs. Organic chemists often draw structures that omit most or all of the lone pairs. These are not true Lewis structures because you must imagine the correct number of nonbonding electrons.

Problem-solving Hint

Lewis structures are the way we write organic chemistry. Learning how to draw them quickly and correctly will help you throughout this course.

PROBLEM 1-2

Draw Lewis structures for the following compounds.

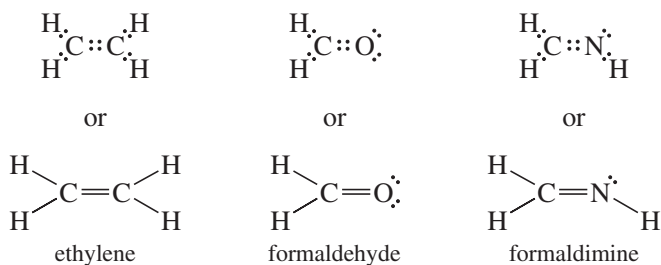
- | | |
|---|--|
| <p>(a) ammonia, NH_3</p> <p>(c) hydroniumion, H_3O^+</p> <p>(e) dimethylamine, CH_3NHCH_3</p> <p>(g) 1-chloropropane, $CH_3CH_2CH_2Cl$</p> <p>(i) borane, BH_3</p> | <p>(b) water, H_2O</p> <p>(d) propane, C_3H_8</p> <p>(f) diethyl ether, $CH_3CH_2OCH_2CH_3$</p> <p>(h) propan-2-ol, $CH_3CH(OH)CH_3$</p> <p>(j) boron trifluoride, BF_3</p> |
|---|--|

Explain what is unusual about the bonding in the compounds in parts (i) and (j).

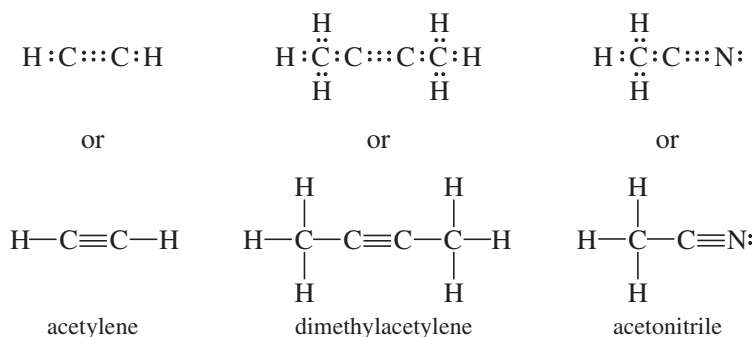
1-5 Multiple Bonding

In drawing Lewis structures in Section 1-4, we placed just one pair of electrons between any two atoms. The sharing of one pair between two atoms is called a **single bond**. Many molecules have adjacent atoms sharing two or even three electron pairs. The sharing of two pairs is called a **double bond**, and the sharing of three pairs is called a **triple bond**.

Ethylene (C_2H_4) is an organic compound with a double bond. When we draw a Lewis structure for ethylene, the only way to show both carbon atoms with octets is to draw them sharing two pairs of electrons. The following examples show organic compounds with double bonds. In each case, two atoms share four electrons (two pairs) to give them octets. A double dash ($=$) symbolizes a double bond.



Acetylene (C_2H_2) has a triple bond. Its Lewis structure shows three pairs of electrons between the carbon atoms to give them octets. The following examples show organic compounds with triple bonds. A triple dash (\equiv) symbolizes a triple bond.



All these Lewis structures show that carbon normally forms four bonds in neutral organic compounds. Nitrogen generally forms three bonds, and oxygen usually forms two. Hydrogen and the halogens usually form only one bond. The number of bonds an atom usually forms is called its **valence**. Carbon is tetravalent, nitrogen is trivalent, oxygen is divalent, and hydrogen and the halogens are monovalent. By remembering the usual number of bonds for these common elements, we can write organic structures more easily. If we draw a structure with each atom having its usual number of bonds, a correct Lewis structure usually results.

SUMMARY Common Bonding Patterns (Uncharged)

	$\begin{array}{c} \\ -\text{C}- \\ \end{array}$	$\begin{array}{c} \cdot \cdot \\ -\text{N}- \\ \cdot \cdot \end{array}$	$\begin{array}{c} \cdot \cdot \\ -\text{O}- \\ \cdot \cdot \end{array}$	$-\text{H}$	$\begin{array}{c} \cdot \cdot \\ -\text{Cl}: \\ \cdot \cdot \end{array}$
	carbon	nitrogen	oxygen	hydrogen	halogens
valence:	4	3	2	1	1
lone pairs:	0	1	2	0	3

PROBLEM 1-3

Write Lewis structures for the following molecular formulas.

- | | | |
|---|--|--|
| (a) N_2 | (b) HCN | (c) HONO |
| (d) CO_2 | (e) CH_3CHNH | (f) HCO_2H |
| (g) $\text{C}_2\text{H}_3\text{Cl}$ | (h) HNNH | (i) C_3H_6 (one double bond) |
| (j) C_3H_4 (two double bonds) | (k) C_3H_4 (one triple bond) | |

PROBLEM 1-4

Circle any lone pairs (pairs of nonbonding electrons) in the structures you drew for Problem 1-3.

Application: FYI

Acetylene is a high-energy gaseous hydrocarbon that is explosive at high pressures. Combined with oxygen, acetylene burns with such a hot flame that it melts steel. Acetylene is commonly used in welding and cutting torches that work anywhere, even underwater. In gas cylinders, acetylene is dissolved in acetone to keep it from getting too concentrated and exploding.

Problem-solving Hint

These "usual numbers of bonds" might be single bonds, or they might be combined into double and triple bonds. For example, three bonds to nitrogen might be three single bonds, one single bond and one double bond, or one triple bond ($:\text{N} \equiv \text{N}:$). In working problems, consider all possibilities.