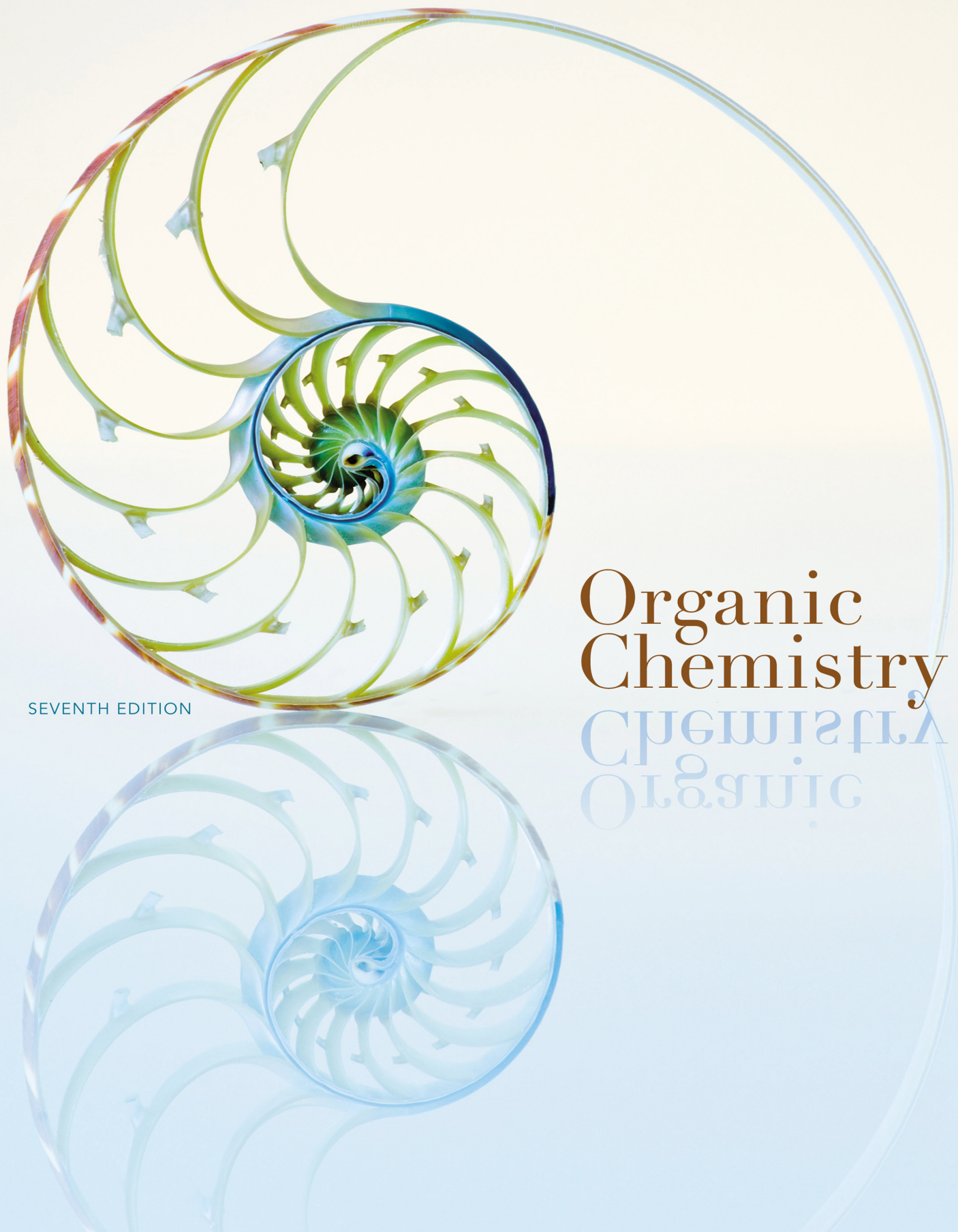


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SEVENTH EDITION

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7th edition

# Organic Chemistry

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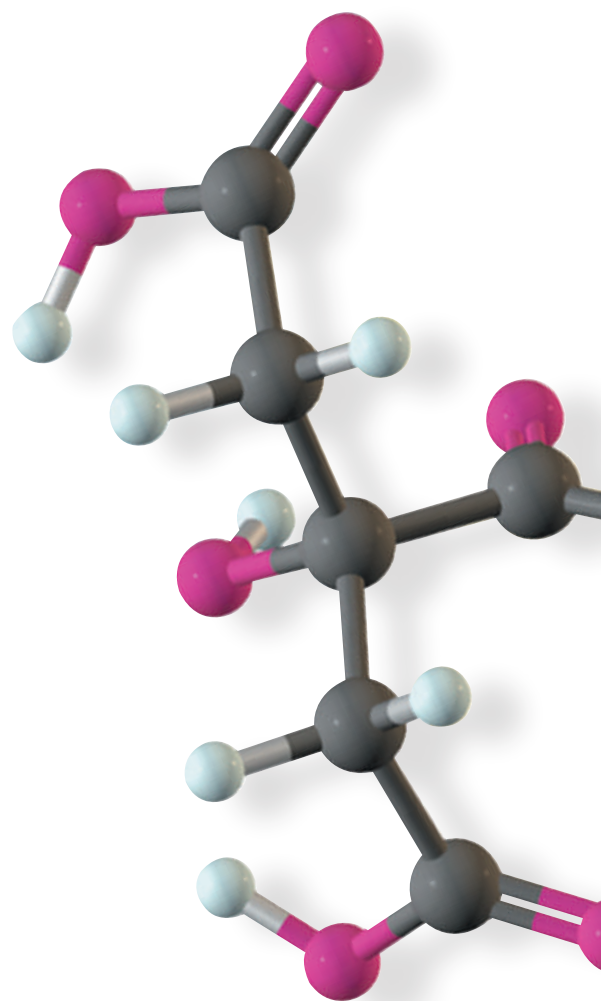
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## Dedication

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This Seventh Edition is dedicated to the memory of our dear friend and colleague, Christopher Foote. Chris's insights, encouragement, and dedication to this project can never be replaced. His kind and nurturing spirit lives on in all who are lucky enough to have known him.

## ABOUT THE AUTHORS

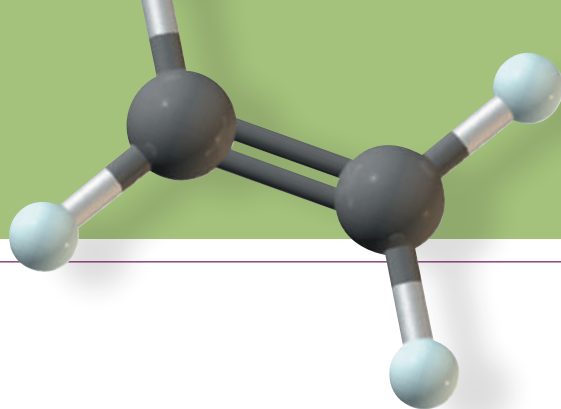
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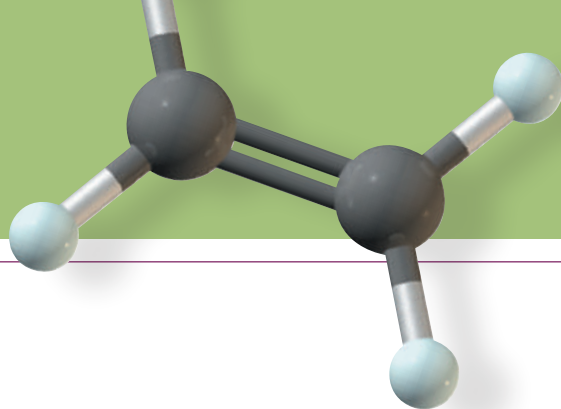
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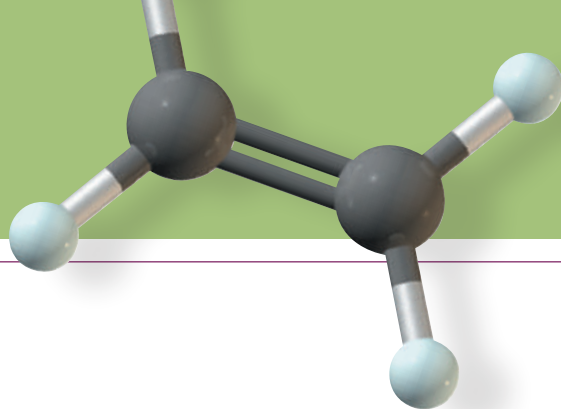
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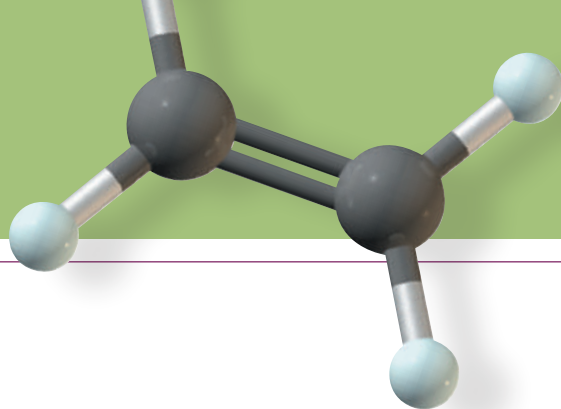
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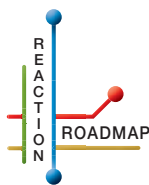
## INTRODUCTION

This seventh edition of *Organic Chemistry* significantly extends the transformation started in the sixth edition. Students taking an organic chemistry course have two objectives: the first is to learn organic chemistry, and the second is to establish the intellectual foundation for other molecular science courses. Most often, these other courses involve biochemistry or specialized topics such as materials science. This textbook addresses these two objectives head-on by first presenting mechanistic and synthetic organic chemistry geared toward giving students a fundamental understanding of organic molecules and reactions as well as their mechanisms and uses in organic synthesis. The text then builds on the fundamentals by emphasizing bridging concepts that will prepare students for subsequent science courses. Several studying and learning features of this text include comprehensive end-of-chapter summaries, a unique paradigm for learning mechanisms, and an enhanced learning tool called Organic Chemistry Reaction Roadmaps.

## A FRESH LOOK AT MECHANISMS

This edition refines a revolutionary paradigm for learning organic chemistry mechanisms. Students are introduced to a small set of individual mechanism elements in a special primer section preceding Chapter 6. In addition, a new special primer section just before Chapter 18 describes how to apply this unique approach to construct the mechanisms for the reactions of carboxylic acid derivatives, historically the make-or-break point for students learning to develop and understand complex reaction mechanisms in the organic chemistry course. In both of these new special sections, the mechanism elements are explained in detail, including when they are appropriate to use. Reaction mechanisms throughout the rest of the book are described as combinations of these individual mechanism elements, which are written in stepwise fashion. This new approach not only simplifies the learning of mechanisms for students but also makes it easier to recognize similarities and differences between related reactions. Most important, it makes the prediction of reaction mechanisms simpler, analogous to a multiple-choice situation in which the correct mechanism element is chosen from a menu of choices. Also, Appendix 10, "Common Mistakes in Arrow Pushing," gives students more hints on writing mechanisms.

To reinforce the mechanism element approach, the uniting concept of nucleophiles reacting with electrophiles is highlighted. Especially helpful is the use of electrostatic potential surface models of reacting molecules. These maps emphasize, in an easily interpreted, color-coded fashion, how the majority of reactions involve areas of higher electron density on one reactant (a nucleophile) interacting with areas of lower electron density on the other reactant (an electrophile).



## A FRESH LOOK AT SYNTHESIS: ORGANIC CHEMISTRY ROADMAPS, AN INNOVATIVE AND POWERFUL WAY TO VISUALIZE ORGANIC REACTIONS

In this seventh edition, we refine an innovation to organic chemistry learning that we refer to as the Organic Chemistry Reaction Roadmap. It is a graphical representation of the different organic reactions taught in the context of the important functional groups. The functional groups of an organic chemistry roadmap are analogous to cities on a real roadmap, and the reactions are like the roads between those cities. Arrows are used to represent known routes between functional groups, and the reagents required to bring about each reaction are written next to the corresponding arrow. Multistep synthesis questions are often very challenging for organic chemistry students even though synthesis is at the core of organic chemistry as a discipline. The power of the organic chemistry reaction roadmap is that it helps students visualize the reactions to interconvert key functional groups in multistep synthesis problems. The construction and use of organic chemistry reaction roadmaps are introduced in the end-of-chapter problems beginning in Chapter 6 and presented in complete form in a new Appendix 11, which students can tear out and use next to a problem.

## A FRESH LOOK AT ORBITALS

An organic chemist's theoretical framework for understanding electron density within molecules is based on atomic and molecular orbitals. Paradoxically, organic chemistry texts generally provide only passing coverage of orbitals, never revealing their true shapes or full significance. The seventh edition paints a detailed picture of the orbital nature of electron density in Chapter 1 by focusing on the interplay between the two complementary approaches to orbital descriptions: valence bond theory and molecular orbital theory. Chapter 1 provides a comprehensive description of how organic chemists use electronic theory to understand structure, bonding, and reactivity. Significantly, students are given easy-to-use guidelines that detail when and how to use electronic theory, even in complex situations, such as molecules described by multiple resonance contributing structures. The inclusion of calculated orbital diagrams alongside the familiar orbital cartoons gives students a greater appreciation for orbital sizes and shapes that are reinforced throughout the book. The intent is to provide students with a strong theoretical foundation that will give them unprecedented insight and intuition into molecular structure and reactivity.

## A FRESH LOOK AT MCAT PREPARATION

A significant number of students taking organic chemistry are doing so to prepare for standardized tests such as the MCAT, DAT, or PCAT. Often, organic chemistry content on the MCAT is in the form of passages followed by a series of multiple-choice questions. Learning to answer questions based on passages requires students to develop increased reading comprehension and analytical skills. The seventh edition of *Organic Chemistry* is the first text to aid students in developing these skills by introducing an extensive series of passages followed by several thought-provoking multiple-choice questions in almost every chapter (*MCAT Practice: Passage and Questions*). The passages cover interesting applications of organic chemistry principles as well as biological and chemical topics. Thus, far from being just test preparation, these passages add considerable enrichment to the material being presented.

Organic chemistry enables the synthesis of thousands of useful molecules. Synthetic applications of the reactions covered in this text are emphasized throughout, partly through the many new challenging synthesis problems, the goal of which is to demonstrate to students how synthetic organic chemistry is used in pharmaceutical research and in the production of useful pharmaceuticals. The text provides applications of the reactions to the synthesis of important molecules, such as Valium, fluoxetine (Prozac), meperidine (Demerol), albuterol (Proventil), tamoxifen, and sildenafil (Viagra). Multistep synthesis problems challenge students to develop their own multistep synthetic plan for converting a relatively simple starting material into a more complex target molecule. Multistep synthesis is supported by an expanded description of retrosynthetic analysis in multiple chapters, including tips on recognizing when to use certain reactions, such as those involving enolates in the construction of complex structures.

## ORGANIC CHEMISTRY APPLIED TO BIOLOGY

The application of organic chemistry principles to important biological molecules is integrated where appropriate to establish a bridge with biochemistry courses. In particular, *Connections to Biological Chemistry* gives special attention to those aspects of organic chemistry that are essential to understanding the chemistry of living systems. For example, the organic chemistry of amino acids is highlighted beginning in Section 3.8, along with the importance of alkene geometry to both membrane fluidity and nutrition. How hydrogen bonding is involved with drug-receptor interactions (Section 10.2) is discussed. Importantly, these Connections to Biological Chemistry features have been added throughout the book, not just at the end, because not all instructors make it through the biological chemistry chapters at the end of the text. Relevance to practical application is also emphasized in an expanded array of essays titled *Chemical Connections*. Topics include medicines such as penicillins and cephalosporins (MCAT Practice: Section 18.8), food supplements such as antioxidants (Section 8.7), and materials science concepts such as spider silk (Chemical Connections: Section 27.6). These sections provide a bridge between the theory of organic chemistry and well-known, current, practical applications. A list of the Chemical Connections as well as Connections to Biological Chemistry essays can be found on the inside back cover of this text.

## MASTERING SKILLS

Mastering organic chemistry requires the development of certain intellectual skills. To this end, 15 How To boxes highlight “survival skills” for organic chemistry students. Five new How To boxes to this edition are *How To Quickly Figure Out Formal Charge*, *How To Quickly Recognize the Hybridization and Geometry of Atoms*, *How To Quickly Draw and Recognize Enantiomers and Diastereomers*, *How To Retrosynthetically Dissect an Amine into the Proper Starting Materials for a Reductive Amination*, and *How To Recognize Aromatic Compounds: Criteria and Caveats*.

## HELPING STUDENTS PREPARE MORE EFFICIENTLY

A key feature of the seventh edition is the end-of-chapter summaries, which are mini study guides designed to help students prepare for class exams and later for standardized tests such as the MCAT. When preparing for exams, students will benefit from the bulleted lists of important concepts with highlighted keywords. These mini study guides

make it easier for students to identify difficult-to-grasp material by referring them to the section of the text for a full explanation and then providing them with end-of-chapter problems that test and reinforce their comprehension. As a companion to the summary outlines, end-of-chapter summaries of key reactions systematically list the reactions covered in each chapter. These include prose descriptions of mechanisms as well as important information such as observed stereochemistry or regiochemistry. Students will find these reaction summaries particularly efficient when preparing for exam questions requiring application of reactions in the context of new molecules or even multistep syntheses. The appendix reference material has been enhanced with two unique items to provide students with a quickly accessible source of important information. The first is a thorough “Summary of Stereochemical Terms” (Appendix 8). Stereochemical terms are subtle and difficult to master, so having them compiled in one location allows students to compare and contrast any new terms with those learned in earlier chapters, as well as prepare for exams. In addition, Appendix 9, “Summary of the Rules of Nomenclature,” provides a practical listing of the nomenclature rules described throughout the text. In response to student requests, this appendix provides a single location for the rules students need when naming complex molecules that contain multiple functional groups.

### UNIQUE ORGANIZATIONAL ELEMENTS

- Together, Chapter 1 (comprehensive description of electronic theory) and Chapter 4 (detailed description of acids and bases in organic chemistry) provide a fundamental grasp of molecular structure and properties, giving students the basis to understand all aspects of the mechanistic discussions that follow. Equipping students with the proper tools from the beginning will give them a predictive command of reactivity and foster chemical intuition, while discouraging superficial memorization.
- Because of the increased use of NMR spectroscopy in chemical and biochemical research, as well as the growing dependence on MRI for medical diagnosis, Chapter 13, “Nuclear Magnetic Resonance Spectroscopy,” is detailed and up to date. The practical and theoretical aspects concerning NMR spectra and signal splitting patterns are highlighted, and a complete description of FT-NMR provides a stronger technical connection to MRI.
- Carbonyl chemistry (Chapters 16–19) is placed earlier than in most texts so that professors have time to teach this material to the majority of students in an organic chemistry class, who are geared toward a life science degree and/or career in the health professions. Carbonyl chemistry is fundamental to the chemistry of living systems, and connections between carbonyl chemistry and the chemistry of carbohydrates is highlighted earlier in the book. This latter change mirrors the increasing importance of carbohydrate chemistry on the MCAT.
- Chapter 24, “Catalytic Carbon-Carbon Bond Formation,” combines content from previous chapters and challenges students to devise syntheses. The intent is to expose students to the excitement and challenge of modern synthetic chemistry.

### WHAT'S NEW

In this edition, we made major changes to provide a better theoretical understanding of organic chemistry as well as to provide better tools to prepare for exams.

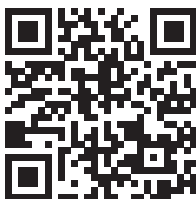
- Two new primer sections were added to better prepare students to understand, as opposed to simply memorize, reaction mechanisms. The first, “Primer I: Reaction Mechanisms,” added prior to Chapter 6, introduces the concept of fundamental mechanistic elements and explains how to predict which mechanistic element is appropriate for a given step in the reaction mechanism being considered. This revolutionary approach promotes student understanding of the similarities and differences between different reactions, and perhaps more important, leads students to an intuitive understanding of how molecules react.

- “Primer II, Carboxylic Acid Derivative Reaction Mechanisms” was added just prior to Chapter 18, the chapter describing the reactions of carboxylic acid derivatives. This is a critical chapter for students because the reaction mechanisms of carboxylic acids have numerous steps with only subtle differences among them. Students who approach mechanisms by trying to memorize them generally do very poorly with this material. On the other hand, by reintroducing the unifying mechanistic element approach in front of this chapter, students are given the appropriate foundation to develop an intuitive understanding of carboxylic acid derivative mechanisms.
- Acknowledging that a significant number of students take organic chemistry courses as preparation for standardized exams such as the MCAT, this new edition is the first and only text on the market to contain MCAT-style passages and accompanying multiple-choice questions in almost every chapter. A significant portion of the organic chemistry section of the MCAT involves passages about intentionally new material that is related to concepts with which students should be familiar, followed by a series of multiple-choice questions intended to test students’ reading comprehension and analytical skills. These new passages not only introduce interesting applications of the material presented in the chapters but also provide students with the reading comprehension and analytical skills they need to do well in the organic chemistry passages sections of the MCAT exam.
- Organic chemistry reaction roadmaps were completely redrawn and highly refined in this edition. This innovation in organic chemistry learning gives students a visual representation of the different reactions and shows how these roadmaps can be used in specific sequences for the multistep synthesis of complex molecules.
- The description of several more modern synthetic methods were added, including the Swern, Dess-Martin, and Pinnick oxidations.

## SPECIAL FEATURES

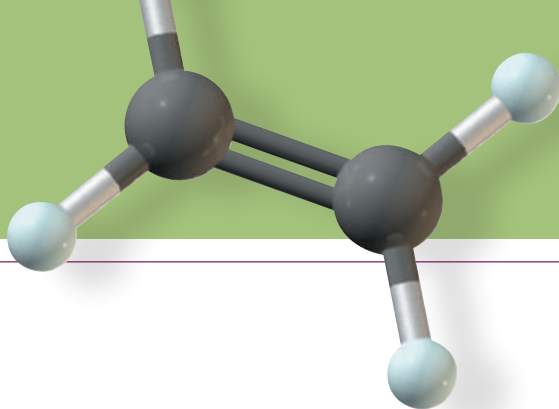
- **New A revolutionary new paradigm** for learning organic chemistry mechanisms is introduced in “Primer I: Reaction Mechanisms” just prior to Chapter 6 and then used throughout the book.
- **New The new mechanism paradigm** for learning organic chemistry mechanisms is reviewed and applied to the mechanisms for carboxylic acid derivatives in a second all-new “Primer II, Carboxylic Acid Derivative Reaction Mechanisms” just prior to Chapter 18.
- **New Several more modern synthetic methods** were added, such as the Swern, Dess-Martin, and Pinnick oxidations.
- **New MCAT Practice: Passage and Questions** are incorporated into almost every chapter. These new passages and questions not only introduce interesting applications of the material presented in the chapters but also provide students with the reading comprehension and analytical skills they need to do well in the organic chemistry passages sections of the MCAT exam.
- **Updated Organic Chemistry Reaction Roadmaps** were completely redrawn to make them even more useful as an innovation in learning organic chemistry. Organic chemistry roadmaps are presented in end-of-chapter problems and in the newly designed Appendix 11 tear-out.
- **Updated Accurate Orbital Diagrams** were added throughout the text to provide students with a more realistic understanding of electronic theory as applied to organic chemistry.
- **Updated Chemical Connections** These essays illustrate applications of organic chemistry to everyday settings. Topics range from Chiral Drugs to Drugs That Lower Plasma Levels of Cholesterol and The Chemistry of Superglue. A complete list can be found on the inside back cover.

- **Updated Connections to Biological Chemistry** Application of organic chemistry to biology is emphasized throughout the text in the Connections to Biological Chemistry essays and in end-of-chapter problems. See the inside back cover for a complete list. New essays include pyridoxine (vitamin B<sub>6</sub>) and electron transfer agents in biological oxidation-reduction reactions.
- **Updated Fifteen How To features** of key tools and topics are included. These describe “survival skills” for the organic chemistry student. Five How To boxes are new to this edition.
- **Updated In-Chapter Examples** There are an abundance of in-chapter examples, each with a detailed solution, so that students can immediately see how the concepts just discussed relate to specific questions and their answers. Following each in-chapter example is a comparable in-chapter problem designed to give students the opportunity to solve a related problem on their own.
- **Updated End-of-Chapter Summaries** highlight, in outline form, all of the important ideas of the chapter. Each concept is keyed to the section in the chapter that provides a full explanation, as well as to the problems that reinforce understanding.
- **Updated End-of-Chapter Summaries of Key Reactions** list the reactions described in the chapter, complete with a prose description of the mechanism and important considerations such as stereochemistry and regiochemistry.
- **Updated End-of-Chapter Problems** There are plentiful end-of-chapter problems, with the majority categorized by topic. A red problem number indicates an applied, real-world problem. There are numerous multistep synthesis problems, many dealing with the synthesis of important pharmaceuticals, and Reactions in Context problems dealing with functional group transformations of more complex molecules.
- **Updated Glossary of Key Terms** Throughout the book, definitions for new terms are placed in the margin for easy reference. In addition, all definitions are collected in a handy glossary at the end of the text and keyed to the section where the term is introduced.
- **Updated Precise Stereochemical Definitions** are compiled in a unique appendix. A comprehensive listing of stereochemical terms in a single collection provides students with a resource they can refer to often as they encounter new terms.
- **Updated A Unique Nomenclature Appendix** This appendix provides a comprehensive listing of all the rules introduced in the text governing nomenclature of complex molecules.
- **Updated A Unique Arrow Pushing Appendix** In this appendix, the correct use of arrow pushing is emphasized and students are encouraged to avoid common mistakes.
- **Updated Full-Color Art Program** One of the most distinctive features of this text is its visual impact. The text’s extensive full-color art program includes a large number of molecular models generated with a three-dimensional look, as well as applied photos. In addition, special colors are used to highlight parts of molecules and to follow the course of reactions.
- **Updated Electrostatic Potential Maps** are provided at appropriate places throughout the text to illustrate the important concepts of resonance, electrophilicity, and nucleophilicity.



## SUPPORTING MATERIALS

Please visit [www.cengage.com/chemistry/brown/organic7e](http://www.cengage.com/chemistry/brown/organic7e) for information about student and instructor resources for this text.



## Acknowledgments

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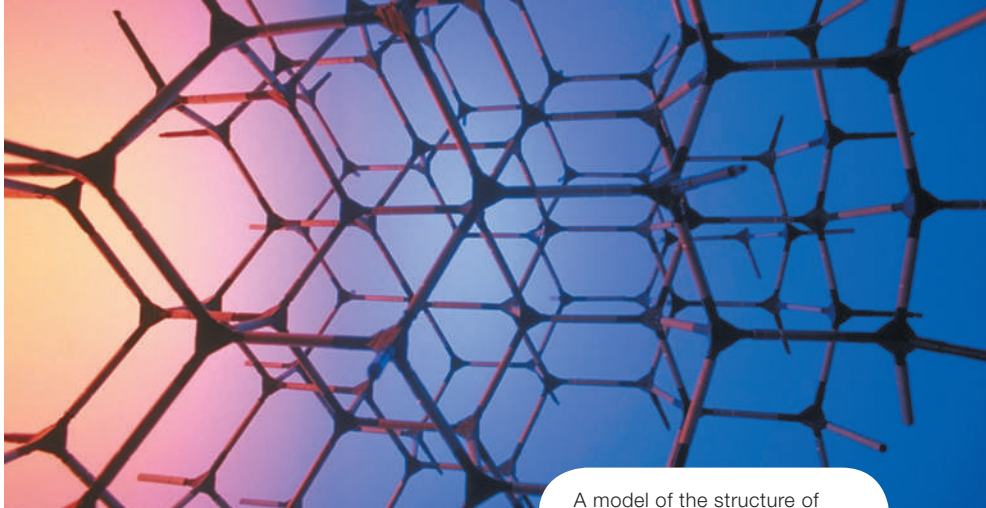
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# 1



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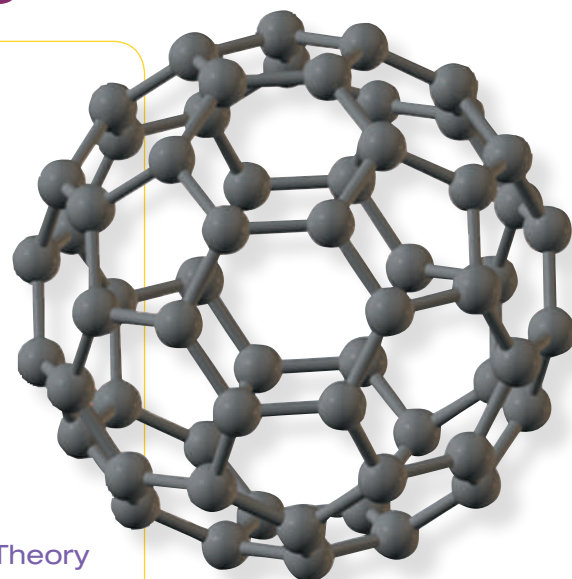
A model of the structure of diamond, one form of pure carbon. Each carbon is bonded to four other carbons at the corners of a tetrahedron.

**Inset:** a model of fullerene ( $C_{60}$ ). See "MCAT Practice: Fullerenes."

## Covalent Bonding and Shapes of Molecules

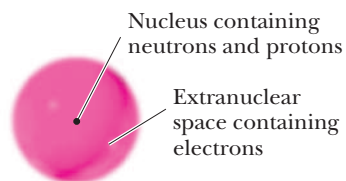
### Outline

- 1.1** Electronic Structure of Atoms
- 1.2** Lewis Model of Bonding
- HOW TO** Quickly Figure Out Formal Charge
- HOW TO** Draw Lewis Structures from Condensed Structural Formulas
- 1.3** Functional Groups
- 1.4** Bond Angles and Shapes of Molecules
- 1.5** Polar and Nonpolar Molecules
- 1.6** Quantum or Wave Mechanics
- 1.7** A Combined Valence Bond and Molecular Orbital Theory Approach to Covalent Bonding
- HOW TO** Quickly Recognize the Hybridization and Geometry of Atoms
- 1.8** Resonance
- HOW TO** Draw Curved Arrows and Push Electrons in Creating Contributing Structures
- 1.9** Molecular Orbitals for Delocalized Systems
- 1.10** Bond Lengths and Bond Strengths in Alkanes, Alkenes, and Alkynes



*According to the simplest definition,* **organic chemistry** is the study of the compounds of carbon. Perhaps its most remarkable feature is that most organic compounds consist of carbon and only a few other elements—chiefly, hydrogen, oxygen,

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← $10^{-10}$  m→

### Figure 1.1

A schematic view of an atom. Most of the mass of an atom is concentrated in its small, dense nucleus.

#### Shell

A region of space around a nucleus that can be occupied by electrons, corresponding to a principal quantum number.

#### Quantized

Having discrete values for energy and momentum.

#### Delocalization

The spreading of electron density over a larger volume of space.

#### Orbital

A region of space that can hold two electrons.

#### Orthogonal

Having no net overlap.

and nitrogen. Chemists have discovered or made well over 10 million compounds composed of carbon and these three other elements. Organic compounds are all around us—in our foods, flavors, and fragrances; in our medicines, toiletries, and cosmetics; in our plastics, films, fibers, and resins; in our paints and varnishes; in our glues and adhesives; in our fuels and lubricants; and, of course, in our bodies and the bodies of all living things.

Let us review how the elements of C, H, O, and N combine by sharing electron pairs to form bonds, and ultimately molecules. No doubt, you have encountered much of this initial material in previous chemistry courses; however, the chapters that follow require your ability to use this knowledge fluently.


## 1.1 Electronic Structure of Atoms

An atom contains a small, dense nucleus made of neutrons and positively charged protons. Most of the mass of an atom is contained in its nucleus. The nucleus is surrounded by an extranuclear space containing negatively charged electrons. The nucleus of an atom has a diameter of  $10^{-14}$  to  $10^{-15}$  meters (m). The electrons occupy a much larger volume with a diameter of approximately  $10^{-10}$  m (Figure 1.1).

**Shells** define the probability of finding an electron in various regions of space relative to the nucleus. The energy of electrons in the shells is quantized. **Quantization** means that only specific values of energy are possible, rather than a continuum of values. These shells occur only at quantized energies in which three important effects balance each other. The first is the electrostatic attraction that draws the electrons toward the nucleus; the second is the electrostatic repulsion between the electrons; and the third is the wavelike nature of an electron that prefers to be delocalized, thereby spreading the electron density away from the nuclei. **Delocalization** describes the spreading of electron density over a larger volume of space.

Electron shells are identified by the principal quantum numbers 1, 2, 3, and so forth. Each shell can contain up to  $2n^2$  electrons, where  $n$  is the number of the shell. Thus, the first shell can contain 2 electrons; the second, 8 electrons; the third, 18 electrons; the fourth, 32 electrons; and so on (Table 1.1). Electrons in the first shell are nearest to the positively charged nucleus and are held most strongly by it; these electrons are lowest in energy. Electrons in higher-numbered shells are farther from the positively charged nucleus and are held less strongly.

Shells are divided into subshells designated by the letters  $s$ ,  $p$ ,  $d$ , and  $f$ , and within these subshells, electrons are grouped in orbitals (Table 1.2). An **orbital** is a region of space that can hold two electrons and has a specific quantized energy. The first shell contains a single orbital called a  $1s$  orbital. The second shell contains one  $s$  orbital and three  $p$  orbitals. The three  $2p$  orbitals reflect orthogonal angular momentum states in three-dimensional space. **Orthogonal** in this context results in  $90^\circ$  angles between the orbitals, but in all cases, orthogonal also means that the orbitals have no net overlap. As a point of reference, to discuss the  $2p$  orthogonal orbitals, we consider them to be directed along the  $x$ -,  $y$ -, and  $z$ -axes and give them designations,  $2p_x$ ,  $2p_y$ , and

Shell	Number of Electrons Shell Can Hold	Relative Energies of Electrons in These Shells
4	32	higher  lower
3	18	
2	8	
1	2	

**Table 1.2** Distribution of Orbitals in Shells

Shell	Orbitals Contained in That Shell
3	$3s, 3p_x, 3p_y, 3p_z$ , plus five $3d$ orbitals
2	$2s, 2p_x, 2p_y, 2p_z$
1	$1s$

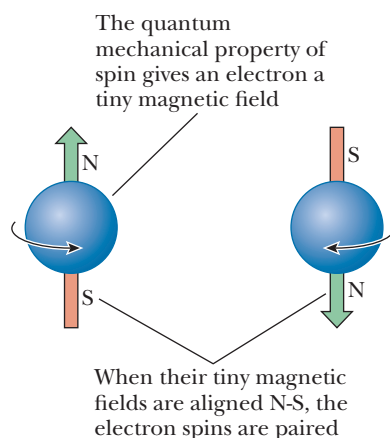
$2p_z$ . The third shell contains one  $3s$  orbital, three  $3p$  orbitals, and five  $3d$  orbitals. The shapes of  $s$  and  $p$  orbitals are shown in Figures 1.8 and 1.9 and are described in more detail in Section 1.6B.

## A. Electron Configuration of Atoms

The electron configuration of an atom is a description of the orbitals its electrons occupy. Every atom has an infinite number of possible electron configurations. At this stage, we are concerned primarily with the **ground-state electron configuration**—the electron configuration of lowest energy. We determine the ground-state electron configuration of an atom by using the following three rules.

**Rule 1: The Aufbau (“Build-Up”) Principle.** Orbitals fill in order of increasing energy, from lowest to highest. In this course, we are concerned primarily with the elements of the first, second, and third periods of the Periodic Table. Orbitals fill in the order  $1s, 2s, 2p, 3s, 3p$ , and so on.

**Rule 2: The Pauli Exclusion Principle.** The Pauli exclusion principle requires that only two electrons can occupy an orbital and that their spins must be paired. To understand what it means to have paired spins, recall from general chemistry that just as the earth has a spin, electrons have a quantum mechanical property referred to as spin. And just as the earth has magnetic north (N) and south (S) poles, so do electrons. As described by quantum mechanics, a given electron can exist in only two different spin states. Two electrons with opposite spins are said to have **paired spins**.



When filling orbitals with electrons, place no more than two in an orbital. For example, with four electrons, the  $1s$  and  $2s$  orbitals are filled and are written  $1s^2 2s^2$ . With an additional six electrons, the set of three  $2p$  orbitals is filled and is written  $2p_x^2 2p_y^2 2p_z^2$ . Alternatively, a filled set of three  $2p$  orbitals may be written  $2p^6$ .

**Rule 3: Hund’s Rule.** Hund’s rule has two parts. The first part states that when orbitals of equal energy (called degenerate) are available but there are not enough

### Ground-state electron configuration

The lowest-energy electron configuration for an atom or a molecule.

### Aufbau principle

Orbitals fill in order of increasing energy, from lowest to highest.

### Pauli exclusion principle

No more than two electrons may be present in an orbital. If two electrons are present, their spins must be paired.

### Hund’s rule

When orbitals of equal energy are available but there are not enough electrons to fill all of them completely, one electron is put in each before a second electron is added to any.

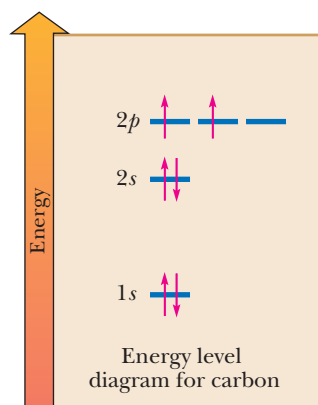
**Table 1.3** Ground-State Electron Configurations for Elements 1–18

First Period*	Second Period	Third Period
H 1 $1s^1$	Li 3 [He] $2s^1$	Na 11 [Ne] $3s^1$
He 2 $1s^2$	Be 4 [He] $2s^2$	Mg 12 [Ne] $3s^2$
	B 5 [He] $2s^2 2p^1$	Al 13 [Ne] $3s^2 3p^1$
	C 6 [He] $2s^2 2p^2$	Si 14 [Ne] $3s^2 3p^2$
	N 7 [He] $2s^2 2p^3$	P 15 [Ne] $3s^2 3p^3$
	O 8 [He] $2s^2 2p^4$	S 16 [Ne] $3s^2 3p^4$
	F 9 [He] $2s^2 2p^5$	Cl 17 [Ne] $3s^2 3p^5$
	Ne 10 [He] $2s^2 2p^6$	Ar 18 [Ne] $3s^2 3p^6$

\*Elements are listed by symbol, atomic number, and simplified ground-state electron configuration.

electrons to fill all of them completely, then one electron is added to each orbital before a second electron is added to any one of them. The second part of Hund's rule states that the spins of the single electrons in the degenerate orbitals should be aligned. Recall that electrons have a negative charge; partially filling orbitals as much as possible minimizes electrostatic repulsion between electrons. After the  $1s$  and  $2s$  orbitals are filled with four electrons, a fifth electron is added to the  $2p_x$  orbital, a sixth to the  $2p_y$  orbital, and a seventh to the  $2p_z$  orbital. Only after each  $2p$  orbital contains one electron is a second electron added to the  $2p_x$  orbital. Carbon, for example, has six electrons, and its ground-state electron configuration is  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$ . Alternatively, it may be simplified to  $1s^2 2s^2 2p^2$ . Table 1.3 shows ground-state electron configurations of the first 18 elements of the Periodic Table.

Chemists routinely write **energy-level diagrams** that pictorially designate where electrons are placed in an electron configuration. For example, the energy-level diagram for the electron configuration of carbon,  $1s^2 2s^2 2p^2$ , shows three energy levels, one each for the  $1s$ ,  $2s$ , and  $2p$  orbitals. Moving up in the diagram means higher energy. Electrons in these diagrams are drawn as arrows. The Aufbau principle tells us to place the first four electrons in the  $1s$  and  $2s$  orbitals, and the Pauli exclusion principle tells us to pair the two electrons in each orbital (shown as arrows with opposing directions). The remaining two electrons are left to go into the  $2p$  level, and because there are three such orbitals, the second part of Hund's rule tells us to place these electrons in different orbitals with their spins aligned (shown as arrows pointing in the same direction). We will use energy-level diagrams later in this chapter to explain bonding and throughout the book when discussing relative energies of orbitals.



**Example 1.1** | **Electron Configurations**

Write the ground-state electron configuration for each element showing the occupancy of each  $p$  orbital. For (c), write the energy-level diagram.

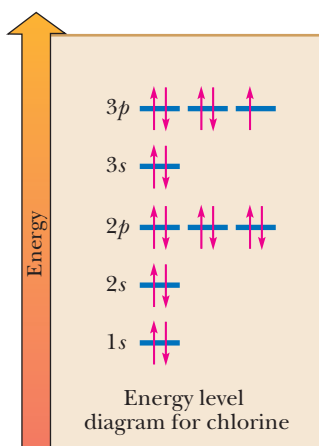
- (a) Lithium                      (b) Oxygen                      (c) Chlorine

**Solution**

(a) Lithium (atomic number 3):  $1s^2 2s^1$

(b) Oxygen (atomic number 8):  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

(c) Chlorine (atomic number 17):  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^1$

**Problem 1.1**

Write and compare the ground-state electron configurations for each pair of elements.

- (a) Carbon and silicon    (b) Oxygen and sulfur    (c) Nitrogen and phosphorus

**B. The Concept of Energy**

In the discussion of energy-level diagrams, the lines were drawn on the diagram to depict relative energy. In the energy-level diagram for carbon, the  $1s$  level is the reference and the  $2s$  and  $2p$  levels are placed higher on the diagram relative to it. But you may be asking, "How is energy defined?"

**Energy** is the ability to do work. The higher in energy an entity is, the more work it can perform. If you hold an object above the ground, it is unstable relative to when it is lying on the ground. You expend energy lifting the object, and this energy is stored in the object as potential energy. The **potential energy** can be released when the object is released. The higher you hold the object, the more energy the object stores and the greater the impact the object will have when it hits the ground.

The force that restores the object to its resting state on the ground is the gravitational attraction of the object to the earth. Interestingly, the farther the object is from the earth, the easier it is to take the object even farther from the earth. As an extreme example, thousands of miles above the earth the object has incredibly large potential energy and could wreak serious damage to a building if dropped. But at that distance, it is relatively easy to remove the object farther from the earth because the gravitational attraction is weak.

We can generalize this example to chemical structures. Unstable structures possess energy waiting to be released. When a structure is higher in energy, the more energy it has stored. When that energy is released, work can be done. In chemistry,

**Energy**

The ability to do work.

**Potential energy**

The energy that can be released if given an opportunity.

### Ground state

The lowest energy state of a system.

### Excited state

A state of a system at higher energy than the ground state.

### First ionization potential

The energy needed to remove the most loosely held electron from an atom or a molecule.

### Valence electrons

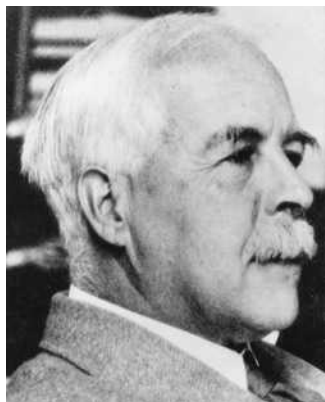
Electrons in the valence (outermost) shell of an atom.

### Valence shell

The outermost occupied electron shell of an atom.

### Lewis dot structure

The symbol of an element surrounded by the number of dots equal to the number of electrons in the valence shell of the atom.



Gilbert N. Lewis (1875–1946) introduced the theory of the electron pair that extended our understanding of covalent bonding and of the concept of acids and bases. It is in his honor that we often refer to an “electron dot” structure as a Lewis structure. © Bettmann/CORBIS

released energy is very often harnessed to do work, such as the burning of gasoline to drive the pistons in an internal combustion engine. In chemical reactions carried out in the laboratory, the release of energy commonly just heats up the reaction vessel.

Let’s return to the energy-level diagram of carbon. In the **ground state** of carbon, the electrons are placed in accordance with the quantum chemistry principles (e.g., Aufbau principle, Hund’s rule, and Pauli exclusion principle) that dictate the lowest energy form of carbon. If we place the electrons in a different manner (as an example, only one electron in  $2s$  and three electrons in  $2p$ ), we would have a higher energy state of carbon, referred to as an **excited state**. All of nature seeks its lowest energy state; when the electrons are rearranged back to this ground state, energy is released.

Note that the electrons in the lowest energy orbital,  $1s$ , are held tightest to the nucleus. It would take the largest amount of energy to remove these electrons relative to the others. The energy it takes to remove an electron from an atom or a molecule is called the **ionization potential**. The  $1s$  electrons, therefore, have the highest ionization potential; however, the electrons in the  $2p$  levels of carbon are the farthest from the nucleus and are held the weakest. They are the easiest to remove from the atom and therefore have the lowest ionization potential. This is analogous to it being easier to remove an object from the earth the farther it is from the surface.

## C. Lewis Dot Structures

Chemists often focus on the electrons in the outermost shell of the atom because these electrons are involved in the formation of chemical bonds and in chemical reactions. Carbon, for example, with the ground-state electron configuration  $1s^2 2s^2 2p^2$ , has four outer-shell electrons. Outer-shell electrons are called **valence electrons**, and the energy level in which they are found is called the **valence shell**. To illustrate the outermost electrons of an atom, chemists commonly use a representation called a **Lewis dot structure**, named after the American chemist Gilbert N. Lewis (1875–1946), who devised it. A Lewis dot structure shows the symbol of the element surrounded by the number of dots equal to the number of electrons in the outer shell of an atom of that element. In Lewis dot structures, the atomic symbol represents the core (i.e., the nucleus and all inner shell electrons). Table 1.4 shows Lewis dot structures for the first 18 elements of the Periodic Table.

The noble gases helium and neon have filled valence shells. The valence shell of helium is filled with two electrons; that of neon is filled with eight electrons. Neon and argon have in common an electron configuration in which the  $s$  and  $p$  orbitals of their valence shells are filled with eight electrons. The valence shells of all other elements shown in Table 1.4 contain fewer than eight electrons.

For C, N, O, and F in period 2 of the Periodic Table, the valence electrons belong to the second shell. With eight electrons, this shell is completely filled. For Si, P, S, and Cl in period 3 of the Periodic Table, the valence electrons belong to the third shell. This shell is only partially filled with eight electrons; the  $3s$  and  $3p$  orbitals are fully occupied, but the five  $3d$  orbitals can accommodate an additional ten electrons.

**Table 1.4** Lewis Dot Structures for Elements 1–18\*

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

\*These dots represent electrons from the valence shell. They are arranged as pairs or single electrons in accordance with Hund’s rule.

In 1916, Lewis devised a beautifully simple model that unified many of the observations about chemical bonding and reactions of the elements. He pointed out that the chemical inertness of the noble gases indicates a high degree of stability of the electron configurations of these elements: helium with a valence shell of two electrons ( $1s^2$ ), neon with a valence shell of eight electrons ( $2s^2 2p^6$ ), and argon with a valence shell of eight electrons ( $3s^2 3p^6$ ). The tendency of atoms to react in ways that achieve an outer shell of eight valence electrons is particularly common among second-row elements of Groups 1A–7A (the main-group elements) and is given the special name **octet rule**.

**Octet rule**

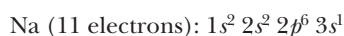
Group 1A–7A elements react to achieve an outer shell of eight valence electrons.

**Example 1.2 | The Octet Rule**

Show how the loss of an electron from a sodium atom leads to a stable octet.

**Solution**

The ground-state electron configurations for Na and  $\text{Na}^+$  are:



Thus,  $\text{Na}^+$  has a complete octet of electrons in its outermost (valence) shell and has the same electron configuration as neon, the noble gas nearest it in atomic number.

**Problem 1.2**

Show how each chemical change leads to a stable octet.

- (a) Sulfur forms  $\text{S}^{2-}$ .      (b) Magnesium forms  $\text{Mg}^{2+}$ .

**A. Formation of Chemical Bonds**

According to Lewis's model, atoms interact in such a way that each participating atom acquires a completed outer-shell electron configuration resembling that of the noble gas nearest to it in atomic number. Atoms acquire completed valence shells in two ways.

1. An atom may become ionic (i.e., lose or gain enough electrons to acquire a completely filled valence shell). An atom that gains electrons becomes an **anion** (a negatively charged ion), and an atom that loses electrons becomes a **cation** (a positively charged ion). A positively charged ion and a negatively charged ion attract each other. This attraction can lead to the formation of ionic crystals such as sodium chloride, in which each positive ion is surrounded by negative ions and vice versa, in a definite geometric arrangement that depends on the crystal. When atoms are held together primarily by attraction of oppositely charged ions, we say that an **ionic interaction** exists between them. (This ionic interaction is often referred to as an ionic bond.)
2. An atom may share electrons with one or more other atoms to complete its valence shell. A chemical bond formed by sharing electrons is called a **covalent bond**.
3. Bonds may be partially ionic and partially covalent; these bonds are called **polar covalent bonds**. Polar covalent bonds are defined more precisely in the next section.

**Anion**

An atom or a group of atoms bearing a negative charge.

**Cation**

An atom or a group of atoms bearing a positive charge.

**Ionic interaction**

Attraction between oppositely charged ions.

**Covalent bond**

A chemical bond formed between two atoms by sharing one or more pairs of electrons.

**B. Electronegativity and Chemical Bonds**

How do we estimate the degree of ionic or covalent character in a chemical bond? One way is to compare the electronegativities of the atoms involved. **Electronegativity** is

**Electronegativity**

A measure of the force of an atom's attraction for electrons.



Linus Pauling (1901–1994) was the first person to receive two unshared Nobel prizes. He received the 1954 Nobel Prize in Chemistry for his contributions to our understanding of chemical bonding. He received the 1962 Nobel Peace Prize for his efforts on behalf of international control of nuclear weapons testing.  
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### Electron affinity

Energy added or released when an electron is added to an atom or a molecule.

**Table 1.5** Electronegativity Values for Some Atoms (Pauling Scale)

1A		2A												3A		4A		5A		6A		7A					
Li 1.0	Be 1.5											H 2.1											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	3B	4B	5B	6B	7B	8B					1B	2B	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0									
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8											
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5											
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2											

	<1.0		1.5 – 1.9		2.5 – 2.9
	1.0 – 1.4		2.0 – 2.4		3.0 – 4.0

a measure of an atom's attraction for electrons that it shares in a chemical bond with another atom. The most widely used scale of electronegativities (Table 1.5) was devised by Linus Pauling in the 1930s.

On the Pauling scale, fluorine, the most electronegative element, is assigned an electronegativity of 4.0 and all other elements are assigned values in relation to fluorine. As you study the electronegativity values in this table, note that they generally increase from left to right within a period of the Periodic Table and generally decrease from top to bottom within a group. Values increase from left to right because the increasing positive charge on the nucleus results in a greater force of attraction for the atom's valence electrons. Electronegativity decreases from top to bottom because the increasing distance of the valence electrons from the nucleus results in a lower attraction between the nucleus and these electrons.

Let's further analyze the trends in the Periodic Table we just discussed. As you proceed from left to right in a row of the Periodic Table, the atoms get smaller. This contraction occurs because as you go across a row, the electrons are placed in the same shell, but the charge on the nuclei is increasing, thereby pulling the electrons in closer. This means that the orbitals get lower in energy as you move from left to right in the table and that the atoms hold their electrons tighter. It therefore takes more energy to remove the electrons from atoms as you move toward the right in the Periodic Table (with some exceptions), meaning that these atoms have a higher first ionization potential.

In contrast, consider adding rather than removing an electron to the atoms. For example, when an electron is added to the halogens (Group 7A), energy is released because these atoms achieve a noble gas configuration. The energy released upon addition of an electron is called the **electron affinity**, which becomes more favorable as you move from left to right in a row of the Periodic Table. In contrast, as you proceed down a column in the Periodic Table, the principal quantum levels increase and the outermost electrons are farther from the nuclei, are held less tightly, and have lower ionization potentials. The atoms also have decreasing electron affinities. Because the electronegativity of an atom reflects its tendency to hold on to and to acquire electrons, the phenomenon arises from a combination of ionization potentials and electron affinities.

When combining the trends of moving from left to right and up to down in the Periodic Table, you can conclude that fluorine must have the most tightly held electrons of any atom that can make bonds. Further, fluorine most tightly holds any electron that it gains during ion formation or covalent bond formation. Hence, fluorine has the highest electronegativity of any atom.



### Example 1.3 | Electronegativity

Judging from their relative positions in the Periodic Table, which element in each set is more electronegative?

- (a) Lithium or carbon      (b) Nitrogen or oxygen      (c) Carbon or oxygen

#### Solution

All of the elements in these sets are in the second period of the Periodic Table. Electronegativity in this period increases from left to right.

- (a)  $C > Li$       (b)  $O > N$       (c)  $O > C$

#### Problem 1.3

Judging from their relative positions in the Periodic Table, which element in each set is more electronegative?

- (a) Lithium or potassium      (b) Nitrogen or phosphorus      (c) Carbon or silicon

## Formation of Ions

Ions are formed by the transfer of electrons from the valence shell of an atom of lower electronegativity to the valence shell of an atom of higher electronegativity. As a rough guideline, we say that ions will form if the difference in electronegativity between interacting atoms is 1.9 or greater. As an example, ions are formed from sodium (electronegativity 0.9) and fluorine (electronegativity 4.0). In the following equation, we use a single-headed (barbed) curved arrow to show the transfer of one electron from sodium to fluorine.



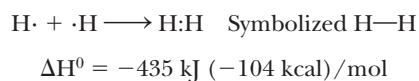
In forming  $\text{Na}^+\text{F}^-$ , the single  $3s$  valence electron of sodium is transferred to the partially filled valence shell of fluorine:



As a result of this transfer of one electron, both sodium and fluorine form ions that have the same electron configuration as neon, the noble gas nearest each in atomic number. The attraction between ions is what permits ionic salts such as sodium fluoride to form a strong crystal lattice and gives them a high melting point.

## Covalent Bonds

A covalent bond is formed between atoms that share one or more pairs of electrons to give a noble gas configuration to each atom. The simplest example occurs in the hydrogen molecule. When two hydrogen atoms bond, the single electrons from each combine to form an electron pair. This shared pair completes the valence shell of each hydrogen. According to the Lewis model, a pair of electrons in a covalent bond functions in two ways simultaneously: it is shared by two atoms and at the same time fills the outer (valence) shell of each. We use a line between the two hydrogens to symbolize the covalent bond formed by the sharing of a pair of electrons.



In this pairing, a large amount of energy is released, meaning that two hydrogen atoms are unstable relative to  $\text{H}_2$ . The same amount of energy, called the **bond dissociation enthalpy** (BDE, also known as the bond dissociation energy) would have to be absorbed to break the bond.

Later in the chapter, we see that electrons have both wave and particle character (Section 1.6). When bonds are formed by the sharing of two electrons between adjacent