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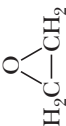

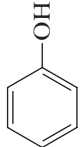
NINTH EDITION

# ORGANIC CHEMISTRY

BROWN | IVERSON | ANSLYN | FOOTE



### Some Important Organic Functional Groups

Functional Group*		IUPAC Name	
Functional Group*	Example	Functional Group*	Example
Acid anhydride	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{—C—O—C—} \\ \text{:O:} \end{array}$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COCCH}_3 \end{array}$	Ethanoic anhydride (Acetic anhydride)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COH} \end{array}$
Acid chloride	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{—C—Cl:} \\ \text{:O:} \end{array}$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCl} \end{array}$	Ethanoyl chloride (Acetyl chloride)	$\text{CH}_3\text{SSCH}_3$
Alcohol	$\text{—}\ddot{\text{O}}\text{H}$	Ethanol (Ethyl alcohol)	$\text{H}_2\text{C—CH}_2$ 
Aldehyde	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{—C—H} \end{array}$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH} \end{array}$	Ethanal (Acetaldehyde)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COCH}_3 \end{array}$
Alkane	-----	Ethane	$\text{CH}_3\text{OCH}_3$
Alkene		Ethene (Ethylene)	$\text{CH}_3\text{CH}_2\text{Cl}$
Alkyne	$\text{—C}\equiv\text{C—}$	Ethyne (Acetylene)	$\text{CH}_3\text{OCH}_3$
Amide	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{—C—N—} \\ \text{:} \end{array}$	Ethanamide (Acetamide)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \\ \text{CH}_3\text{—C}\equiv\text{N} \end{array}$
Amine, primary	$\text{—}\ddot{\text{N}}\text{H}_2$	Ethylamine	$\text{CH}_3\text{NO}_2$
Amine, secondary	$\text{—}\ddot{\text{N}}\text{H—}$	Diethylamine	
Amine, tertiary	$\text{—}\ddot{\text{N}}\text{—}$	Triethylamine	$\text{CH}_3\text{SCH}_3$
			$\text{CH}_3\text{CH}_2\text{SH}$

\* Where bonds to an atom are not specified, the atom is assumed to be bonded to one or more carbon or hydrogen atoms in the rest of the molecule.

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# Organic Chemistry

Ninth Edition

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# Dedication

This Ninth 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.





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# Preface

## Learning Through Understanding

---

*The best way to master organic chemistry is to first develop an intuitive understanding of basic principles, and then understand how to apply those principles to new and increasingly complex situations.*

The learning of organic chemistry is analogous to putting together a complex jigsaw puzzle—and at least two distinct approaches can be imagined. The first approach, unfortunately, reflects the way many students approach their first organic chemistry class: by memorizing each new piece of the puzzle individually, with no context, and then trying to blindly guess where it is to be placed by trial and error. We can all agree that a much better approach to finishing a jigsaw puzzle (as well as learning organic chemistry) is to keep the overall picture of the completed puzzle in one's mind and then evaluate each new piece being considered in the context of where it might fit into the emerging image. This book has been written in alignment with the far more effective second approach to learning by providing a strong foundation of basic concepts at the beginning, and then consistently emphasizing a “big picture” understanding as each new concept and functional group is presented in context. To accomplish this, the Ninth Edition uses two key innovations from previous editions that teach students how to learn two of the most important elements of organic chemistry: mechanisms and synthesis.

- **Mechanisms** We present a revolutionary paradigm for learning organic chemistry mechanisms. Students are introduced to a small set of individual mechanism elements, and importantly, when each of these mechanism elements is to be used. The four most important of these elements are:
  - ♦ Make a bond between a nucleophile and an electrophile
  - ♦ Break a bond to create stable molecules or ions
  - ♦ Add a proton
  - ♦ Take a proton away

Reaction mechanisms throughout the book are written in stepwise fashion and described as logical combinations of the individual mechanism elements. This new approach not only simplifies the learning of mechanisms for students but also makes it easier for them to recognize similarities and differences between related reactions. Most important, this approach makes the prediction of reaction mechanisms a straightforward, multiple-choice situation in which the correct mechanism



- element for a given step of each new reaction mechanism is systematically chosen from a small menu of options.
- **Synthesis** We present another important innovation in 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 that are appropriate 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 the Appendix section of this book, which students can tear out and use.

## What’s New in the Ninth Edition?

Each new feature is intended to enhance student engagement and learning.

**New Section Overview:** Each section begins with a bulleted summary of the content, providing highlights, “crib notes,” and key reactions.

**New Examples with Step-by-Step Solutions:** All Solutions to the Examples have been rewritten in a stepwise fashion so that students learn how to master complicated problems. Students are first reminded of relevant, important concepts, then walked through a systematic approach to arriving at the correct solution.

**New Think–Pair–Share:** Think–Pair–Share activities pose a question to students, who first consider it independently, and then discuss with one or two other students before settling on a final answer. This is a great way to motivate students and promote higher-level thinking. Sometimes this group discussion “sharing” is followed up with a larger classroom discussion. Some Think–Pair–Share activities are short “quick-response Think–Pair–Shares,” and sometimes the activities may be a longer and more involved “extended Think–Pair–Share.”

### 4.37 Think–Pair–Share

HI and  $\text{NaOCH}_3$  react in an acid–base reaction.

- Write out a reaction equation for these two reagents.
- Identify which covalent bonds are formed and which covalent bonds are broken in the reaction.
- Use curved arrow notation to show electron pair movement to go from reactants to products.
- Draw the transition state for the reaction.

**New Things You Should Know: Key Principles:** There are important transitions between distinct topics in the sequence of the book that are good checkpoints to stop, reflect, and take stock of important concepts or ideas that will be needed

going forward. “Things You Should Know” appropriately emphasize key principles from the chapters, while preserving reading fluency. When students read and fully digest these primers, they will be better prepared to approach critical topics in following sections. Things You Should Know recap the most important lessons and principles from quantum mechanics and other essential pieces of information that the students must use to understand many different aspects of molecular structure, properties, reactions, and mechanisms. Such overarching principles include “Delocalization of charge over a larger area is stabilizing,” and “Delocalization of  $\pi$  electron density over a larger area is stabilizing.”

### ► Things You Should Know

#### Key Principle

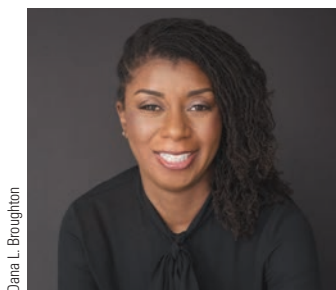
There are two possible arrangements of four different groups around a tetrahedral atom.

The two different arrangements are mirror images of each other, a property referred to as chirality and often compared to handedness.

*Very important:* Your goal should be to understand, not memorize, the material presented in your organic chemistry course. Thoroughly understanding key principles presented throughout this text will allow you to develop an intuitive feel for organic chemistry that

avoids the necessity of resorting to the far less effective use of extensive memorization. The key principle above has a basis in symmetry operations, and should be used as a foundation for building your understanding throughout the course. As appropriate, these principles will be mentioned in the margins of various future chapters as a reminder of just how extensively we fall back on these notions to explain organic chemistry.

**New Careers in Chemistry:** These profiles of diverse individuals showcase various career paths that students can take after studying organic chemistry. By showing a diverse, inclusive, and equitable chemical community, all students know that they have a future in chemistry-related jobs.



Dana L. Broughton

#### Careers in Chemistry

Dana L. Broughton, PhD, Esq. is a patent attorney with GlaxoSmithKline (GSK).

**New and Revised Exercises:** About 140 new and over 250 revised exercises were added to the book and online course to keep the content current.

## New to the Online OWL Course

**New Targeted Feedback:** Over 30 percent of the problems in OWLv2 now have targeted feedback on common errors that students make. The targeted feedback explains why the student’s answer is incorrect and guides them toward a correct solution.

**New Laddered Assessments:** Conceptual mastery modules have been combined with more traditional homework questions into one structured learning path, organized by topic at the chapter level.

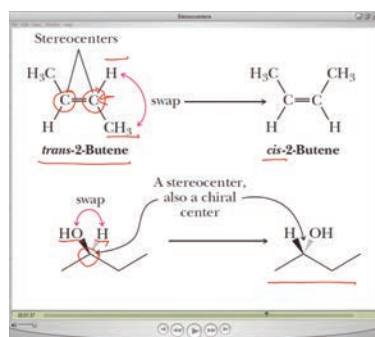
**Content Audit:** All online exercises and randomizations were reviewed for accuracy and to ensure that they align with the textbook so that students are tested on content that they have learned.

**Drawing Tool Enhancements:** The drawing tool now allows multiple structures to be drawn in one canvas, and new curved arrows for mechanisms were added.

**OWLv2 Help:** Resources have been streamlined and improved to make it easier for instructors and students to master OWL.

## Major Features of Organic Chemistry, Ninth Edition

**Videos:** The leading authors, Eric Anslyn and Brent Iverson, created over 90 short videos for the eBook and online course. The videos provide students with an on-demand resource that provides insight into the most difficult and important material. Icons in the margin of the text indicate to students when a video is available to walk them through problems and key figures in the text. These videos have been thoroughly student tested and approved.



The screenshot shows a table titled 'Infrared Stretching Frequencies of Selected Functional Groups'. The table lists bond types, their stretching frequencies in cm<sup>-1</sup>, and their intensity. Red circles and arrows highlight the O-H, N-H, and C-H bonds, and the C=O bond.

Bond	Stretching Frequency (cm <sup>-1</sup> )	Intensity
O-H	3200-3650	Weak to strong (strongest when H-bonded)
N-H	3100-3550	Medium
C-H	2700-3300	Weak to medium
C=C	1600-1680	Weak to medium
C=O	1630-1820	Strong
C-O	1000-1250	Strong

**Margin Bullets:** A series of bullet points emphasizing key foundational ideas that recur throughout the book guide the discussions of topics in future chapters. Their objective is to reiterate that the same fundamental principles are used throughout the text to explain patterns of molecular structure, properties, and reactivity.

► Delocalization of charge over a larger area is stabilizing.

**Survival 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. These include the following:

- 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
- How to Recognize Aromatic Compounds: Criteria and Caveats

**MCAT Preparation:** A significant number of students taking organic chemistry will take standardized tests such as the MCAT, DAT, or PCAT. Organic chemistry content on the MCAT, or similar exams, is generally 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. Our textbook is the first 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. These passages add considerable enrichment to the material being presented.

**Unique Chapter Sequence:** Carbonyl chemistry (Chapters 16–19) is placed earlier than in most texts so that instructors have time to teach this material to their students who have selected a life science degree and/or career in the health professions. Carbonyl chemistry is fundamental to the chemistry of living systems; therefore, the connections between carbonyl chemistry and the chemistry of carbohydrates are highlighted earlier in the book. This latter change mirrors the increasing importance of carbohydrate chemistry as well as other biological molecules on the MCAT.

**Applications to Synthesis:** Organic chemistry enables the synthesis of useful molecules. Synthetic applications of the reactions covered in this text are emphasized throughout, partly through the challenging end-of-chapter synthesis problems. The goal 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 the Organic Chemistry Reaction Roadmaps as well as an expanded description of retrosynthetic analysis in multiple chapters. We include tips on recognizing when to use certain reactions, such as those involving enolates in the construction of complex structures.

**Applications 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. It is important to note that 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.

**Chemical Connections:** Relevance to practical application is also emphasized in an expanded array of essays titled “Chemical Connections.” Topics include

medicines such as penicillin 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.

## Instructor and Student Resources

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Additional instructor and student resources are available online. Instructor assets include the following:

- Instructor Manual
- Guide to Teaching Online
- Transition Guide from the Eighth Edition to the Ninth Edition
- Educator's Guide
- Lecture Notes PowerPoint® slides
- Image Library PowerPoint® slides
- Solution and Answer Guide
- Organic Chemistry Reaction Roadmaps
- Test Bank

# Acknowledgments

This book is the product of collaboration of many individuals—some obvious, others not so obvious. It is with gratitude that we herein acknowledge the contributions of the many.

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We are also indebted to the many reviewers of our manuscript who helped shape its contents. With their guidance, we have revised this text to better meet the needs of students everywhere.

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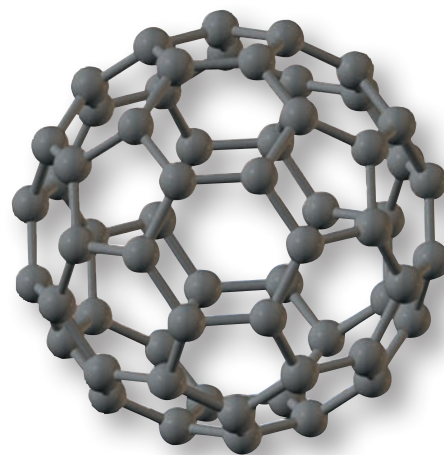
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# Covalent Bonding and Shapes of Molecules

## 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

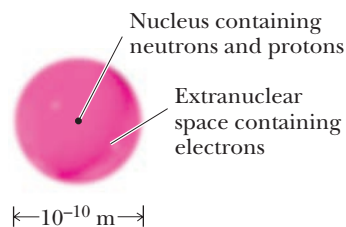
A model of the structure of diamond, one form of pure carbon. Each carbon is bonded to four other carbons at the corners of a tetrahedron. **Above:** a model of fullerene ( $C_{60}$ ). See "MCAT Practice: Fullerenes."  
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According to the simplest definition, **organic chemistry** is the study of the compounds of carbon. Remarkably most organic compounds consist of carbon and only a few other elements—chiefly, hydrogen, oxygen, and nitrogen. 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.

## 1.1 Electronic Structure of Atoms

» **SECTION OVERVIEW** Atoms consist of a small, dense nucleus and electrons distributed about the nucleus in regions of space called **shells**.

- Each shell can contain as many as  $2n^2$  electrons, where  $n$  is the number of the shell.
- Each principal energy level is subdivided into regions of space called **orbitals**. The **valence shell** is the outermost occupied shell, and it contains the **valence electrons**. Valence electrons are important because they take part in chemical bonding.
- The **Lewis dot structure** of an atom shows the symbol of the atom surrounded by a number of dots equal to the number of electrons in the valence shell of the atom.



**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.

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.

**Table 1.1** Distribution of Electrons in Shells

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

**Table 1.2** Distribution of Orbitals in Shells

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

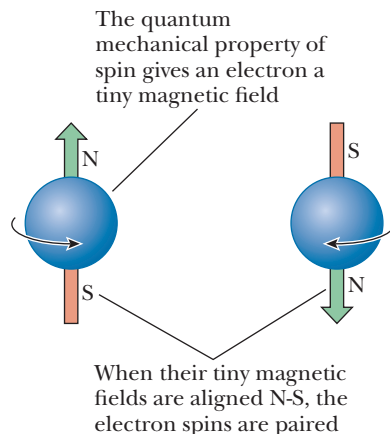
Shells are divided into subshells designated by the letters  $s$ ,  $p$ ,  $d$ , and  $f$ , and within these subshells, electrons are grouped in orbitals (Table 1.2). An **orbital** is a region of space that can hold two electrons and has a specific quantized energy. The first shell contains a single 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, consider them to be directed along the  $x$ -,  $y$ -, and  $z$ -axes and give them designations,  $2p_x$ ,  $2p_y$ , and  $2p_z$ . 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. At this stage, we are concerned primarily with the **ground-state electron configuration**—the electron configuration of lowest energy. Determine the ground-state electron configuration of an atom by using the following three rules.

**Rule 1: The Aufbau (“Build-Up”) Principle.** According to the **Aufbau principle**, orbitals fill in order of increasing energy, from lowest to highest. In this course, you will be 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**.



### Orbital

A region of space that can hold two electrons.

### Orthogonal

Having no net overlap.

### 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.

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  $2p^6$ .

### 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.

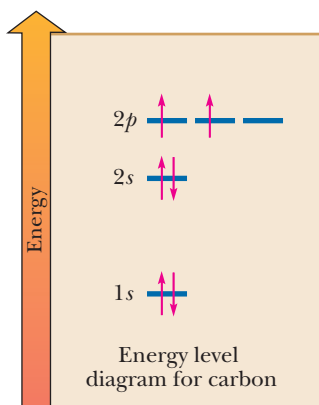
**Rule 3: Hund's Rule.** **Hund's rule** has two parts. The first part states that when orbitals of equal energy (called degenerate) are available, but there are not enough electrons to fill all of them completely, then one electron is added to each orbital before a second electron is added to any one 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 on the next page means higher energy. Electrons in these diagrams are drawn as arrows. The Aufbau principle says to place the first four electrons in the  $1s$  and  $2s$  orbitals, and the Pauli exclusion principle says 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, Hund's rule says to place these electrons in different orbitals with their spins aligned (shown as arrows pointing in the same direction).

**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.



## 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

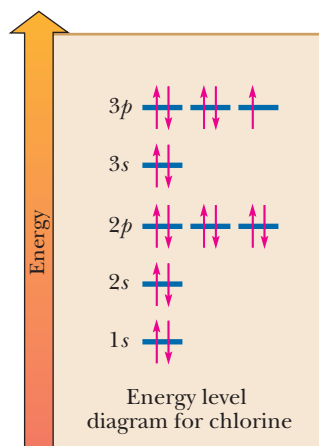
### Solution

**STEP 1** Determine the atomic number of the element from the Periodic Table. This is the number of electrons in the ground state.

**STEP 2** Fill the orbitals from the lowest energy to the highest energy using Table 1.2 as a guide. Remember to place 2 electrons in the lowest energy first shell, up to 8 electrons in the second shell, and up to 18 electrons in the third shell until all of the electrons are placed in an orbital.

**NOTE** The group number for each element gives the number of electrons in the outermost (valence) shell.

- (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

The ability to do work.

### Potential energy

The energy that can be released if given an opportunity.

**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 has 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.

You 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, released energy is very often harnessed to do work, such as the burning of gasoline to drive the pistons in an internal combustion engine.

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 (such as Aufbau principle, Pauli exclusion principle, and Hund’s rule) that dictate the lowest energy form of carbon. If you place the electrons in a different manner (as an example, only one electron in  $2s$  and three electrons in  $2p$ ), you 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 the 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.

### Ground state

The lowest energy state of a system.

### Excited state

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

### Ionization potential

The energy needed to remove an 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.

## 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 (that is, the nucleus and all inner shell

**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.

electrons). Table 1.4 shows Lewis dot structures for the first 18 elements of the Periodic Table.

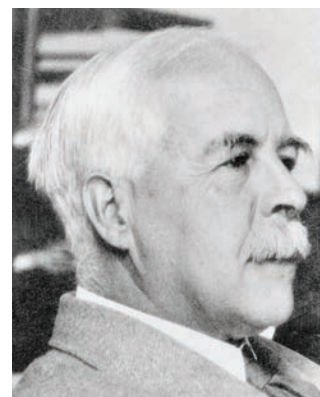
The noble gases helium and neon have filled valence shells. The valence shell of helium is filled with two electrons; that of neon is filled with eight electrons. Neon and argon have in common an electron configuration in which the *s* and *p* orbitals of their valence shells are filled with eight electrons. 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 as with Ne, 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.

## 1.2 Lewis Model of Bonding

» **SECTION OVERVIEW** According to the Lewis model of covalent bonding, atoms bond together in such a way that each atom participating in a chemical bond acquires a completed valence-shell electron configuration resembling that of the noble gas nearest it in atomic number.

- **Anions** and **cations** attract each other but do not form bonds with defined directionality.
- A **covalent bond** is a chemical bond formed by the sharing of electron pairs between adjacent atoms.
- The tendency of main-group elements (Groups 1A–7A) to achieve an outer shell of eight valence electrons is called the **octet rule**.
- **Electronegativity** is a measure of the force of attraction by an atom for electrons it shares in a chemical bond with another atom. In the context of the Periodic Table, the electronegativity of elements increases from left to right with a period (increasing positive charge of the nucleus) and decreases from the top to bottom within a group (increasing distance of electrons from the nucleus).
- A **nonpolar covalent bond** is a covalent bond in which the difference in electronegativity of the bonded atoms is less than 0.5.
- A **polar covalent bond** is a covalent bond in which the difference in electronegativity of the bonded atoms is between 0.5 and 1.9.
- In a polar covalent bond, the more electronegative atom bears a partial negative charge ( $\delta^-$ ) and the less electronegative atom bears a partial positive charge ( $\delta^+$ ).
- A polar bond has a bond dipole moment equal to the product of the absolute value of the partial charge times the distance between the dipolar charges (the bond length).



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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.

- An acceptable Lewis structure for a molecule or an ion must show (1) the correct connectivity of atoms, (2) the correct number of valence electrons, (3) no more than two electrons in the outer shell of hydrogen and no more than eight electrons in the outer shell of any second-period element, and (4) all formal charges.
- There are some apparent exceptions to the octet rule: neutral compounds of boron and aluminum can have only six valence electrons.

In 1916, Lewis 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 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.

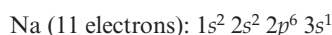
### Solution

**RECALL** The octet rule states that a high degree of stability is achieved when an element has a filled outermost (valence) shell with 8 electrons.

**STEP 1** Determine the ground-state electron configuration for each atom as shown in the previous example.

**STEP 2** Add an electron to the configuration for each negative charge and take away an electron for each positive charge of the ion. The most stable ions have a filled octet in the valence shell.

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 (that is, 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. When atoms are held together primarily by attraction of oppositely charged ions, it is said that an **ionic bond** exists between them.

- 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**.
- Bonds may be partially ionic and partially covalent; these bonds are called **polar covalent bonds**.

## B. Electronegativity and Chemical Bonds

How do you 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 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.

**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

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, while 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 ionization potential.

### 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 bond

Attraction between oppositely charged ions.

### Covalent bond

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

### Electronegativity

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



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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.