Introduction to Organic Chemistry



WILLIAM H. BROWN

THOMAS POON

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Introduction to **Organic Chemistry**

FIFTH EDITION

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FIFTH EDITION

THOMAS POON

Claremont McKenna College Scripps College Pitzer College

WILLIAM H. BROWN

Beloit College

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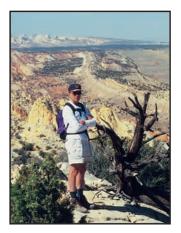
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10 9 8 7 6 5 4 3 2 1

To Carolyn, with whom life is a joy Bill Brown

> To Sophia, sky, fish, fireworks Тномаs Рооп

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WILLIAM H. BROWN is Professor Emeritus at Beloit College, where he was twice named Teacher of the Year. He is also the author of two other college textbooks: *Organic Chemistry* 5/e, coauthored with Chris Foote, Brent Iverson, and Eric Anslyn, published in 2009, and *General, Organic, and Biochemistry* 9/e, coauthored with Fred Bettelheim, Mary Campbell, and Shawn Farrell, published in 2010. He received his Ph.D. from Columbia University under the direction of Gilbert Stork and did postdoctoral work at California Institute of Technology and the University of Arizona. Twice he was Director of a Beloit College World Affairs Center seminar at the University of Glasgow, Scotland. In 1999, he retired from Beloit College to devote more time to writing and development of educational materials. Although officially retired, he continues to teach Special Topics in Organic Synthesis on a yearly basis.

Bill and his wife Carolyn enjoy hiking in the canyon country of the Southwest. In addition, they both enjoy quilting and quilts.



THOMAS POON is Professor of Chemistry in the W.M. Keck Science Department of Claremont McKenna, Pitzer, and Scripps Colleges, three of the five undergraduate institutions that make up the Claremont Colleges in Claremont, California. He received his B.S. degree from Fairfield University (CT) and his Ph.D. from the University of California, Los Angeles under the direction of Christopher S. Foote. Poon was a Camille and Henry Dreyfus Postdoctoral Fellow under Bradford P. Mundy at Colby College (ME) before joining the faculty at Randolph-Macon College (VA) where he received the Thomas Branch Award for Excellence in Teaching in 1999. He was a visiting scholar at Columbia University (NY) in 2002 (and again in 2004) where he worked on projects in both research and education with his friend and mentor, Nicholas J. Turro. He has taught organic chemistry, forensic chemistry, upper-level courses in advanced laboratory techniques, and a first-year seminar class titled *Science of Identity*. His favorite activity is working alongside undergraduates in the laboratory on research problems involving the investigation of synthetic methodology in zeolites, zeolite photochemistry, natural products isolation, and reactions of singlet oxygen.

When not in the lab, he likes to play guitar and sing chemistry songs to his daughter Sophie.

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Goals of This Text

This text is designed for an introductory course in organic chemistry and assumes, as background, a prior course of general chemistry. Both its form and content have been shaped by our experiences in the classroom and by our assessment of the present and future direction of the brief organic course.

A brief course in organic chemistry must achieve several goals. First, most students who elect this course are oriented toward careers in science, but few if any intend to become professional chemists; rather, they are preparing for careers in areas that require a grounding in the essentials of organic chemistry. Here is the place to examine the structure, properties, and reactions of rather simple molecules. Students can then build on this knowledge in later course work and professional life.

Second, an introductory course must portray something of the scope and content of organic chemistry as well as its tremendous impact on the ways we live and work. To do this, we have included specific examples of pharmaceuticals, plastics, soaps and detergents, natural and synthetic textile fibers, petroleum refining, petrochemicals, pesticides, artificial flavoring agents, chemical ecology, and so on at appropriate points in the text.

Third, a brief course must convince students that organic chemistry is more than just a catalog of names and reactions. There are certain organizing themes or principles, which not only make the discipline easier to understand, but also provide a way to analyze new chemistry. The relationship between molecular structure and chemical reactivity is one such theme. Electronic theory of organic chemistry, including Lewis structures, atomic orbitals, the hybridization of atomic orbitals, and the theory of resonance are presented in Chapter 1. Chapter 2 explores the relationship between molecular structure and one chemical property, namely, acidity and basicity. Variations in acidity and basicity among organic compounds are correlated using the concepts of electronegativity, the inductive effect, and resonance. These same concepts are used throughout the text in discussions of molecular structure and chemical reactivity. Stereochemistry is a second theme that recurs throughout the text. The concept and importance of the spatial arrangement of atoms is introduced in Chapter 3 with the concept of conformations in alkanes and cycloalkane, followed by cis/trans isomerism in Chapters 3 (in cycloalkanes) and 4 (in alkenes). Molecular symmetry and asymmetry, enantiomers and absolute configuration, and the significance of asymmetry in the biological world are discussed in Chapter 6. The concept of a mechanistic understanding of the reactions of organic substances is a third major theme. Reaction mechanisms are first presented in Chapter 5; they not only help to minimize memory work but also provide a satisfaction that comes from an understanding of the molecular logic that governs how and why organic reactions occur as they do. In this chapter we present a set of five fundamental patterns that are foundational to the molecular logic of organic reactions. An understanding and application of these patterns will not only help to minimize memory work but also provide a satisfaction that comes from an understanding of how and why organic reactions occur as they do.

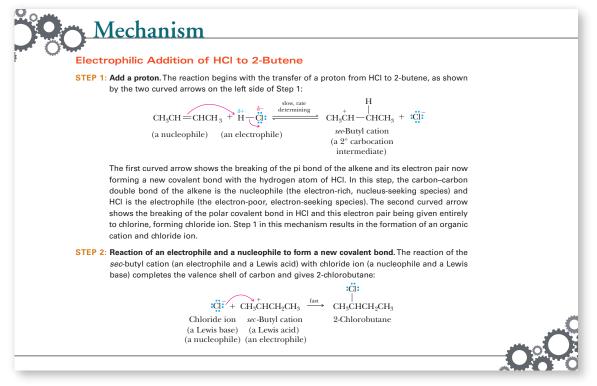
The Audience

This book provides an introduction to organic chemistry for students who intend to pursue careers in the sciences and who require a grounding in organic chemistry. For this reason, we make a special effort throughout to show the interrelation between organic chemistry and other areas of science, particularly the biological and health sciences. While studying with this book, we hope that students will see that organic chemistry is a tool for these many disciplines, and that organic compounds, both natural and synthetic, are all around them—in pharmaceuticals, plastics, fibers, agrochemicals, surface coatings, toiletry preparations and cosmetics, food additives, adhesives,

and elastomers. Furthermore, we hope that students will recognize that organic chemistry is a dynamic and ever-expanding area of science waiting openly for those who are prepared, both by training and an inquisitive nature, to ask questions and explore.

New to This Edition

• "Mechanism" boxes have been added for each mechanism in the book. These Mechanism boxes serve as road maps and are a new way of presenting mechanisms using basic steps and recurring themes that are common to most organic reaction mechanisms. This approach allows students to see that reactions have many steps in common, and it makes the reactions easier to understand and remember. By graphically highlighting the mechanisms in the text, we emphasize the importance of mechanisms for learning organic chemsitry, and mechanisms are easier for the students to locate quickly.



• New "Group Learning Activities" appear with the end-of-chapter problems, and provide students with the opportunity to learn organic chemistry collaboratively. This will encourage students to work in groups and foster more active learning in their studying.

GROUP LEARNING ACTIVITIES Take turns guizzing each other on the reactions Using a piece of paper or, preferably, a whiteboard 5.55 5.56 presented in this chapter in the following ways: or chalkboard, take turns drawing the mechanisms of each reaction in this chapter from memory. If you (a) Say the name of a reaction and ask each other forget a step or make a mistake, another member of to come up with the reagents and products of the group should step in and finish it. that reaction. For example, if you say "catalytic hydrogenation of an alkene" the answer should 5.57 With the exception of ethylene to ethanol, the acidbe "H₂/Pt reacts to give an alkane." catalyzed hydration of alkenes cannot be used for the (b) Describe a set of reagents and ask each other synthesis of primary alcohols. Explain why this is so. what functional group(s) the reagents react with. For example, if you say "H₂/Pt," the answer should be "alkenes" and "alkynes." (c) Name a functional group or class of compound as a product of a reaction and ask what functional group or class of compound could be used to synthesize that product. For example,

if you say "alkene," the answer should be

"alkvne."

X1X

- Due to overwhelming demand, we have combined the chapters on organic spectroscopic techniques into one chapter, Chapter 11, while still providing a sound conceptual treatise on organic spectroscopy. In combining the chapters, students are shown that the absorption of electromagnetic radiation and transitions between energy states are common themes to both infrared spectroscopy and NMR spectroscopy.
- "Key Terms and Concepts" now appear within the "Summary of Key Questions." In doing so, we shift the emphasis from simply memorizing a list of terms to seeing the terms (high-lighted in bold) in the context of important conceptual questions.
- We have reduced the length of the text. Using reviewer input and feedback from instructors who have used the text, we removed material that we identified as being less important to our audience's learning of organic chemistry. We also moved some chapters online, to the text website and to *WileyPLUS*. The result is a manageable amount of material that still provides a thorough introduction to organic chemistry. Chapter 20, Nucleic Acids, and Chapter 21, The Organic Chemistry of Metabolism, will be available in *WileyPLUS* and at the text website: www.wiley.com/college/brown.

Special Features

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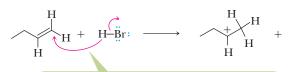
HOW TO

"How To" Boxes: Have your students ever wished for an easy-to-follow, step-by-step guide to understanding a problem or concept? We have identified topics in nearly every chapter that often give students a difficult time and created step-by-step *How To* guides for approaching them.

Draw Mechanisms

Mechanisms show how bonds are broken and formed. Although individual atoms may change positions in a reaction, the curved arrows used in a mechanism are only for the purpose of showing electron movement. Therefore, it is important to remember that curved arrow notation always shows the arrow originating from a bond or from an unshared electron pair (not the other way around). Correct use of curved arrows...

Incorrect use of curved arrows...



a common mistake is to use curved arrows to indicate the movement of atoms rather than electrons

Chemical Connection Boxes include applications of organic chemistry to the world around us, particularly to the biochemical, health, and biological sciences. The topics covered in these boxes represent real-world applications of organic chemistry and highlight the relevance between organic chemistry and the students' future careers.

"Putting It Together" Cumulative Review Questions: In this text, end-of-chapter problems are organized by section, allowing students to easily refer back to the chapter if difficulties arise. This way of organizing practice problems is very useful for learning new material. Wouldn't it be help-ful for students to know whether they could do a problem that wasn't categorized for them (i.e., to know whether they could recognize that problem in a different context, such as an exam setting)? To help students in this regard, we have added a section called *Putting It Together* (PIT) at the end of Chapters 3, 6, 10, 14, and 17. Each PIT section is structured much like an exam would be organized, with questions of varying type (multiple choice, short answer, naming, mechanism problems, predict the products, synthesis problems, etc.) and difficulty (often requiring knowledge of concepts from two or more previous chapters). Students' performance on the PIT questions will

aid them in assessing their knowledge of the concepts from these groupings of chapters. The solutions to the Putting It Together questions appear in the Student Solutions Manual.

Problem-Solving Strategies: One of the greatest difficulties students often encounter when attempting to solve problems is knowing where to begin. To help students overcome this challenge, we include a *Strategy* step for every worked example in the text. The strategy step will help students to determine the starting point for each of the example problems. Once students are familiar with the strategy, they can apply it to all problems of that type.

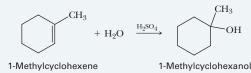
EXAMPLE 5.5

Draw a structural formula for the product of the acid-catalyzed hydration of 1-methylcyclohexene.

STRATEGY

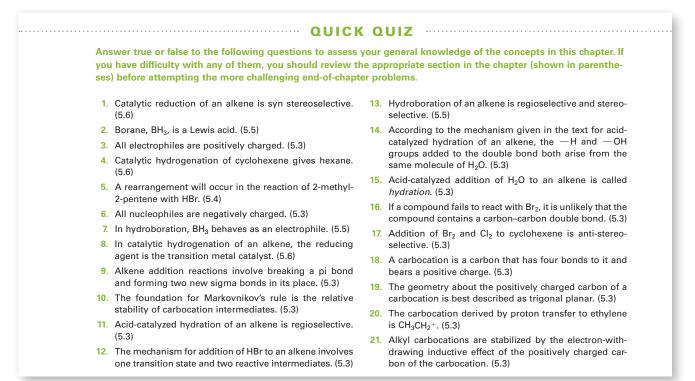
Use Markovnikov's rule, which states that the H adds to the carbon of the carbon–carbon double bond bearing the greater number of hydrogens and that OH adds to the carbon bearing the lesser number of hydrogens.

SOLUTION



See problems 5.19, 5.20, 5.28, 5.32

Quick Quizzes: Research on reading comprehension has shown that good readers self-monitor their understanding of what they have just read. We have provided a tool that will allow students to do this, called the *Quick Quiz*. Quick quizzes are a set of true or false questions at the end of every chapter designed to test students' understanding of the basic concepts presented in the chapter. The questions are not designed to be an indicator of their readiness for an exam. Rather, they are provided for students to assess whether they have the bare minimum of knowledge needed



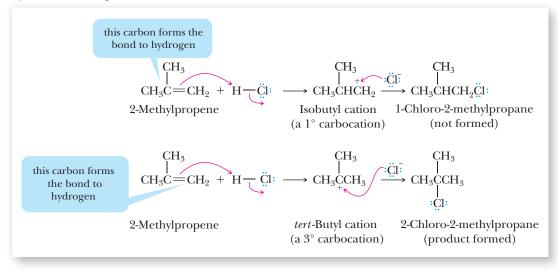
XX1

to begin approaching the end-of-chapter problems. The answers to the quizzes are provided at the bottom of the page, so that students can quickly check their progress, and if necessary, return to the appropriate section in the chapter to review the material.

More Practice Problems: It is widely agreed that one of the best ways to learn the material in organic chemistry is to have students do as many of the practice problems available as possible. We have increased the number of practice problems in the text by 15%, providing students with even more opportunities to learn the material. For example, we've included a section called *Chemical Transformations* in nearly every chapter, which will help students to familiarize themselves with the reactions covered both in that chapter and in previous chapters. These problems provide a constructivist approach to learning organic chemistry. That is, they illustrate how concepts constantly build on each other throughout the course.

Organic Synthesis: In this text, we treat organic synthesis and all of the challenges it presents as a teaching tool. We recognize that the majority of students taking this course are intending to pursue careers in the health and biological sciences, and that very few intend to become synthetic organic chemists. We also recognize that what organic chemists do best is to synthesize new compounds; that is, they make things. Furthermore, we recognize that one of the keys to mastering organic chemistry is extensive problem solving. To this end, we have developed a large number of synthetic problems in which the target molecule is one with an applied, real-world use. Our purpose in this regard is to provide drills in recognizing and using particular reactions within the context of real syntheses. It is not our intent, for example, that students be able to propose a synthesis for procaine (Novocaine), but rather that when they are given an outline of the steps by which it can be made, they can supply necessary reagents.

Greater Attention to Visual Learning: Research in knowledge and cognition has shown that visualization and organization can greatly enhance learning. We have increased the number of callouts (short dialog bubbles) to highlight important features of many of the illustrations throughout the text. This places most of the important information in one location. When students try to recall a concept or attempt to solve a problem, we hope that they will try to visualize the relevant illustration from the text. They may be pleasantly surprised to find that the visual cues provided by the callouts help them to remember the content as well as the context of the illustration.



Organization: An Overview

Chapters 1–10 begin a study of organic compounds by first reviewing the fundamentals of covalent bonding, the shapes of molecules, and acid–base chemistry. The structures and typical reactions of several important classes of organic compounds are then discussed: alkanes, alkenes and alkynes, haloalkanes, alcohols and ethers, benzene and its derivatives, and amines, aldehydes, and ketones, and finally carboxylic acids and their derivatives.

Chapter 11 introduces IR spectroscopy, and ¹H-NMR and ¹³C-NMR spectroscopy. Discussion of spectroscopy requires no more background than what students receive in general chemistry. The chapter is freestanding and can be taken up in any order appropriate to a particular course.

Chapters 12–16 continue the study of organic compounds, including aldehydes and ketones, carboxylic acids, and finally carboxylic acids and their derivatives. Chapter 15 concludes with an introduction to the aldol, Claisen, and Michael reactions, all three of which are important means for the formation of new carbon–carbon bonds. Chapter 16 provides a brief introduction to organic polymer chemistry.

Chapters 17–20 present an introduction to the organic chemistry of carbohydrates, amino acids and proteins, nucleic acids, and lipids. Chapter 21, The Organic Chemistry of Metabolism, demonstrates how the chemistry developed to this point can be applied to an understanding of three major metabolic pathways—glycolysis, the β -oxidation of fatty acids, and the citric acid cycle.

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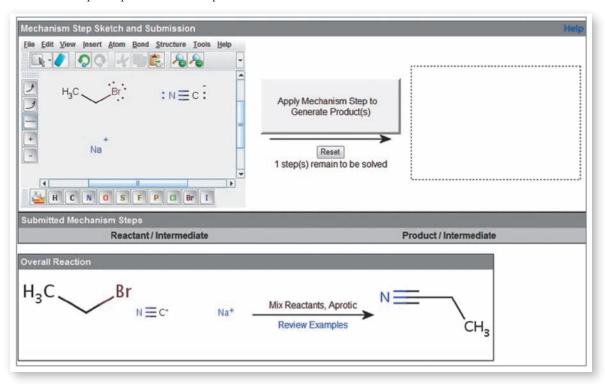
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Reaction Explorer—Students' ability to understand mechanisms and predict synthesis reactions greatly impacts their level of success in the course. **Reaction Explorer** is an interactive system for **learning and practicing reactions**, **syntheses**, and **mechanisms** in organic chemistry with advanced support for the automatic generation of random problems and curved arrow mechanism diagrams.

Mechanism Explorer provides valuable practice of reactions and mechanisms:

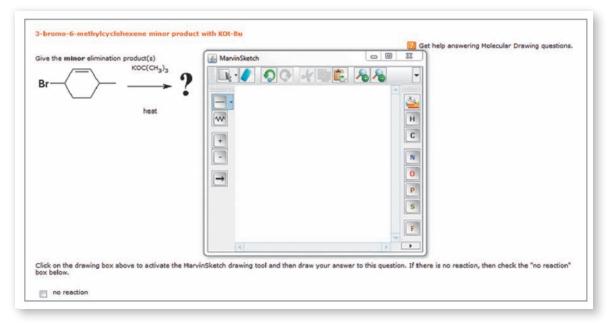


Synthesis Explorer provides meaningful practice of single and multistep synthesis:

eactants forme 2 Add	Reagents	Target Product 207078 WLinks
Br — CH ₃	1. Mix Reactants in DMSO or THF (solvent) (2. H2O (Aqueous workup))	E N CH ₂
H ₃ C Br	Mix Reactants in Alcohol (solvent)	Select a reagent from the reagent frame.
athway (0.000 sec)		-
Reactants	Reagents	Products
Select a Reactant	Select a Reagent	Apply Reaction to Generate Product(s)
l	-	

End-of-Chapter Problems—A subset of the end-of-chapter problems is included for use in *WileyPLUS*. Many of the problems are algorithmic and feature structure drawing/assessment functionality using MarvinSketch, with immediate answer feedback.

Prebuilt Concept Mastery Assignments—Students must continuously practice and work organic chemistry problems in order to master the concepts and skills presented in the course. **Prebuilt concept mastery assignments** offer students ample opportunities for practice in each chapter. Each assignment is organized by topic and features **feedback for incorrect answers**. These assignments pull from a unique database of over 25,000 questions, over half of which require students to draw a structure using MarvinSketch.



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Support Package for Students

Student Solutions Manual: Authored by Felix Lee, of The University of Western Ontario. The Student Study Guide contains detailed solutions to all problems, including the Quick Quiz questions and the Putting It Together questions.

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All Instructor Resources are available within *WileyPLUS* or they can be accessed by contacting your local Wiley Sales Representative.

PowerPoint Presentations: Authored by William Brown, the PPT lecture slides provide a prebuilt set of approximately 700 slides corresponding to every chapter in the text. The slides include examples and illustrations that help reinforce and test students' grasp of organic chemistry concepts. An additional set of PPT slides, featuring the illustrations, figures, and tables from the text, are also available. All PPT slide presentations are customizable to fit your course.

Test Bank: Authored by Stefan Bossmann of Kansas State University, the Test Bank for this edition has been revised and updated to include over 2,000 short-answer, multiple-choice, and true-false questions. It is available in both printed and computerized versions.

Digital Image Library: Images from the text are available online in JPEG format. Instructors may use these to customize their presentations and to provide additional visual support for quizzes and exams.

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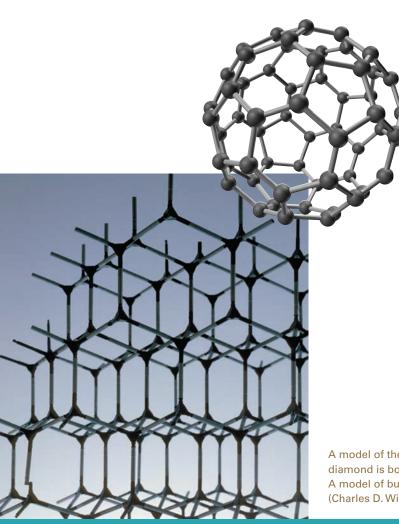
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Introduction to **Organic Chemistry**

FIFTH EDITION

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Covalent Bonding and Shapes of Molecules

A model of the structure of diamond, one form of pure carbon. Each carbon atom in diamond is bonded to four other carbon atoms at the corners of a tetrahedron. Inset: A model of buckyball, a form of carbon with a molecular formula of C_{60} . (Charles D. Winters)

KEY QUESTIONS

- 1.1 How Do We Describe the Electronic Structure of Atoms?
- 1.2 What Is the Lewis Model of Bonding?
- 1.3 How Do We Predict Bond Angles and the Shapes of Molecules?
- 1.4 How Do We Predict If a Molecule Is Polar or Nonpolar?
- 1.5 What Is Resonance?
- 1.6 What Is the Orbital Overlap Model of Covalent Bonding?

1.7 What Are Functional Groups?

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1.1 How to Draw Lewis Structures for Molecules and lons

CHEMICAL CONNECTIONS

1A Buckyball: A New Form of Carbon

ACCORDING TO the simplest definition, **organic chemistry** is the study of the compounds of carbon. As you study this text, you will realize that organic compounds are everywhere 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; and, of course, in our bodies and in all living things.

Perhaps the most remarkable feature of organic chemistry is that it is the chemistry of carbon and only a few other elements-chiefly hydrogen, oxygen, and nitrogen. Chemists

have discovered or made well over 10 million organic compounds. While the majority of them contain carbon and just those three elements, many also contain sulfur, phosphorus, and a halogen (fluorine, chlorine, bromine, or iodine).

Let us begin our study of organic chemistry with a review of how carbon, hydrogen, oxygen, and nitrogen combine by sharing electron pairs to form molecules.

Shell A region of space around a nucleus where electrons are found.

Orbital A region of space where an electron or pair of electrons spends 90 to 95% of its time.

1.1 How Do We Describe the Electronic Structure of Atoms?

You are already familiar with the fundamentals of the electronic structure of atoms from a previous study of chemistry. Briefly, an atom contains a small, dense nucleus made of neutrons and positively charged protons (Figure 1.1a).

Electrons do not move freely in the space around a nucleus, but rather are confined to regions of space called **principal energy levels** or, more simply, **shells**. We number these shells 1, 2, 3, and so forth from the inside out (Figure 1.1b).

Shells are divided into subshells designated by the letters *s*, *p*, *d*, and *f*, and within these subshells, electrons are grouped in orbitals (Table 1.1). An **orbital** is a region of space that can hold 2 electrons. In this course, we focus on compounds of carbon with hydrogen, oxygen, and nitrogen, all of which use only electrons in *s* and *p* orbitals for covalent bonding. Therefore, we are concerned primarily with *s* and *p* orbitals.

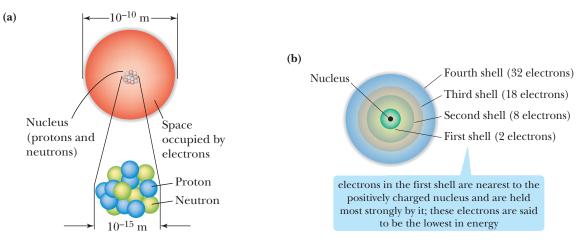


FIGURE 1.1

A schematic view of an atom. (a) Most of the mass of an atom is concentrated in its small, dense nucleus, which has a diameter of 10^{-14} to 10^{-15} meter (m). (b) Each shell can contain up to $2n^2$ electrons, where *n* is the number of the shell. Thus, the first shell can hold 2 electrons, the second 8 electrons, the third 18, the fourth 32, and so on. (Table 1.1).

the first shell contains a single orbital called a 1*s* orbital. The second shell contains one 2*s* orbital and three 2*p* orbitals. All *p* orbitals come in sets of three and can hold up to 6 electrons. The third shell contains one 3*s* orbital, three 3*p* orbitals, and five 3*d* orbitals. All *d* orbitals come in sets of five and can hold up to 10 electrons. All *f* orbitals come in sets of seven and can hold up to 14 electrons

TABLE 1.1 Distribution of Orbitals within Shells

	Shell	Orbitals Contained in Each Shell	Maximum Number of Electrons Shell Can Hold	Relative Energies of Electrons in Each Shell
	4	One 4 <i>s</i> , three 4 <i>p</i> , five 4 <i>d</i> , and seven 4 <i>f</i> orbitals	2 + 6 + 10 + 14 = 32	Higher
-	3	One 3 <i>s</i> , three 3 <i>p</i> , and five 3 <i>d</i> orbitals	2 + 6 + 10 = 18	
	2	One 2 <i>s</i> and three 2 <i>p</i> orbitals	2 + 6 = 8	
	l_1	One 1 <i>s</i> orbital	2	Lower

Ground-state electron configuration The

molecule, or ion.

electron configuration of

lowest energy for an atom,

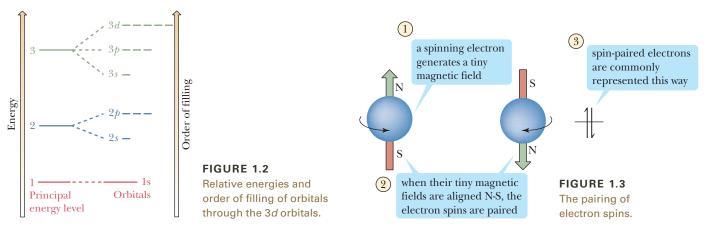
TAE	BLE 1	.2	Ground-State Electron Configuration	ns for Elements 1–18*		Rule 1. Orbitals in these
First Period	Н	1	1 <i>s</i> ¹			elements fill in the order 1 <i>s</i> , 2 <i>s</i> , 2 <i>p</i> , 3 <i>s</i> , and 3 <i>p</i> .
Fii Per	He	2	1 <i>s</i> ²			,,,
	Li	3	1 <i>s</i> ² <i>s</i> ¹	[He]2 <i>s</i> ¹		
	Be	4	1 <i>s</i> ² 2 <i>s</i> ²	[He]2 <i>s</i> ²		Rule 2. Notice that
Period	В	5	$1s^22s^22p_x^{-1}$	[He] $2s^2 2p_x^1$		each orbital contains a maximum of two electrons.
l Per	С	6	$1s^2 2s^2 2p_x^{-1} 2p_y^{-1}$	[He] $2s^2 2p_x^1 2p_y^1$		In neon. there are six
Second	Ν	7	$1s^2 2s^2 2p_x^{-1} 2p_y^{-1} 2p_z^{-1}$	[He] $2s^2 2p_x^1 2p_y^1 2p_z^1$		additional electrons after the 1s and 2s orbitals are
Sec	0	8	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	[He] $2s^22p_x^22p_y^{-1}2p_z^{-1}$		filled. These are written as
	F	9	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	[He] $2s^22p_x^22p_y^22p_z^1$		$2p_x^2 2p_y^2 2p_z^2$. Alternatively, we can group the three
	Ne	10	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	[He] $2s^22p_x^22p_y^22p_z^2$		filled 2 <i>p</i> orbitals and write
	Na	11	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$	[Ne] 3 <i>s</i> ¹		them in a condensed form as $2p^6$.
	Mg	12	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2$	[Ne] 3 <i>s</i> ²		101111 as 2p.
po	AI	13	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1$	[Ne] $3s^2 3p_x^1$		
Third Period	Si	14	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1 3p_y^1$	[Ne] $3s^2 3p_x^{-1} 3p_y^{-1}$		Rule 3. Because the p_x , p_y ,
ird	Р	15	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^13p_z^1$	[Ne] $3s^2 3p_x^{-1} 3p_y^{-1} 3p_z^{-1}$		and p_z orbitals are equal in energy, we fill each with
Тh	S	16	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^13p_z^1$	[Ne] $3s^2 3p_x^2 3p_y^1 3p_z^1$		one electron before adding
	CI	17	$1s^22s^22p_x^22p_y^22p_z^23s^33p_x^23p_y^33p_z^1$	[Ne] $3s^2 3p_x^2 3p_y^2 3p_z^1$		a second electron. That is,
	Ar	18	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^23p_z^2$	[Ne] $3s^2 3p_x^2 3p_y^2 3p_z^2$		only after each 3 <i>p</i> orbital contains one electron do
	*Elements are listed by symbol, atomic number, ground-state electron configuration, and shorthand notation for the ground-state electron configuration, in that order.					we add a second electron to the $3p_x$ orbital.

A. Electron Configuration of Atoms

The electron configuration of an atom is a description of the orbitals the electrons in the atom occupy. Every atom has an infinite number of possible electron configurations. At this stage, we are concerned only with the **ground-state electron configuration**—the electron configuration of lowest energy. Table 1.2 shows ground-state electron configurations for the first 18 elements of the Periodic Table. We determine the ground-state electron configuration of an atom with the use of the following three rules:

Rule 1. Orbitals fill in order of increasing energy from lowest to highest (Figure 1.2).

- **Rule 2.** *Each orbital can hold up to two electrons with their spins paired. Spin pairing* means that each electron spins in a direction opposite that of its partner (Figure 1.3). We show this pairing by writing two arrows, one with its head up and the other with its head down.
- **Rule 3.** When orbitals of equivalent energy are available, but there are not enough electrons to fill them completely, then we add one electron to each equivalent orbital before we add a second electron to any one of them.



EXAMPLE 1.1

Write ground-state electron configurations for these elements:

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

STRATEGY

Locate each atom in the PeriodicTable and determine its atomic number. The order of filling of orbitals is 1s, 2s, $2p_{x}$, $2p_{y}$, $2p_{z}$, and so on.

SOLUTION

(a) Lithium (atomic number 3): $1s^22s^1$. Alternatively, we can write the ground-state electron configuration as [He] $2s^1$.

PROBLEM 1.1

Write and compare the ground-state electron configurations for the elements in each set. What can be said about the outermost shell of orbitals for each pair of elements?

- (b) Oxygen (atomic number 8): $1s^22s^22p_x^22p_y^{-1}2p_z^{-1}$. Alternatively, we can group the four electrons of the 2p orbitals together and write the ground-state electron configuration as $1s^22s^22p^4$. We can also write it as [He] $2s^22p^4$.
- (c) Chlorine (atomic number 17): $1s^22s^22p^63s^23p^5$. Alternatively, we can write it as [Ne] $3s^23p^5$.

See problems 1.17–1.20

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

B. Lewis Structures

In discussing the physical and chemical properties of an element, chemists often focus on the outermost shell of its atoms, because electrons in this shell are the ones involved in the formation of chemical bonds and in chemical reactions. We call outer-shell electrons **valence electrons**, and we call the energy level in which they are found the **valence shell**. Carbon, for example, with a ground-state electron configuration of $1s^22s^22p^2$, has four valence (outer-shell) electrons.

To show the outermost electrons of an atom, we commonly use a representation called a **Lewis structure**, after the American chemist Gilbert N. Lewis (1875–1946), who devised this notation. A Lewis structure shows the symbol of the element, surrounded by a number of dots equal to the number of electrons in the outer shell of an atom of that element. In Lewis structures, the atomic symbol represents the nucleus and all filled inner shells. Table 1.3 shows Lewis structures for the first 18 elements of the Periodic Table. As you study the entries in the table, note that, with the exception of helium, the number of valence electrons of the element corresponds to the group number of the element in the Periodic Table; for example, oxygen, with six valence electrons, is in Group 6A.

At this point, we must say a word about the numbering of the columns (families or groups) in the Periodic Table. Dmitri Mendeleev gave them numerals and added the letter A for some columns and B for others. This pattern remains in common use in the United

TABLI	E 1.3 L	ewis Stru	ictures fo	r Element	ts 1–18 of	the Perio	dic Table	helium and neon have filled valence shells
1A	2A	ЗA	4A	5A	6A	7A	8A	
H·							He	neon and argon have in common an electron
Li	Be:	ġ:	٠Ċ٠	Ň	; ġ:	: <u>F</u> :	:Ne:	configuration in which the s and p orbitals of their
Na•	Mg:	Ål:	· si :	·P·	÷Ś÷	÷Ċl÷	:Är:	valence shells are filled with eight electrons

Valence electrons

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

Valence shell The outermost electron shell of an atom.

Lewis structure of an atom The symbol of an element surrounded by a number of dots equal to the number of electrons in the valence shell of the atom. States today. In 1985, however, the International Union of Pure and Applied Chemistry (IUPAC) recommended an alternative system in which the columns are numbered 1 to 18 beginning on the left and without added letters. Although we use the original Mendeleev system in this text, the Periodic Table on the inside back cover of the text shows both.

Notice from Table 1.3 that, for C, N, O, and F in period 2 of the Periodic Table, the valence electrons belong to the second shell. It requires 8 electrons to fill this shell. For Si, P, S, and Cl in period 3 of the Periodic Table, the valence electrons belong to the third shell. With 8 electrons, this shell is only partially filled: The 3s and 3p orbitals are fully occupied, but the five 3d orbitals can accommodate an additional 10 valence electrons. Because of the differences in number and kind of valence shell orbitals available to elements of the second and third periods, significant differences exist in the covalent bonding of oxygen and sulfur and of nitrogen and phosphorus. For example, although oxygen and nitrogen can accommodate no more than 8 electrons in their valence shells, many phosphoruscontaining compounds have 10 electrons in the valence shell of phosphorus, and many sulfur-containing compounds have 10 and even 12 electrons in the valence shell of sulfur.

1.2 What Is the Lewis Model of Bonding?

A. Formation of lons

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 (Group 8A) 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 $(2s^22p^6)$, argon with a valence shell of eight electrons $(3s^23p^6)$, and so forth. The tendency of atoms to react in ways that achieve

an outer shell of eight valence electrons is particularly common among elements of Groups 1A–7A (the main-group elements). We give this tendency the special name, the **octet rule**. An atom with almost eight valence electrons tends to gain the needed electrons to have eight electrons in its valence shell and an electron configuration like that of the noble gas nearest it in atomic number. In gaining electrons, the atom becomes a negatively charged ion called an **anion**. An atom with only one or two valence electrons tends to lose the number of electrons required to have the same electron configuration as the noble gas nearest it in atomic number. In losing one or more electrons, the atom becomes a positively charged ion called a **cation**.

EXAMPLE 1.2

Show how the loss of one electron from a sodium atom to form a sodium ion leads to a stable octet:

Na	\longrightarrow	Na^+	+	e
A sodium		A sodium		An
atom		ion		electron

STRATEGY

To see how this chemical change leads to a stable octet, write the condensed ground-state electron configuration for a sodium atom and for a sodium ion, and then compare the two to that of neon, the noble gas nearest to sodium in atomic number.

SOLUTION

Noble

Gas

He

Ne

Ar

Kr

Xe

Noble Gas

Notation

[He] $2s^2 2p^6$

[Ne] 3s²3p⁶

 $[Ar] 4s^2 4p^6 3d^{10}$

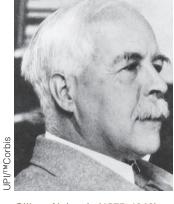
 $[Kr] 5s^2 5p^6 4d^{10}$

 $1s^2$

A sodium atom has one electron in its valence shell. The loss of this one valence electron changes the sodium atom to a sodium ion, Na^+ , which has a complete octet of electrons in its valence shell and the same electron configuration as neon, the noble gas nearest to it in atomic number.

Na (11 electrons): $1s^2 2s^2 2p^6 3s^1$ Na⁺ (10 electrons): $1s^2 2s^2 2p^6$ Ne (10 electrons): $1s^2 2s^2 2p^6$

See problems 1.22, 1.23



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.

Octet rule The tendency among atoms of Group 1A–7A elements to react in ways that achieve an outer shell of eight valence electrons.

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

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

$\mathbf{P} \mathbf{R} \mathbf{O} \mathbf{B} \mathbf{L} \mathbf{E} \mathbf{M} \qquad \mathbf{1.2}$

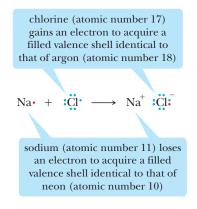
Show how the gain of two electrons by a sulfur atom to form a sulfide ion leads to a stable octet:

 $S + 2e^- \longrightarrow S^{2-}$

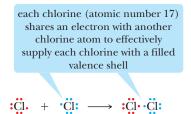
B. Formation of Chemical Bonds

According to the Lewis model of bonding, atoms interact with each other in such a way that each atom participating in a chemical bond acquires a valence-shell electron configuration the same as that of the noble gas closest to it in atomic number. Atoms acquire completed valence shells in two ways:

1. An atom may lose or gain enough electrons to acquire a filled valence shell. An atom that gains electrons becomes an anion, and an atom that loses electrons becomes a cation. A chemical bond between an anion and a cation is called an **ionic bond**.



2. An atom may share electrons with one or more other atoms to acquire a filled valence shell. A chemical bond formed by sharing electrons is called a **covalent bond**.



We now ask how we can find out whether two atoms in a compound are joined by an ionic bond or a covalent bond. One way to answer this question is to consider the relative positions of the two atoms in the Periodic Table. Ionic bonds usually form between a metal and a nonmetal. An example of an ionic bond is that formed between the metal sodium and the nonmetal chlorine in the compound sodium chloride, Na⁺Cl⁻. By contrast, when two nonmetals or a metalloid and a nonmetal combine, the bond between them is usually covalent. Examples of compounds containing covalent bonds between nonmetals include Cl_2 , H_2O , CH_4 , and NH_3 . Examples of compounds containing covalent bonds between a metalloid and a nonmetal include BF_3 , $SiCl_4$, and AsH_4 .

Another way to identify the type of bond is to compare the electronegativities of the atoms involved, which is the subject of the next subsection.

lonic bond A chemical bond resulting from the electrostatic attraction of an anion and a cation.

Covalent bond A chemical bond resulting from the sharing of one or more pairs of electrons.

Electronegativity A

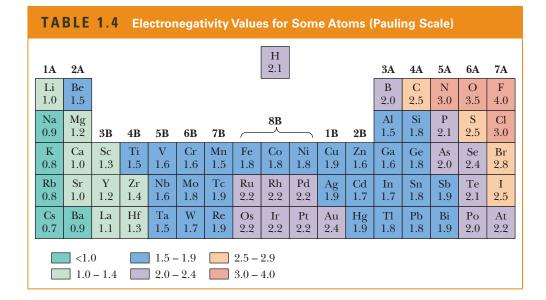
measure of the force of an atom's attraction for electrons it shares in a chemical bond with another atom.

C. Electronegativity and Chemical Bonds

Electronegativity is a measure of the force 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 1.4) 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 increase from bottom to top within a group. Values increase from left to right because of the increasing positive charge on the nucleus, which leads to a stronger attraction for electrons in the valence shell. Values increase going up a column because of the decreasing distance of the valence electrons from the nucleus, which leads to stronger attraction between a nucleus and its valence electrons.

Note that the values given in Table 1.4 are only approximate. The electronegativity of a particular element depends not only on its position in the Periodic Table, but also on its oxidation state. The electronegativity of Cu(I) in Cu_2O , for example, is 1.8, whereas the electronegativity of Cu(II) in CuO is 2.0. In spite of these variations, electronegativity is still a useful guide to the distribution of electrons in a chemical bond.





Linus Pauling (1901–1994) was the first person ever to receive two unshared Nobel Prizes. He received the Nobel Prize for Chemistry in 1954 for his contributions to the nature of chemical bonding. He received the Nobel Prize for Peace in 1962 for his efforts on behalf of international control of nuclear weapons and against nuclear testing.

 H
 Secondary

 Electronegativity increases
 Image: Secondary

 Li Be
 B C N O F

 Na Mg
 AI Si P S CI

 K Ca
 Br

 Image: Secondary
 Image: Secondary

 <td

Partial Periodic Table showing commonly encountered elements in organic chemistry. Electronegativity generally increases from left to right within a period and from bottom to top within a group. Hydrogen is less electronegative than the elements in red and more electronegative than those in blue. Hydrogen and phosphorus have the same electronegativity on the Pauling scale.

Ionic Bonds

An ionic bond forms 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. The more electronegative atom gains one or more valence electrons and becomes an anion; the less electronegative atom loses one or more valence electrons and becomes a cation.

EXAMPLE 1.3

Judging from their relative positions in the Periodic Table, which element in each pair has the larger electronegativity?

(a) Lithium or carbon

(b) Nitrogen or oxygen

(c) Carbon or oxygen

STRATEGY

Determine whether the pair resides in the same period (row) or group (column) of the Periodic Table. For those in the same period, electronegativity increases from left to right. For those in the same group, electronegativity increases from bottom to top.

SOLUTION

The elements in these pairs are all in the second period of the Periodic Table. Electronegativity in this period increases from left to right.

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

See problem 1.24

PROBLEM 1.3

Judging from their relative positions in the Periodic Table, which element in each pair has the larger electronegativity?

(a) Lithium or potassium

(b) Nitrogen or phosphorus

(c) Carbon or silicon

As a guideline, we say that this type of electron transfer to form an ionic compound is most likely to occur if the difference in electronegativity between two atoms is approximately 1.9 or greater. A bond is more likely to be covalent if this difference is less than 1.9. Note that the value 1.9 is somewhat arbitrary: Some chemists prefer a slightly larger value, others a slightly smaller value. The essential point is that the value 1.9 gives us a guidepost against which to decide whether a bond is more likely to be ionic or more likely to be covalent.

An example of an ionic bond is that formed between sodium (electronegativity 0.9) and fluorine (electronegativity 4.0). The difference in electronegativity between these two elements is 3.1. In forming Na^+F^- , the single 3*s* valence electron of sodium is transferred to the partially filled valence shell of fluorine:

$$Na(1s^{2} 2s^{2} 2p^{6} 3s^{1}) + F(1s^{2} 2s^{2} 2p^{5}) \longrightarrow Na^{+}(1s^{2} 2s^{2} 2p^{6}) + F^{-}(1s^{2} 2s^{2} 2p^{6})$$

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 closest to each in atomic number. In the following equation, we use a single-headed curved arrow to show the transfer of one electron from sodium to fluorine:

$$Na + F \longrightarrow Na^+ F$$

Covalent Bonds

A covalent bond forms when electron pairs are shared between two atoms whose difference in electronegativity is 1.9 or less. According to the Lewis model, an electron pair in a covalent bond functions in two ways simultaneously: It is shared by two atoms, and, at the same time, it fills the valence shell of each atom.

The simplest example of a covalent bond is that in a hydrogen molecule, H_2 . When two hydrogen atoms bond, the single electrons from each atom combine to form an electron pair with the release of energy. A bond formed by sharing a pair of electrons is called a *single bond* and is represented by a single line between the two atoms. The electron pair shared between the two hydrogen atoms in H_2 completes the valence shell of each hydrogen. Thus, in H_2 , each hydrogen has two electrons in its valence shell and an electron configuration like that of helium, the noble gas nearest to it in atomic number:

 $H \cdot + \cdot H \longrightarrow H - H$ $\Delta H^0 = -435 \text{ kJ/mol} (-104 \text{ kcal/mol})$

The Lewis model accounts for the stability of covalently bonded atoms in the following way: In forming a covalent bond, an electron pair occupies the region between two nuclei and serves to shield one positively charged nucleus from the repulsive force of the other positively charged nucleus. At the same time, an electron pair attracts both nuclei. In other words, an electron pair in the space between two nuclei bonds them together and fixes the internuclear distance to within very narrow limits. The distance between nuclei participating in a chemical bond is called a **bond length**. Every covalent bond has a definite bond length. In H—H, it is 74 pm, where 1 pm = 10^{-12} m.

Although all covalent bonds involve the sharing of electrons, they differ widely in the degree of sharing. We classify covalent bonds into two categories—nonpolar covalent and polar covalent—depending on the difference in electronegativity between the bonded atoms. In a **nonpolar covalent bond**, electrons are shared equally. In a **polar covalent bond**, they are shared unequally. It is important to realize that no sharp line divides these two categories, nor, for that matter, does a sharp line divide polar covalent bonds and ionic bonds. Nonetheless, the rule-of-thumb guidelines in Table 1.5 will help you decide whether a given bond is more likely to be nonpolar covalent, polar covalent, or ionic.

A covalent bond between carbon and hydrogen, for example, is classified as nonpolar covalent because the difference in electronegativity between these two atoms is 2.5 - 2.1 = 0.4 unit. An example of a polar covalent bond is that of H—Cl. The difference in electronegativity between chlorine and hydrogen is 3.0 - 2.1 = 0.9 unit.

Nonpo	lar coval	ent bond
-------	-----------	----------

A covalent bond between atoms whose difference in electronegativity is less than approximately 0.5.

Polar covalent bond

A covalent bond between atoms whose difference in electronegativity is between approximately 0.5 and 1.9.

TABLE 1.5 Classification of Chemical Bonds							
Difference in Electronegativity between Bonded Atoms	Type of Bond	Most Likely Formed Between					
Less than 0.5	Nonpolar covalent	Two nonmetals or a nonmetal					
0.5 to 1.9	Polar covalent \int	and a metalloid					
Greater than 1.9	Ionic	A metal and a nonmetal					

EXAMPLE 1.4

Classify each bond as nonpolar covalent, polar covalent, or ionic:

- (a) O-H
- (b) N-H
- (c) Na-F
- (d) C-Mg

STRATEGY

Use the difference in electronegativity between the two atoms and compare this value with the range of values given in Table 1.5.

SOLUTION

On the basis of differences in electronegativity between the bonded atoms, three of these bonds are polar covalent and one is ionic:

Bond	Difference in Electronegativity	Type of Bond
(a) O—H	3.5 - 2.1 = 1.4	polar covalent
(b) N—H	3.0 - 2.1 = 0.9	polar covalent
(c) Na—F	4.0 - 0.9 = 3.1	ionic
(d) C-Mg	2.5 - 1.2 = 1.3	polar covalent

See problem 1.25

PROBLEM 1.4

Classify each bond as nonpolar covalent, polar covalent, or ionic: (a) S-H (b) P-H (c) C-F (d) C-CI