



Organic Chemistry

SECOND EDITION

DAVID KLEIN

WILEY



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DAVID KLEIN

Johns Hopkins University

WILEY

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Dedication

To Larry,

By inspiring me to pursue a career in organic chemistry instruction, you served as the spark for the creation of this book. You showed me that any subject can be fascinating (even organic chemistry!) when presented by a masterful teacher. Your mentorship and friendship have profoundly shaped the course of my life, and I hope that this book will always serve as a source of pride and as a reminder of the impact you've had on your students.

To my wife, Vered,

This book would not have been possible without your partnership. As I worked for years in my office, you shouldered all of our life responsibilities, including taking care of all of the needs of our five amazing children. This book is our collective accomplishment and will forever serve as a testament of your constant support that I have come to depend on for everything in life. You are my rock, my partner, and my best friend. I love you.



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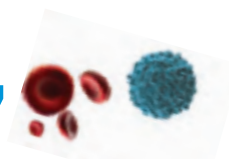


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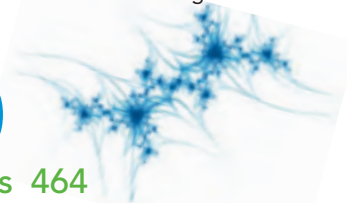
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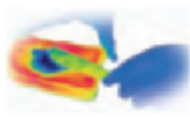
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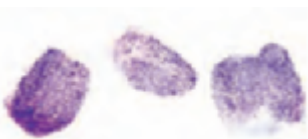
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WHY I WROTE THIS BOOK

Students who perform poorly on organic chemistry exams often report having invested countless hours studying. Why do many students have difficulty preparing themselves for organic chemistry exams? Certainly, there are several contributing factors, including inefficient study habits, but perhaps the most dominant factor is a fundamental *disconnect* between what students learn in the lecture hall and the tasks expected of them during an exam. To illustrate the disconnect, consider the following analogy.

Imagine that a prestigious university offers a course entitled “Bike-Riding 101.” Throughout the course, physics and engineering professors explain many concepts and principles (for example, how bicycles have been engineered to minimize air resistance). Students invest significant time studying the information that was presented, and on the last day of the course, the final exam consists of riding a bike for a distance of 100 feet. A few students may have innate talents and can accomplish the task without falling. But most students will fall several times, slowly making it to the finish line, bruised and hurt; and many students will not be able to ride for even one second without falling. Why? Because there is a *disconnect* between what the students learned and what they were expected to do for their exam.

Many years ago, I noticed that a similar disconnect exists in traditional organic chemistry instruction. That is, learning organic chemistry is much like bicycle riding; just as the students in the bike-riding analogy were expected to ride a bike after attending lectures, it is often expected that organic chemistry students will independently develop the necessary skills for solving problems. While a few students have innate talents and are able to develop the necessary skills independently, most students require guidance. This guidance was not consistently integrated within existing textbooks, prompting me to write the first edition of my textbook, *Organic Chemistry, 1e*. The main goal of my text was to employ a skills-based approach to bridge the gap between theory (concepts) and practice (problem-solving skills). The phenomenal success of the first edition has been extremely gratifying because it provides strong evidence that my skills-based approach is indeed effective at bridging the gap described above.

I firmly believe that the scientific discipline of organic chemistry is NOT merely a compilation of principles, but rather, it is a disciplined method of thought and analysis. Students must certainly understand the concepts and principles, but more importantly, students must learn to think like organic chemists . . . that is, they must learn to become proficient at approaching new situations methodically, based on a repertoire of skills. That is the true essence of organic chemistry.

A SKILLS-BASED APPROACH

To address the disconnect in organic chemistry instruction, I have developed a *skills-based approach* to instruction. The textbook includes all of the concepts typically covered in an organic chemistry textbook, complete with *conceptual checkpoints* that promote mastery of the concepts, but special emphasis is placed on skills development through SkillBuilders to support these concepts. Each SkillBuilder contains 3 parts:

Learn the Skill: contains a solved problem that demonstrates a particular skill.

Practice the Skill: includes numerous problems (similar to the solved problem in *Learn the Skill*) that give students valuable opportunities to practice and master the skill.

Apply the Skill: contains one or two more challenging problems in which the student must apply the skill in a slightly different environment. These problems include conceptual, cumulative, and applied problems that encourage students to think outside of the box. Sometimes problems that foreshadow concepts introduced in later chapters are also included.



At the end of each SkillBuilder, a *Need More Practice?* reference suggests end-of-chapter problems that students can work to practice the skill.

This emphasis upon skills development will provide students with a greater opportunity to develop proficiency in the key skills necessary to succeed in organic chemistry. Certainly, not all necessary skills can be covered in a textbook. However, there are certain skills that are fundamental to all other skills.

As an example, resonance structures are used repeatedly throughout the course, and students must become masters of resonance structures early in the course. Therefore a significant portion of Chapter 2 is devoted to pattern-recognition for drawing resonance structures. Rather than just providing a list of rules and then a few follow-up problems, the skills-based approach provides students with a series of skills, each of which must be mastered in sequence. Each skill is reinforced with numerous practice problems. The sequence of skills is designed to foster and develop proficiency in drawing resonance structures.

As another example of the skills-based approach, Chapter 7, Substitution Reactions, places special emphasis on the skills necessary for drawing all of the mechanistic steps for S_N2 and S_N1 processes. Students are often confused when they see an S_N1 process whose mechanism is comprised of four or five mechanistic steps (proton transfers, carbocation rearrangements, etc.). This chapter contains a novel approach that trains students to identify the number of mechanistic steps required in a substitution process. Students are provided with numerous examples and are given ample opportunity to practice drawing mechanisms.

The skills-based approach to organic chemistry instruction is a unique approach. Certainly, other textbooks contain tips for problem solving, but no other textbook consistently presents skills development as the primary vehicle for instruction.

WHAT'S NEW IN THIS EDITION

Peer review played a very strong role in the development of the first edition of *Organic Chemistry*. Specifically, the first edition manuscript was reviewed by nearly 500 professors and over 5,000 students. In preparing the second edition, peer review has played an equally prominent role. We have received a tremendous amount of input from the market, including surveys, class tests, diary reviews, and phone interviews. All of this input has been carefully culled and has been instrumental in identifying the focus of the second edition.

Literature-based Challenge Problems

The first edition of my textbook, *Organic Chemistry 1e*, was written to address a gap between theory (concepts) and practice (problem-solving skills). In *Organic Chemistry 2e*, I have endeavored to bridge yet another gap between theory and practice. Specifically, students who have studied organic chemistry for an entire year are often left profoundly disconnected from the dynamic and exciting world of research in the field of organic chemistry. That is, students are not exposed to actual research performed by practicing organic chemists around the world. To bridge this gap and to address market feedback suggesting that the text would benefit from a larger number of challenge problems, I've created literature-based Challenge Problems for this edition. These problems will expose students to the fact that organic chemistry is an evolving, active branch of science, central to addressing global challenges.

The literature-based Challenge Problems are more challenging than the problems presented in the text's SkillBuilders because they require the students to think "outside the box" and to predict or explain an unexpected observation. Over 225 new literature-based Challenge Problems have been added in *Organic Chemistry, 2e*. All of these problems are based on the chemical literature and include references. The problems are all designed to be thought-provoking puzzles that are challenging, but possible to solve with the principles and skills developed in the textbook. The inclusion of literature-based problems will expose students to exciting real-world examples of chemical research being conducted in real laboratories. Students will see that organic chemistry is a vibrant field of study, with endless possibilities for exploration and research that can benefit the world in very concrete ways. Most chapters of *Organic Chemistry, 2e* will have 8-10 literature-based Challenge Problems. These problems are all coded for assigning and grading in

WileyPLUS. In addition, within the WileyPLUS course for *Organic Chemistry, 2e*, I've created problem solving videos that provide key strategies for solving a subset of these problems.

Rewriting for Clarity

In response to market feedback a few sections in the textbook have been rewritten for clarity:

Chapter 7: Substitution Reactions/Section 7.5: The S_N1 Mechanism

- The discussion of the rate-determining step has been revised to focus on the highest energy transition state. A more detailed discussion of the thermodynamic principles involved is now included.

Chapter 20: Aldehydes and Ketones/Section 20.7: Mechanism Strategies

- The section on hydrolysis, as well as the corresponding SkillBuilder, have been rewritten for clarity.

Chapter 20: Aldehydes and Ketones/Section 20.10: Carbon Nucleophiles

- The discussion of the Wittig reaction mechanism has been revised to better reflect the observations and insights discussed in the literature.

Applications and Chapter Openers

Much like the literature-based Challenge Problems underscore the relevance of organic chemistry to current research in the field, the Medically Speaking and Practically Speaking applications demonstrate how the first principles of organic chemistry are relevant to practicing physicians and have everyday commercial applications. We have received very positive feedback from the market regarding these applications. In recognition of the fact that some applications generate more interest than others, we've replaced approximately 10% of the applications, to make them even more relevant and exciting. Since these applications are often foreshadowed in the Chapter Openers, many Chapter Openers have been revised as well.

Reference Materials

An appendix containing rules for naming polyfunctional compounds as well as a reference table of pK_a values are now included.

In addition, all known errors, inaccuracies, or ambiguities have been corrected in the second edition.

TEXT ORGANIZATION

The sequence of chapters and topics in *Organic Chemistry, 2e* do not differ markedly from that of other organic chemistry textbooks. Indeed, the topics are presented in the traditional order, based on functional groups (alkenes, alkynes, alcohols, ethers, aldehydes and ketones, carboxylic acid derivatives, etc.). Despite this traditional order, a strong emphasis is placed on mechanisms, with a focus on pattern recognition to illustrate the similarities between reactions that would otherwise appear unrelated (for example, acetal formation and enamine formation, which are mechanistically quite similar). No shortcuts were taken in any of the mechanisms, and all steps are clearly illustrated, including all proton transfer steps.

Two chapters (6 and 12) are devoted almost entirely to skill development and are generally not found in other textbooks. Chapter 6, *Chemical Reactivity and Mechanisms*, emphasizes skills that are necessary for drawing mechanisms, while Chapter 12, *Synthesis*, prepares the students for proposing syntheses. These two chapters are strategically positioned within the traditional order described above and can be assigned to the students for independent study. That is, these two chapters do not need to be covered during precious lecture hours, but can be, if so desired.

The traditional order allows instructors to adopt the skills-based approach without having to change their lecture notes or methods. For this reason, the spectroscopy chapters (Chapters 15 and 16) were written to be stand-alone and portable, so that instructors can cover these chapters in any order desired. In fact, five of the chapters (Chapters 2, 3, 7, 13, and 14) that precede the spectroscopy chapters include end-of-chapter spectroscopy problems, for those students who

covered spectroscopy earlier. Spectroscopy coverage also appears in subsequent functional group chapters, specifically Chapter 18 (Aromatic Compounds), Chapter 20 (Aldehydes and Ketones), Chapter 21 (Carboxylic Acids and Their Derivatives), Chapter 23 (Amines), Chapter 24 (Carbohydrates), and Chapter 25 (Amino Acids, Peptides, and Proteins).

THE WileyPLUS ADVANTAGE

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New to WileyPLUS for Organic Chemistry, 2e

WileyPLUS for *Organic Chemistry, 2e* highlights David Klein's innovative pedagogy and teaching style:

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- **NEW Guided Online (GO) Tutorials** walk students step-by-step through solving the problem using David Klein's problem-solving pedagogy.
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ADDITIONAL INSTRUCTOR RESOURCES

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PowerPoint Lecture Slides with Answer Slides Authored by James Beil, *Lorain County Community College*.

PowerPoint Art Slides Images selected by Christine Hermann, *Radford University*.

Personal Response System (“Clicker”) Questions Authored by Cynthia Lamberty, *Cloud County Community College, Geary County Campus*, Neal Tonks, *College of Charleston*, Christine Whitlock, *Georgia Southern University*.

STUDENT RESOURCES

Student Study Guide and Solutions Manual (ISBN 9781118700815) Authored by David Klein. The second edition of the *Student Study Guide and Solutions Manual* to accompany *Organic Chemistry, 2e* contains:

- More detailed explanations within the solutions for every problem.
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- SkillBuilder Review Exercises
- Reaction Review Exercises
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Mushtaq Khan, Union County College
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A Review of General Chemistry

1

ELECTRONS, BONDS, AND MOLECULAR PROPERTIES

DID YOU EVER WONDER... what causes lightning?

Believe it or not, the answer to this question is still the subject of debate (that's right... scientists have not yet figured out everything, contrary to popular belief). There are various theories that attempt to explain what causes the buildup of electric charge in clouds. One thing is clear, though—lightning involves a flow of electrons. By studying the nature of electrons and how electrons flow, it is possible to control where lightning will strike. A tall building can be protected by installing a lightning rod (a tall metal column at the top of the building) that attracts any nearby lightning bolt, thereby preventing a direct strike on the building itself. The lightning rod on the top of the Empire State Building is struck over a hundred times each year.

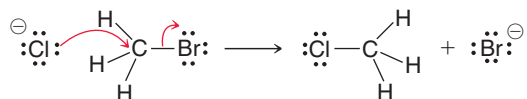
Just as scientists have discovered how to direct electrons in a bolt of lightning, chemists have also discovered how to direct electrons in chemical reactions. We will soon see that although organic chemistry is literally defined as the study of compounds containing carbon atoms, its true essence is actually the study of electrons, not atoms. Rather than thinking of reactions in terms of the motion of atoms, we

continued >

- 1.1 Introduction to Organic Chemistry
- 1.2 The Structural Theory of Matter
- 1.3 Electrons, Bonds, and Lewis Structures
- 1.4 Identifying Formal Charges
- 1.5 Induction and Polar Covalent Bonds
- 1.6 Atomic Orbitals
- 1.7 Valence Bond Theory
- 1.8 Molecular Orbital Theory
- 1.9 Hybridized Atomic Orbitals
- 1.10 VSEPR Theory: Predicting Geometry
- 1.11 Dipole Moments and Molecular Polarity
- 1.12 Intermolecular Forces and Physical Properties
- 1.13 Solubility



must recognize that *reactions occur as a result of the motion of electrons*. For example, in the following reaction the curved arrows represent the motion, or flow, of electrons. This flow of electrons causes the chemical change shown:

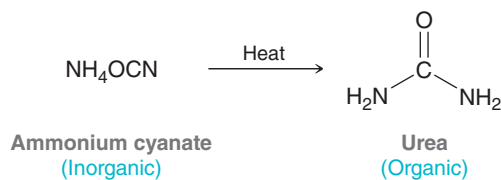


Throughout this course, we will learn how, when, and why electrons flow during reactions. We will learn about the barriers that prevent electrons from flowing, and we will learn how to overcome those barriers. In short, we will study the behavioral patterns of electrons, enabling us to predict, and even control, the outcomes of chemical reactions.

This chapter reviews some relevant concepts from your general chemistry course that should be familiar to you. Specifically, we will focus on the central role of electrons in forming bonds and influencing molecular properties.

1.1 Introduction to Organic Chemistry

In the early nineteenth century, scientists classified all known compounds into two categories: *Organic compounds* were derived from living organisms (plants and animals), while *inorganic compounds* were derived from nonliving sources (minerals and gases). This distinction was fueled by the observation that organic compounds seemed to possess different properties than inorganic compounds. Organic compounds were often difficult to isolate and purify, and upon heating, they decomposed more readily than inorganic compounds. To explain these curious observations, many scientists subscribed to a belief that compounds obtained from living sources possessed a special “vital force” that inorganic compounds lacked. This notion, called vitalism, stipulated that it should be impossible to convert inorganic compounds into organic compounds without the introduction of an outside vital force. Vitalism was dealt a serious blow in 1828 when German chemist Friedrich Wöhler demonstrated the conversion of ammonium cyanate (a known inorganic salt) into urea, a known organic compound found in urine:



BY THE WAY

There are some carbon-containing compounds that are traditionally excluded from organic classification. For example, ammonium cyanate (seen on this page) is still classified as inorganic, despite the presence of a carbon atom. Other exceptions include sodium carbonate (Na_2CO_3) and potassium cyanide (KCN), both of which are also considered to be inorganic compounds. We will not encounter many more exceptions.

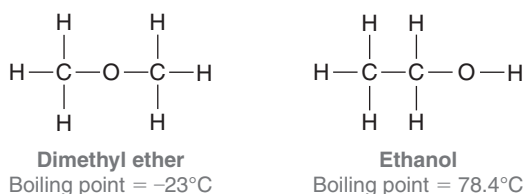
Over the decades that followed, other examples were found, and the concept of vitalism was gradually rejected. The downfall of vitalism shattered the original distinction between organic and inorganic compounds, and a new definition emerged. Specifically, organic compounds became defined as those compounds containing carbon atoms, while inorganic compounds generally were defined as those compounds lacking carbon atoms.

Organic chemistry occupies a central role in the world around us, as we are surrounded by organic compounds. The food that we eat and the clothes that we wear are comprised of organic compounds. Our ability to smell odors or see colors results from the behavior of organic compounds. Pharmaceuticals, pesticides, paints, adhesives, and plastics are all made from organic compounds. In fact, our bodies are constructed mostly from organic compounds (DNA, RNA, proteins, etc.) whose behavior and function are determined by the guiding principles of organic chemistry. The responses of our bodies to pharmaceuticals are the results of reactions guided by the principles of organic chemistry. A deep understanding of those principles enables the design of new drugs that fight disease and improve the overall quality of life and longevity. Accordingly, it is not surprising that organic chemistry is required knowledge for anyone entering the health professions.



1.2 The Structural Theory of Matter

In the mid-nineteenth century three individuals, working independently, laid the conceptual foundations for the structural theory of matter. August Kekulé, Archibald Scott Couper, and Alexander M. Butlerov each suggested that substances are defined by a specific arrangement of atoms. As an example, consider the following two compounds:



These compounds have the same molecular formula ($\text{C}_2\text{H}_6\text{O}$), yet they differ from each other in the way the atoms are connected—that is, they differ in their constitution. As a result, they are called **constitutional isomers**. Constitutional isomers have different physical properties and different names. The first compound is a colorless gas used as an aerosol spray propellant, while the second compound is a clear liquid, commonly referred to as “alcohol,” found in alcoholic beverages.

According to the structural theory of matter, each element will generally form a predictable number of bonds. For example, carbon generally forms four bonds and is therefore said to be **tetravalent**. Nitrogen generally forms three bonds and is therefore **trivalent**. Oxygen forms two bonds and is **divalent**, while hydrogen and the halogens form one bond and are **monovalent** (Figure 1.1).

<i>Tetravalent</i>	<i>Trivalent</i>	<i>Divalent</i>	<i>Monovalent</i>
$\begin{array}{c} \\ -\text{C}- \\ \end{array}$	$\begin{array}{c} -\text{N}- \\ \end{array}$	$-\text{O}-$	$\begin{array}{c} \text{H}- & \text{X}- \\ \text{(where X = F, Cl, Br, or I)} \end{array}$
Carbon generally forms four bonds.	Nitrogen generally forms three bonds.	Oxygen generally forms two bonds.	Hydrogen and halogens generally form one bond.

FIGURE 1.1
Valencies of some common elements encountered in organic chemistry.

SKILLBUILDER



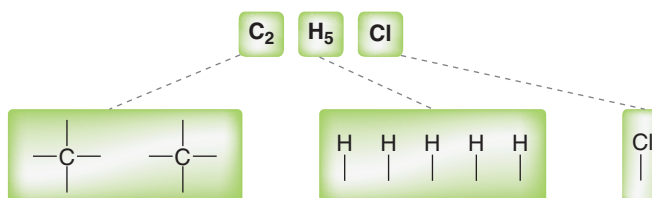
1.1 DETERMINING THE CONSTITUTION OF SMALL MOLECULES

LEARN the skill

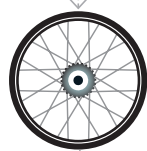
There is only one compound that has molecular formula $\text{C}_2\text{H}_5\text{Cl}$. Determine the constitution of this compound.

SOLUTION

The molecular formula indicates which atoms are present in the compound. In this example, the compound contains two carbon atoms, five hydrogen atoms, and one chlorine atom. Begin by determining the valency of each atom that is present in the compound. Each carbon atom is expected to be tetravalent, while the chlorine and hydrogen atoms are all expected to be monovalent:



STEP 1
Determine the valency of each atom in the compound.



STEP 2

Determine how the atoms are connected—atoms with the highest valency should be placed at the center and monovalent atoms should be placed at the periphery.

**PRACTICE the skill**

1.1 Determine the constitution of the compounds with the following molecular formulas:

**APPLY the skill**

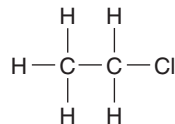
1.2 There are two constitutional isomers with molecular formula C₃H₇Cl, because there are two possibilities for the location of the chlorine atom. It can be connected either to the central carbon atom or to one of the other two (equivalent) carbon atoms. Draw both isomers.

1.3 Draw three constitutional isomers that have molecular formula C₃H₈O.

1.4 Draw all constitutional isomers that have molecular formula C₄H₁₀O.

need more **PRACTICE?** Try Problems 1.34, 1.46, 1.47, 1.54

Now we must determine how these atoms are connected. The atoms with the most bonds (the carbon atoms) are likely to be in the center of the compound. In contrast, the chlorine atom and hydrogen atoms can each form only one bond, so those atoms must be placed at the periphery. In this example, it does not matter where the chlorine atom is placed. All six possible positions are equivalent.



1.3 Electrons, Bonds, and Lewis Structures

What Are Bonds?

As mentioned, atoms are connected to each other by bonds. That is, bonds are the “glue” that hold atoms together. But what is this mysterious glue and how does it work? In order to answer this question, we must focus our attention on electrons.

The existence of the electron was first proposed in 1874 by George Johnstone Stoney (National University of Ireland), who attempted to explain electrochemistry by suggesting the existence of a particle bearing a unit of charge. Stoney coined the term *electron* to describe this particle. In 1897, J. J. Thomson (Cambridge University) demonstrated evidence supporting the existence of Stoney’s mysterious electron and is credited with discovering the electron. In 1916, Gilbert Lewis (University of California, Berkeley) defined a **covalent bond** as the result of *two atoms sharing a pair of electrons*. As a simple example, consider the formation of a bond between two hydrogen atoms:



Each hydrogen atom has one electron. When these electrons are shared to form a bond, there is a decrease in energy, indicated by the negative value of ΔH . The energy diagram in Figure 1.2 plots the energy of the two hydrogen atoms as a function of the distance between them. Focus on the right side of the diagram, which represents the hydrogen atoms separated by a large distance. Moving toward the left on the diagram, the hydrogen atoms approach each other, and there are several forces that must be taken into account: (1) the force of repulsion between the two negatively charged electrons, (2) the force of repulsion between the two positively charged nuclei, and (3) the forces of attraction between the positively charged nuclei and the negatively charged electrons. As the hydrogen atoms get closer to each other, all of these forces get stronger. Under these

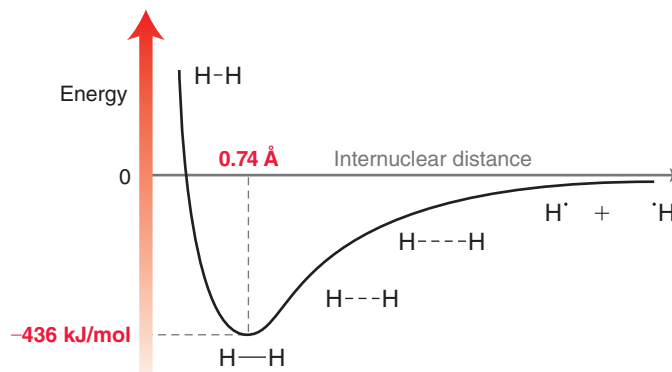


FIGURE 1.2

An energy diagram showing the energy as a function of the internuclear distance between two hydrogen atoms.

BY THE WAY

$1 \text{ \AA} = 10^{-10}$ meters.

circumstances, the electrons are capable of moving in such a way so as to minimize the repulsive forces between them while maximizing their attractive forces with the nuclei. This provides for a net force of attraction, which lowers the energy of the system. As the hydrogen atoms move still closer together, the energy continues to be lowered until the nuclei achieve a separation (internuclear distance) of 0.74 angstroms (\AA). At that point, the force of repulsion between the nuclei begins to overwhelm the forces of attraction, causing the energy of the system to increase. The lowest point on the curve represents the lowest energy (most stable) state. This state determines both the bond length (0.74 \AA) and the bond strength (436 kJ/mol).

Drawing the Lewis Structure of an Atom

Armed with the idea that a bond represents a pair of shared electrons, Lewis then devised a method for drawing structures. In his drawings, called **Lewis structures**, the electrons take center stage. We will begin by drawing individual atoms, and then we will draw Lewis structures for small molecules. First, we must review a few simple features of atomic structure:

- The nucleus of an atom is comprised of protons and neutrons. Each proton has a charge of +1, and each neutron is electrically neutral.
- For a neutral atom, the number of protons is balanced by an equal number of electrons, which have a charge of -1 and exist in shells. The first shell, which is closest to the nucleus, can contain two electrons, and the second shell can contain up to eight electrons.
- The electrons in the outermost shell of an atom are called the valence electrons. The number of valence electrons in an atom is identified by its group number in the periodic table (Figure 1.3).

The Lewis dot structure of an individual atom indicates the number of valence electrons, which are placed as dots around the periodic symbol of the atom (C for carbon, O for oxygen, etc.). The placement of these dots is illustrated in the following SkillBuilder.

1A								8A			
H	2A							He			
Li	Be					B	C	N	O	F	Ne
Na	Mg					Al	Si	P	S	Cl	Ar
K	Ca					Ga	Ge	As	Se	Br	Kr
Rb	Sr					In	Sn	Sb	Te	I	Xe
Cs	Ba					Tl	Pb	Bi	Po	At	Rn
				Transition Metal Elements							

FIGURE 1.3

A periodic table showing group numbers.

SKILLBUILDER



1.2 DRAWING THE LEWIS DOT STRUCTURE OF AN ATOM



LEARN the skill

Draw the Lewis dot structure of (a) a boron atom and (b) a nitrogen atom.



SOLUTION

STEP 1

Determine the number of valence electrons.

STEP 2

Place one valence electron by itself on each side of the atom.

STEP 3

If the atom has more than four valence electrons, the remaining electrons are paired with the electrons already drawn.



PRACTICE the skill

1.5 Draw a Lewis dot structure for each of the following atoms:

- (a) Carbon (b) Oxygen (c) Fluorine (d) Hydrogen
 (e) Bromine (f) Sulfur (g) Chlorine (h) Iodine



APPLY the skill

1.6 Compare the Lewis dot structure of nitrogen and phosphorus and explain why you might expect these two atoms to exhibit similar bonding properties.

1.7 Name one element that you would expect to exhibit bonding properties similar to boron. Explain.

1.8 Draw a Lewis structure of a carbon atom that is missing one valence electron (and therefore bears a positive charge). Which second-row element does this carbon atom resemble in terms of the number of valence electrons?

1.9 Draw a Lewis structure of a carbon atom that has one extra valence electron (and therefore bears a negative charge). Which second-row element does this carbon atom resemble in terms of the number of valence electrons?



- (b) Nitrogen belongs to group 5A on the periodic table, and it therefore has five valence electrons. The periodic symbol for nitrogen (N) is drawn, and each electron is placed by itself (unpaired) on a side of the N until all four sides are occupied:

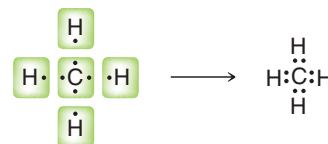


Any remaining electrons must be paired up with the electrons already drawn. In the case of nitrogen, there is only one more electron to place, so we pair it up with one of the four unpaired electrons (it doesn't matter which one we choose):



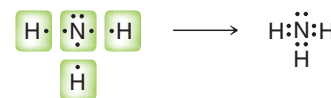
Drawing the Lewis Structure of a Small Molecule

The Lewis dot structures of individual atoms are combined to produce Lewis dot structures of small molecules. These drawings are constructed based on the observation that atoms tend to bond in such a way so as to achieve the electron configuration of a noble gas. For example, hydrogen will form one bond to achieve the electron configuration of helium (two valence electrons), while second-row elements (C, N, O, and F) will form the necessary number of bonds so as to achieve the electron configuration of neon (eight valence electrons).





This observation, called the **octet rule**, explains why carbon is tetravalent. As just shown, it can achieve an octet of electrons by using each of its four valence electrons to form a bond. The octet rule also explains why nitrogen is trivalent. Specifically, it has five valence electrons and requires three bonds in order to achieve an octet of electrons. Notice that the nitrogen atom contains one pair of unshared, or nonbonding, electrons, called a **lone pair**.



In the next chapter, we will discuss the octet rule in more detail; in particular, we will explore when it can be violated and when it cannot be violated. For now, let's practice drawing Lewis structures.

SKILLBUILDER



1.3 DRAWING THE LEWIS STRUCTURE OF A SMALL MOLECULE

LEARN the skill

Draw the Lewis structure of CH_2O .

SOLUTION

There are four discrete steps when drawing a Lewis structure: First determine the number of valence electrons for each atom:



Then, connect any atoms that form more than one bond. Hydrogen atoms only form one bond each, so we will save those for last. In this case, we connect the C and the O:



Next, connect all hydrogen atoms. We place the hydrogen atoms next to carbon, because carbon has more unpaired electrons than oxygen:



Finally, check to see if each atom (except hydrogen) has an octet. In fact, neither the carbon nor the oxygen has an octet, so in a situation like this, the unpaired electrons are shared as a double bond between carbon and oxygen:



Now all atoms have achieved an octet. When drawing Lewis structures, remember that you cannot simply add more electrons to the drawing. For each atom to achieve an octet the existing electrons must be shared. The total number of valence electrons should be correct when you are finished. In this example, there was one carbon atom, two hydrogen atoms, and one oxygen atom, giving a total of 12 valence electrons ($4 + 2 + 6$). The drawing above MUST have 12 valence electrons, no more and no less.

PRACTICE the skill

1.10 Draw a Lewis structure for each of the following compounds:

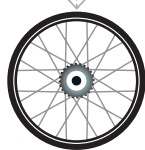
- (a) C_2H_6 (b) C_2H_4 (c) C_2H_2
 (d) C_3H_8 (e) C_3H_6 (f) CH_3OH

APPLY the skill

1.11 Borane (BH_3) is very unstable and quite reactive. Draw a Lewis structure of borane and explain the source of the instability.

1.12 There are four constitutional isomers with molecular formula $\text{C}_3\text{H}_9\text{N}$. Draw a Lewis structure for each isomer and determine the number of lone pairs on the nitrogen atom in each case.

need more PRACTICE? Try Problems 1.35, 1.38, 1.42



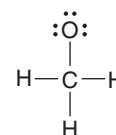
1.4 Identifying Formal Charges

A **formal charge** is associated with any atom that does not exhibit the appropriate number of valence electrons. When such an atom is present in a Lewis structure, the formal charge must be drawn. Identifying a formal charge requires two discrete tasks:

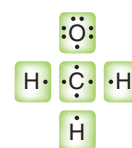
1. Determine the appropriate number of valence electrons for an atom.
2. Determine whether the atom exhibits the appropriate number of electrons.

The first task can be accomplished by inspecting the periodic table. As mentioned earlier, the group number indicates the appropriate number of valence electrons for each atom. For example, carbon is in group 4A and therefore has four valence electrons. Oxygen is in group 6A and has six valence electrons.

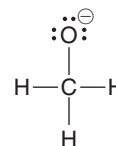
After identifying the appropriate number of electrons for each atom in a Lewis structure, the next task is to determine if any of the atoms exhibit an unexpected number of electrons. For example, consider the following structure:



Each line represents two shared electrons (a bond). For our purposes, we must split each bond apart equally, and then count the number of electrons on each atom:



Each hydrogen atom has one valence electron, as expected. The carbon atom also has the appropriate number of valence electrons (four), but the oxygen atom does not. The oxygen atom in this structure exhibits seven valence electrons, but it should only have six. In this case, the oxygen atom has one extra electron, and it must therefore bear a negative formal charge, which is indicated like this:



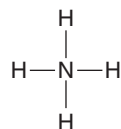
SKILLBUILDER



1.4 CALCULATING FORMAL CHARGE

LEARN the skill

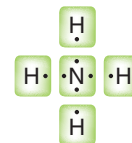
Consider the nitrogen atom in the structure below and determine if it has a formal charge:



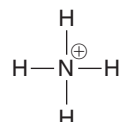
SOLUTION

We begin by determining the appropriate number of valence electrons for a nitrogen atom. Nitrogen is in group 5A of the periodic table, and it should therefore have five valence electrons.

Next, we count how many valence electrons are exhibited by the nitrogen atom in this particular example:



In this case, the nitrogen atom exhibits only four valence electrons. It is missing one electron, so it must bear a positive charge, which is shown like this:



STEP 1

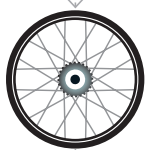
Determine the appropriate number of valence electrons.

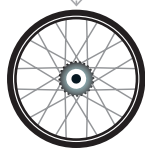
STEP 2

Determine the actual number of valence electrons in this case.

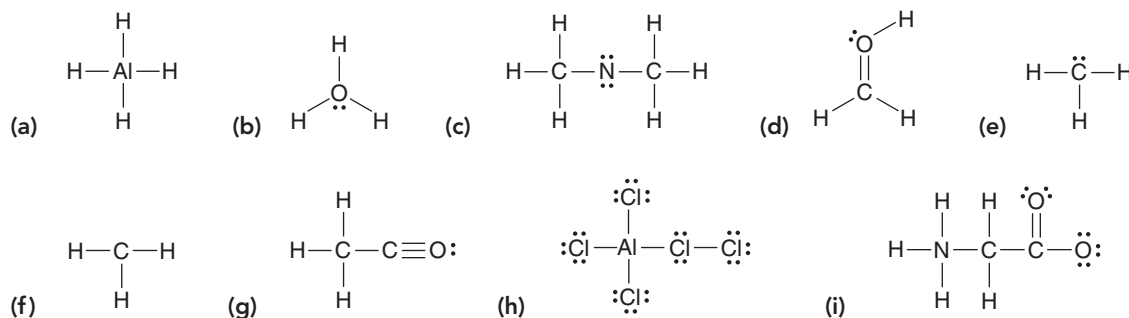
STEP 3

Assign a formal charge.





PRACTICE the skill 1.13 Identify any formal charges in the structures below:



APPLY the skill

1.14 Draw a structure for each of the following ions; in each case, indicate which atom possesses the formal charge:



need more PRACTICE? Try Problem 1.41

1.5 Induction and Polar Covalent Bonds

Chemists classify bonds into three categories: (1) covalent, (2) polar covalent, and (3) ionic. These categories emerge from the electronegativity values of the atoms sharing a bond. Electronegativity is a measure of the ability of an atom to attract electrons. Table 1.1 gives the electronegativity values for elements commonly encountered in organic chemistry.

TABLE 1.1 ELECTRONEGATIVITY VALUES OF SOME COMMON ELEMENTS

Increasing electronegativity \rightarrow

			H 2.1				
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Increasing electronegativity \uparrow
K 0.8						Br 2.8	

When two atoms form a bond, one critical consideration allows us to classify the bond: What is the difference in the electronegativity values of the two atoms? Below are some rough guidelines:

If the difference in electronegativity is less than 0.5, the electrons are considered to be equally shared between the two atoms, resulting in a covalent bond. Examples include C—C and C—H:



The C—C bond is clearly covalent, because there is no difference in electronegativity between the two atoms forming the bond. Even a C—H bond is considered to be covalent, because the difference in electronegativity between C and H is less than 0.5.

If the difference in electronegativity is between 0.5 and 1.7, the electrons are not shared equally between the atoms, resulting in a **polar covalent bond**. For example, consider a bond between carbon and oxygen (C—O). Oxygen is significantly more electronegative (3.5) than carbon (2.5), and therefore oxygen will more strongly attract the electrons of the bond.