

ORGANIC CHEMISTRY

THIRD EDITION

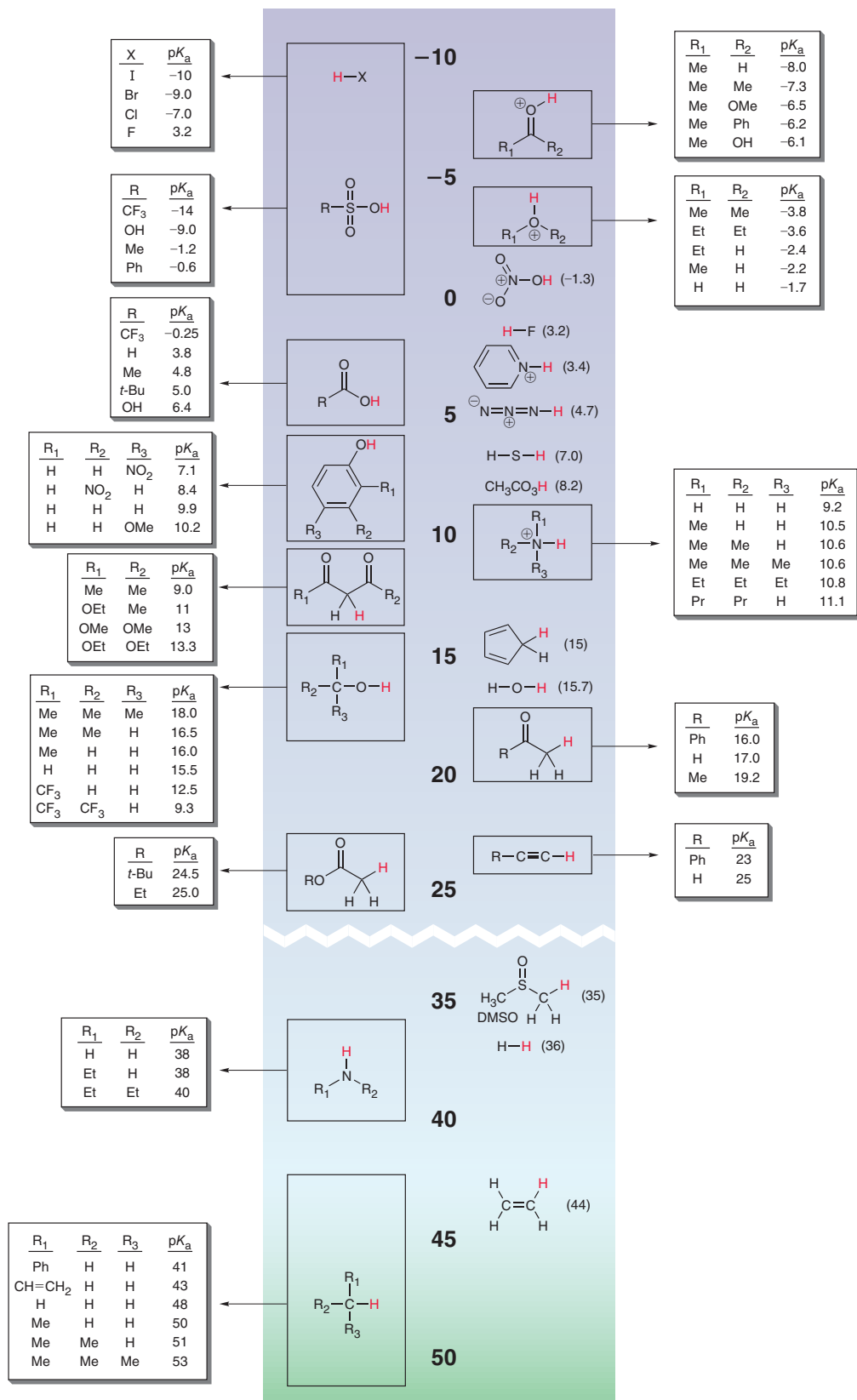


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Approximate pK_a Values for Commonly Encountered Structural Types



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ORGANIC CHEMISTRY

THIRD EDITION



DAVID KLEIN

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WILEY

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Dedication

To my father and mother,

You have saved me (quite literally) on so many occasions, always steering me in the right direction. I have always cherished your guidance, which has served as a compass for me in all of my pursuits. You repeatedly urged me to work on this textbook (“write the book!”, you would say so often), with full confidence that it would be appreciated by students around the world. I will forever rely on the life lessons that you have taught me and the values that you have instilled in me. I love you.

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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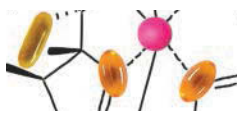
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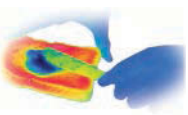


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Preface

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*. 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 second edition further supported this goal by introducing hundreds of additional problems based on the chemical literature, thereby exposing students to exciting real-world examples of chemical research being conducted in real laboratories. The phenomenal success of the first two editions has been extremely gratifying because it provided 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 three 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 problems in which the student must apply the skill to solve real-world problems (as reported in the chemical literature). 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 provides 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.

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 and second editions of *Organic Chemistry*. Specifically, the first edition manuscript was reviewed by nearly 500 professors and over 5,000 students, and the second edition manuscript was based on

comments received from 300 professors and 900 students. In preparing the third 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 third edition.

New Features in the Third Edition

- A new chapter on organometallic reactions covers modern synthetic techniques, including Stille coupling, Suzuki coupling, Negishi coupling, the Heck reaction, and alkene metathesis.
- Substitution and elimination reactions have been combined into one chapter. This chapter (Chapter 7) also features a new section covering the preparation and reactions of alkyl tosylates, as well as a new section covering kinetic isotope effects. In addition, a new section introducing retrosynthesis has been added to the end of the chapter, so that synthesis and retrosynthesis are now introduced much earlier.
- For most SkillBuilders throughout the text, the Apply the Skill problem(s) have been replaced with moderate-level, literature-based problems. There are at least 150 of these new problems, which 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 concrete ways.
- Throughout the text, the distribution of problems has been improved by reducing the number of easy problems, and increasing the number of moderate-level, literature-based problems.
- Each chapter now includes a problem set that mimics the style of the ACS Organic Chemistry Exam.
- The section covering oxidation of alcohols (in Chapter 12, and then again in Chapter 19) has been enhanced to include modern oxidation methods, such as Swern and DMP-based oxidations.
- Coverage of Wittig reactions has been updated to include stereochemical outcomes and the Horner–Wadsworth–Emmons variation.
- Section 2.11 has been revised (Assessing the relative importance of resonance structures). The rules have been completely rewritten to focus on the importance of octets and locations of charges. The improved rules will provide students with a deeper conceptual understanding.
- In Chapter 2, a new section covers the skills necessary for drawing a resonance hybrid.
- At the end of Chapter 5 (Stereoisomerism), a new section introduces chiral compounds that lack chiral centers, including chiral allenes and chiral biphenyls.
- A new section in Chapter 11 (Synthesis) introduces “green chemistry” (atom economy, toxicology issues, etc.).
- Coverage of *E-Z* nomenclature has been moved earlier. It now appears in Chapter 5, which covers stereoisomerism.

TEXT ORGANIZATION

The sequence of chapters and topics in *Organic Chemistry, 3e* does 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. No shortcuts were taken in any of the mechanisms, and all steps are clearly illustrated, including all proton transfer steps.

Two chapters (6 and 11) 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 11, *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 14 and 15) 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, 12, and 13) 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 17 (*Aromatic Compounds*), Chapter 19 (*Aldehydes and Ketones*), Chapter 20 (*Carboxylic Acids and Their Derivatives*), Chapter 22 (*Amines*), Chapter 24 (*Carbohydrates*), and Chapter 25 (*Amino Acids, Peptides, and Proteins*).

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ADDITIONAL INSTRUCTOR RESOURCES

Testbank Prepared by Christine Hermann, *Radford University*.

PowerPoint Lecture Slides with Answer Slides Prepared by Adam Keller, *Columbus State Community College*.

PowerPoint Art Slides Prepared by Kevin Minbiole, *Villanova University*.

Personal Response System ("Clicker") Questions Prepared by Dalila Kovacs, *Grand Valley State University* and Randy Winchester, *Grand Valley State University*.

STUDENT RESOURCES

Student Study Guide and Solutions Manual (ISBN 9781118700815) Authored by David Klein. The third edition of the *Student Study Guide and Solutions Manual* to accompany *Organic Chemistry, 3e* contains:

- More detailed explanations within the solutions for every problem.

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- Concept Review Exercises
- SkillBuilder Review Exercises
- Reaction Review Exercises
- A list of new reagents for each chapter, with a description of their function.
- A list of "Common Mistakes to Avoid" in every chapter.

Molecular Visions™ Model Kit To support the learning of organic chemistry concepts and allow students the tactile experience of manipulating physical models, we offer a molecular modeling kit from the Darling Company. The model kit can be bundled with the textbook or purchased stand alone.

CONTRIBUTORS TO ORGANIC CHEMISTRY, 3E

I owe special thanks to my contributors for their collaboration, hard work, and creativity. Many of the new, literature-based, SkillBuilder problems were written by Laurie Starkey, *California State Polytechnic University, Pomona*; Tiffany Gierasch, *University of Maryland, Baltimore County*; Seth Elsheimer, *University of Central Florida*; and James Mackay, *Elizabethtown College*. Sections 2.11 and 19.10 were rewritten by Laurie Starkey, and Section 2.12 was written by Tiffany Gierasch. Many of the new Medically Speaking and Practically Speaking applications throughout the text were written by Ron Swisher, *Oregon Institute of Technology*.

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Despite my best efforts, as well as the best efforts of the reviewers, accuracy checkers, and class testers, errors may still exist. I take full responsibility for any such errors and would encourage those using my textbook to contact me with any errors that you may find.

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A Review of General Chemistry

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 must recognize that

continued >

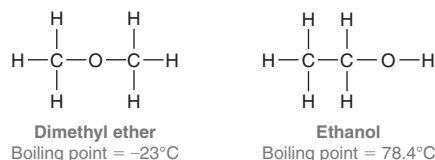
- 1.1 Introduction to Organic Chemistry
- 1.2 The Structural Theory of Matter
- 1.3 Electrons, Bonds, and Lewis Structures
- 1.4 Identifying Formal Charges
- 1.5 Induction and Polar Covalent Bonds
- 1.6 Atomic Orbitals
- 1.7 Valence Bond Theory
- 1.8 Molecular Orbital Theory
- 1.9 Hybridized Atomic Orbitals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





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>
$\begin{array}{c} \\ -\text{C}- \\ \end{array}$	$\begin{array}{c} -\text{N}- \\ \end{array}$	$-\text{O}-$	$\text{H}-\quad \text{X}-$ (where X = F, Cl, Br, or I)
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 DRAWING CONSTITUTIONAL ISOMERS OF SMALL MOLECULES

LEARN the skill

Draw all constitutional isomers that have the molecular formula $\text{C}_3\text{H}_8\text{O}$.

STEP 1

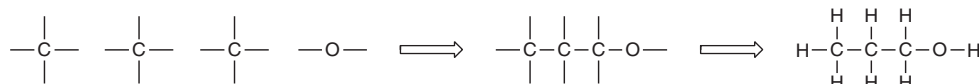
Determine the valency of each atom that appears in the molecular formula.

STEP 2

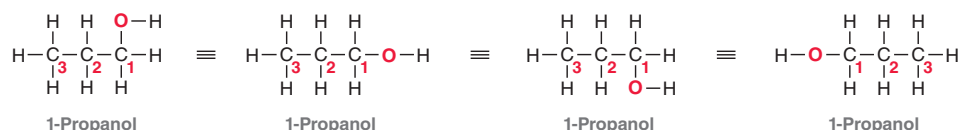
Connect the atoms of highest valency, and place the monovalent atoms at the periphery.

SOLUTION

Begin by determining the valency of each atom that appears in the molecular formula. Carbon is tetravalent, hydrogen is monovalent, and oxygen is divalent. The atoms with the highest valency are connected first. So, in this case, we draw our first isomer by connecting the three carbon atoms, as well as the oxygen atom, as shown below. The drawing is completed when the monovalent atoms (H) are placed at the periphery:



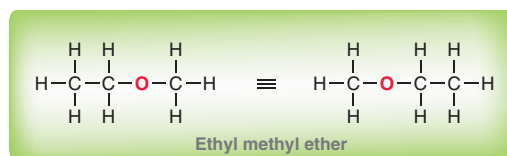
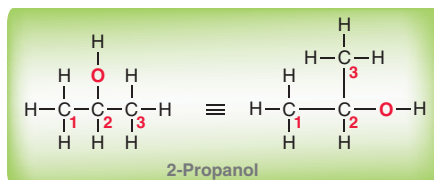
This isomer (called 1-propanol) can be drawn in many different ways, some of which are shown here:



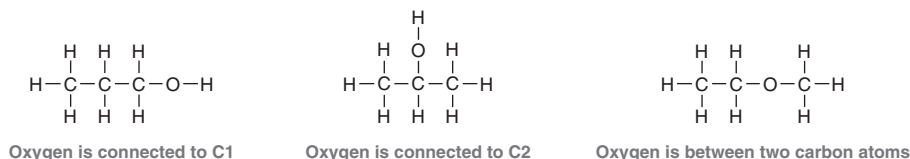
All of these drawings represent the same isomer. If we number the carbon atoms (C1, C2, and C3), with C1 being the carbon atom connected to oxygen, then all of the drawings above show the same connectivity: a three-carbon chain with an oxygen atom attached at one end of the chain.

STEP 3
Consider other ways to connect the atoms.

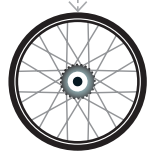
Thus far, we have drawn just one isomer that has the molecular formula $\text{C}_3\text{H}_8\text{O}$. Other constitutional isomers can be drawn if we consider other possible ways of connecting the three carbon atoms and the oxygen atom. For example, the oxygen atom can be connected to C2 (rather than C1), giving a compound called 2-propanol (shown below). Alternatively, the oxygen atom can be inserted between two carbon atoms, giving a compound called ethyl methyl ether (also shown below). For each isomer, two of the many acceptable drawings are shown:



If we continue to search for alternate ways of connecting the three carbon atoms and the oxygen atom, we will not find any other ways of connecting them. So in summary, there are a total of three constitutional isomers with the molecular formula $\text{C}_3\text{H}_8\text{O}$, shown here:



Additional skills (not yet discussed) are required to draw constitutional isomers of compounds containing a ring, a double bond, or a triple bond. Those skills will be developed in Section 14.16.



PRACTICE the skill 1.1 Draw all constitutional isomers with the following molecular formula.

(a) $\text{C}_3\text{H}_7\text{Cl}$ (b) C_4H_{10} (c) C_5H_{12} (d) $\text{C}_4\text{H}_{10}\text{O}$ (e) $\text{C}_3\text{H}_6\text{Cl}_2$



APPLY the skill

1.2 Chlorofluorocarbons (CFCs) are gases that were once widely used as refrigerants and propellants. When it was discovered that these molecules contributed to the depletion of the ozone layer, their use was banned, but CFCs continue to be detected as contaminants in the environment.¹ Draw all of the constitutional isomers of CFCs that have the molecular formula $\text{C}_2\text{Cl}_3\text{F}_3$.

need more PRACTICE? Try Problems 1.35, 1.46, 1.47, 1.54

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 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 if the atoms are brought any closer together. 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).

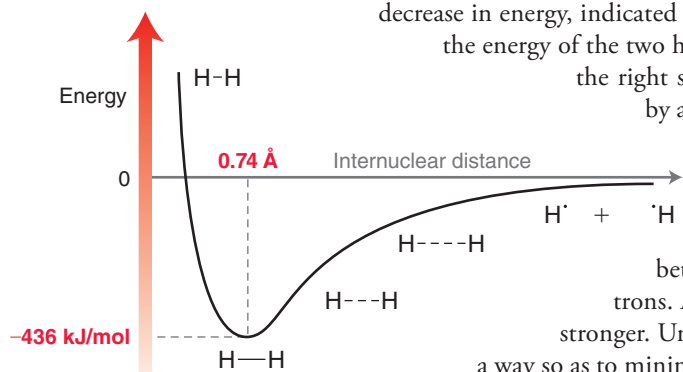


FIGURE 1.2

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.

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).

1A	2A						3A	4A	5A	6A	7A	8A
H	He						B	C	N	O	F	Ne
Li	Be						Al	Si	P	S	Cl	Ar
Na	Mg	Transition Metal Elements					Ga	Ge	As	Se	Br	Kr
K	Ca						In	Sn	Sb	Te	I	Xe
Rb	Sr						Tl	Pb	Bi	Po	At	Rn
Cs	Ba											

FIGURE 1.3

A periodic table showing group numbers.

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.

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.

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.

SOLUTION

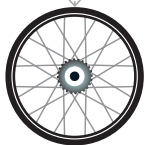
(a) In a Lewis dot structure, only valence electrons are drawn, so we must first determine the number of valence electrons. Boron belongs to group 3A on the periodic table, and it therefore has three valence electrons. The periodic symbol for boron (B) is drawn, and each electron is placed by itself (unpaired) around the B, like this:



(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):



PRACTICE the skill

1.3 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

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

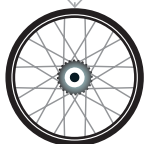
1.5 Name one element that you would expect to exhibit bonding properties similar to boron. Explain.

1.6 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?

1.7 Lithium salts have been used for decades to treat mental illnesses, including depression and bipolar disorder. Although the treatment is effective, researchers are still trying to determine how lithium salts behave as mood stabilizers.²

(a) Draw a Lewis structure of an uncharged lithium atom, Li.

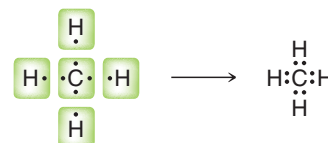
(b) Lithium salts contain a lithium atom that is missing one valence electron (and therefore bears a positive charge). Draw a Lewis structure of the lithium cation.



APPLY the skill

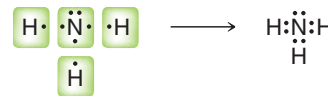
Drawing the Lewis Structure of a Small Molecule

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

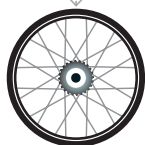
1.8 Draw a Lewis structure for each of the following compounds:

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

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

1.10 There are four constitutional isomers with the 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.

1.11 Smoking tobacco with a water pipe, or hookah, is often perceived as being less dangerous than smoking cigarettes, but hookah smoke has been found to contain the same

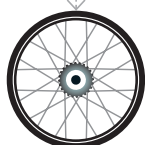


STEP 1
Draw all individual atoms.

STEP 2
Connect atoms that form more than one bond.

STEP 3
Connect the hydrogen atoms.

STEP 4
Pair any unpaired electrons so that each atom achieves an octet.



APPLY the skill

variety of toxins and carcinogens (cancer-causing compounds) as cigarette smoke.³ Draw a Lewis structure for each of the following dangerous compounds found in tobacco smoke:

- (a) HCN (hydrogen cyanide) (b) CH₂CHCHCH₂ (1,3-butadiene)

→ need more **PRACTICE?** Try Problem 1.39

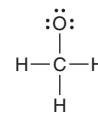
1.4 Identifying Formal Charges

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:

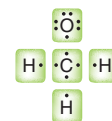
1. Determine the appropriate number of valence electrons for an atom.
2. Determine whether the atom exhibits the appropriate number of electrons.

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.

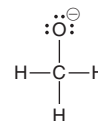
After identifying the appropriate number of electrons for each atom in a Lewis structure, the next task is to determine if any of the atoms exhibit an unexpected number of electrons. For example, consider the following structure.



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.



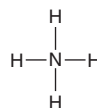
SKILLBUILDER



1.4 CALCULATING FORMAL CHARGE

LEARN the skill

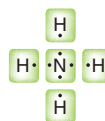
Consider the nitrogen atom in the structure below and determine if it has a formal charge:



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.

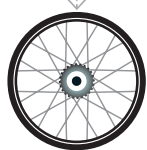


STEP 1

Determine the appropriate number of valence electrons.

STEP 2

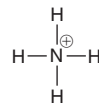
Determine the actual number of valence electrons in this case.



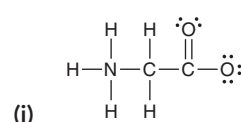
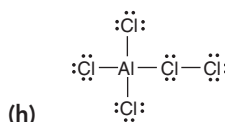
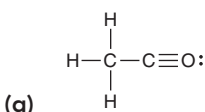
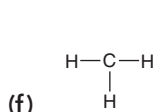
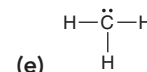
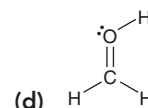
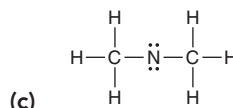
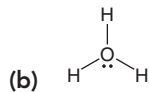
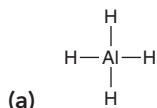


STEP 3
Assign a formal charge.

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:



PRACTICE the skill 1.12 Identify any formal charges in the structures below:

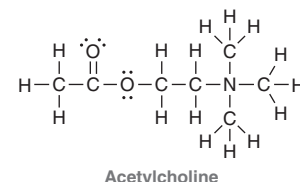


1.13 Draw a structure for each of the following ions; in each case, indicate which atom possesses the formal charge:



APPLY the skill

1.14 If you are having trouble paying attention during a long lecture, your levels of acetylcholine (a neurotransmitter) may be to blame.⁴ Identify any formal charges in acetylcholine.



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

Increasing electronegativity \uparrow

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. The withdrawal of electrons toward oxygen is called **induction**, which is often indicated with an arrow like this.



Induction causes the formation of partial positive and partial negative charges, symbolized by the Greek symbol delta (δ). The partial charges that result from induction will be very important in upcoming chapters.



If the difference in electronegativity is greater than 1.7, the electrons are not shared at all. For example, consider the bond between sodium and oxygen in sodium hydroxide (NaOH).



The difference in electronegativity between O and Na is so great that both electrons of the bond are possessed solely by the oxygen atom, rendering the oxygen negatively charged and the sodium positively charged. The bond between oxygen and sodium, called an **ionic bond**, is the result of the force of attraction between the two oppositely charged ions.

The cutoff numbers (0.5 and 1.7) should be thought of as rough guidelines. Rather than viewing them as absolute, we must view the various types of bonds as belonging to a spectrum without clear cutoffs (Figure 1.4).

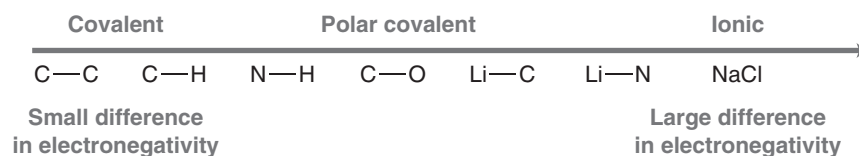
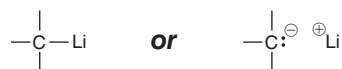


FIGURE 1.4
The nature of various bonds commonly encountered in organic chemistry.

This spectrum has two extremes: covalent bonds on the left and ionic bonds on the right. Between these two extremes are the polar covalent bonds. Some bonds fit clearly into one category, such as C—C bonds (covalent), C—O bonds (polar covalent), or NaCl bonds (ionic). However, there are many cases that are not so clear-cut. For example, a C—Li bond has a difference in electronegativity of 1.5, and this bond is often drawn either as polar covalent or as ionic. Both drawings are acceptable:



Another reason to avoid absolute cutoff numbers when comparing electronegativity values is that the electronegativity values shown above are obtained via one particular method developed by Linus Pauling. However, there are at least seven other methods for calculating electronegativity values, each of which provides slightly different values. Strict adherence to the Pauling scale would suggest that C—Br and C—I bonds are covalent, but these bonds will be treated as polar covalent throughout this course.

SKILLBUILDER



1.5 LOCATING PARTIAL CHARGES RESULTING FROM INDUCTION

LEARN the skill

Consider the structure of methanol. Identify all polar covalent bonds and show any partial charges that result from inductive effects:

