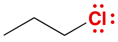
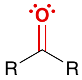
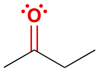
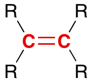
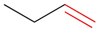
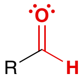
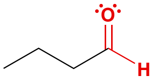
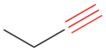
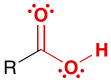
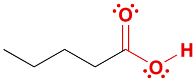
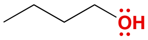
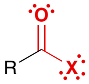
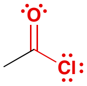
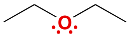
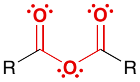
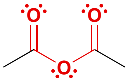
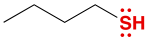
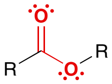
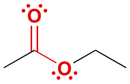
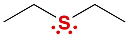
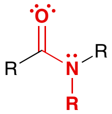
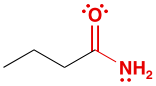
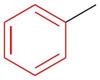
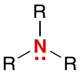
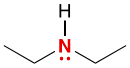
ORGANIC CHEMISTRY

DAVID KLEIN

FOURTH EDITION

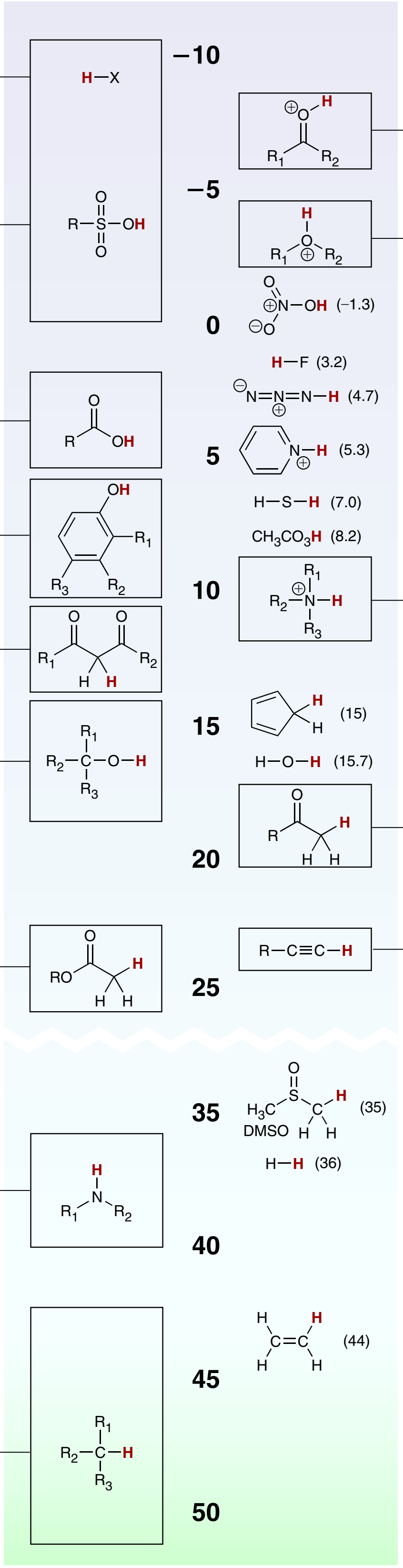
WILEY

EXAMPLES OF COMMON FUNCTIONAL GROUPS

FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER	FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER
$\mathrm{R{-}X}$ (X = Cl, Br or I)	Alkyl halide	 ***n*-Propyl chloride**	7		Ketone	 **2-Butanone**	19
	Alkene	 **1-Butene**	7, 8		Aldehyde	 **Butanal**	19
$\mathrm{R{-}C{\equiv}C{-}R}$	Alkyne	 **1-Butyne**	9		Carboxylic acid	 **Pentanoic acid**	20
$\mathrm{R{-}OH}$	Alcohol	 **1-Butanol**	12		Acyl halide	 **Acetyl chloride**	20
$\mathrm{R{-}O{-}R}$	Ether	 **Diethyl ether**	13		Anhydride	 **Acetic anhydride**	20
$\mathrm{R{-}SH}$	Thiol	 **1-Butanethiol**	13		Ester	 **Ethyl acetate**	20
$\mathrm{R{-}S{-}R}$	Sulfide	 **Diethyl sulfide**	13		Amide	 **Butanamide**	20
	Aromatic (or arene)	 **Methylbenzene**	17, 18		Amine	 **Diethylamine**	22

* The "R" refers to the remainder of the compound, usually carbon and hydrogen atoms.

Approximate pK_a Values for Commonly Encountered Structural Types



X	pK_a
I	−10
Br	−9.0
Cl	−7.0
F	3.2

R	pK_a
CF_3	−14
OH	−9.0
Me	−1.2
Ph	−0.6

R	pK_a
CF_3	−0.25
H	3.8
Me	4.8
t-Bu	5.0
OH	6.4

R_1	R_2	R_3	pK_a
H	H	NO_2	7.1
H	NO_2	H	8.4
H	H	H	9.9
H	H	OMe	10.2

R_1	R_2	pK_a
Me	Me	9.0
OEt	Me	11
OMe	OMe	13
OEt	OEt	13.3

R_1	R_2	R_3	pK_a
Me	Me	Me	18.0
Me	Me	H	16.5
Me	H	H	16.0
H	H	H	15.5
CF_3	H	H	12.5
CF_3	CF_3	H	9.3

R	pK_a
t-Bu	24.5
Et	25.0

R_1	R_2	pK_a
H	H	38
Et	H	38
Et	Et	40

R_1	R_2	R_3	pK_a
Ph	H	H	41
$CH{=}CH_2$	H	H	43
H	H	H	48
Me	H	H	50
Me	Me	H	51
Me	Me	Me	53

R_1	R_2	pK_a
Me	H	−8.0
Me	Me	−7.3
Me	OMe	−6.5
Me	Ph	−6.2
Me	OH	−6.1

R_1	R_2	pK_a
Me	Me	−3.8
Et	Et	−3.6
Et	H	−2.4
Me	H	−2.2
H	H	−1.7

R_1	R_2	R_3	pK_a
H	H	H	9.2
Me	H	H	10.5
Me	Me	H	10.6
Me	Me	Me	9.8
Et	Et	Et	10.8
Pr	Pr	H	11.1

R	pK_a
Ph	16.0
H	17.0
Me	19.2

R	pK_a
Ph	23
H	25

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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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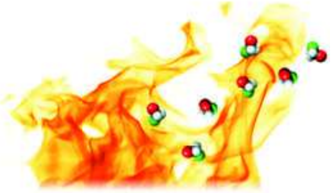

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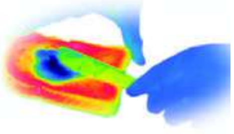

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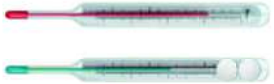

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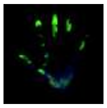

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Preface

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 and third editions 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 three 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 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, second, and third editions of *Organic Chemistry*. For each edition, the manuscript was reviewed by several hundred professors and several thousand students. In preparing the fourth 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 fourth edition.

New Features in the Fourth Edition

- Treatment of synthesis was strengthened throughout the text, with a greater focus on retrosynthetic strategies. The coverage of synthesis and retrosynthesis in Chapter 7 has been expanded (with additional examples and more problems in SkillBuilder 7.8); and in Chapter 8, alkenes are considered both as synthetic targets and possible starting materials. In Chapter 9, the coverage of synthesis with alkynide ions has been expanded, with a focus on retrosynthesis. Indeed, the coverage of retrosynthesis has been expanded similarly in each chapter, gradually developing a scaffold of advanced synthetic skills.
- The introduction of bond-line drawings has been moved from Chapter 2 to Chapter 1. This enables the use of bond-line drawings when covering the material in Chapter 1.
- SkillBuilder 2.1 (converting between condensed structures and bond-line structures) has been rewritten to show students how to interpret the condensed structures of aldehydes (RCHO) and carboxylic acids (RCO_2H).
- In Chapter 3 (acids and bases), a new section covers the relative acidity of cationic acids (with a new SkillBuilder), as well as the relative basicity of their uncharged conjugate bases. This new section (Section 3.5) covers the relative acidity of ammonium ions and the relative basicity of amines.
- In Chapter 6, the section describing nucleophilic centers and electrophilic centers has been entirely rewritten. The previous treatment (3e) would suggest that methyl chloride is a nucleophile, because of the lone pairs on the chlorine atom. Furthermore, the previous treatment (3e) would suggest that methanol is an electrophile, because the carbon atom is connected directly to an electron-withdrawing element. Both of these conclusions are false, so this section was rewritten so that students don't arrive at these false conclusions.
- Section 7.2 (nomenclature of alkyl halides) has been revised to introduce the prefix "*n*" in alkyl substituents (for example, *n*-butyl or *n*-propyl). This terminology is revisited again in Section 12.1 (nomenclature of alcohols) as well as throughout the text, where appropriate.
- In Chapter 7, when reagents are covered, a discussion has been included to explicitly show that NaOEt/EtOH represents NaOEt dissolved in EtOH as the solvent. This was not obvious to students, and it is now explicitly shown.
- Sodium hydride is not an appropriate base for performing an E2 reaction. A quick literature search shows no such examples. NaH has been removed from Chapter 7.
- Chapter 7 (substitution and elimination) has been reorganized in the following ways.
  - Nomenclature of alkenes has been moved out of Chapter 7 and into Chapter 8 (addition reactions of alkenes).
  - Biological methylating agents have been moved into a BioLinks box (rather than being a numbered section of the chapter).
  - Kinetic isotope effects have been moved into a Special Topic box (rather than being a numbered section of the chapter).
  - Solvent effects have been moved to the end of the chapter.
- In Chapter 9, the coverage of dissolving metal reductions has been revised to show that terminal alkynes cannot be reduced by this method (only internal alkynes can be reduced with a dissolving metal reduction). To reduce a terminal alkyne, it is best to perform hydrogenation with a poisoned catalyst.
- In Chapter 15 (NMR spectroscopy), the discussion of complex splitting has been revised to reflect the reality that *J* values are generally similar (~7 Hz), so a triplet of quartets or a quartet of triplets would be extremely rare. A sextet will be much more common when a signal arises from protons that have three neighbors on one side and two neighbors on the other side (for example, the protons on C2 in 1-bromopropane). The entire discussion of complex splitting has been revised accordingly.
- In the previous edition (3e), throughout Chapter 21 (alpha carbon chemistry), after enolates were first introduced, enolates were then represented throughout the chapter by showing the minor contributor to the resonance hybrid (the resonance structure with a negative charge on C, rather than O). While this simplified the mechanisms for students, it is more accurate to show the major contributor. Throughout Chapter 21, all instances of enolates (in all mechanisms) have been modified to show the major contributor to the resonance hybrid (with a negative charge on O), rather than the minor contributor.
- The end of each chapter has been enhanced with additional multiple-choice questions that mimic the style of questions on standardized exams, including the ACS, DAT, and PCAT exams. The previous edition (3e) had approximately 3 such questions at the end of each chapter. The new edition (4e) now has between 7 and 10 such questions per chapter.
- Many students have requested that an answer key (for selected problems) be included at the end of the text. This much-desired feature has been provided in the fourth edition. The end of the book now has a section with answers to selected problems.

TEXT ORGANIZATION

The sequence of chapters and topics in *Organic Chemistry, 4e* 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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New to *WileyPLUS for Organic Chemistry, 4e*

Students regularly report that they prefer to work with eBooks and online problems. The ability to receive instant feedback and always having access to course materials from any mobile device adds to the appeal of an online environment. Within WileyPLUS, students can interact with all (>5,000) problems that appear throughout the textbook, both within the chapters (SkillBuilder problems and Conceptual Checkpoints problems) and at the end of the chapters (Practice, ACS-style, Integrated, and Challenge problems). For the 4th edition, all WileyPLUS problems have been reimagined by instructional designers to make them as efficient as possible. The redesigned problems are more streamlined and better focused on the learning objectives being targeted. Improvements include:

- Clear instructions are provided, and excessive drawing has been eliminated.
- Predict-the-product problems often provide a copy of the starting material in the sketch box, so students can focus on the reactive functional group(s).

- Synthesis problems are open-ended to better reflect classroom assessments.
- Mechanism problems now begin with an overview before moving into arrow-pushing.
- Advanced problems model problem-solving with guided inquiry.
- Feedback is provided to *explain* each solution, and newly written hints are now available for each problem.

In addition to the enhancements above, over 100 new videos have been created by the author using lightboard technology. Each video (5–10 minutes in duration) covers one of the boxed (numbered) mechanisms appearing in the text. In each of these mechanism videos, each step of the mechanism is described in detail, and the student sees the entire mechanism unfolding in a step-by-step fashion. The author shows how to draw the resulting intermediate and how to decide what happens next when drawing the mechanism. The reason for each step is explained, and experimental observations (regiochemical and stereochemical) are justified. The function of each reagent is explained, and curved arrows are drawn one at a time, with a discussion of how each arrow should be drawn. These new mechanism videos are designed to foster a solid grasp of the skills necessary for drawing mechanisms. Mechanisms are foundational to the study of organic chemistry, and these videos provide students with a step-by-step explanation of each boxed mechanism that appears in the text.

Adaptive Practice for *Organic Chemistry, 4e*

WileyPLUS for *Organic Chemistry, 4e* is also supported by an **adaptive practice** learning module that provides students with a personalized learning experience so that they can build and track their proficiency. The database has over 25,000 problems, all of which have been vetted by the author (a process that took almost a year of work), and are continuously updated based on user feedback. Each problem drills a single concept or skill, so that students can track which concepts and skills they need to spend more time learning. Once a student's areas of weakness have been identified (all of which are tracked and plotted), the student is provided with links to the relevant portions of the text, as well as additional problems that will develop proficiency in those areas of weakness. This provides for a personalized experience that *adapts* to each student's needs, thus the term "adaptive practice."

ADDITIONAL INSTRUCTOR RESOURCES

All resources updated and revised under guidance of Laurie Starkey, *California State Polytechnic University, Pomona.*

Testbank Revised for this edition by Mackay Steffensen, *Southern Utah University* and Ann Paterson, *Williams Baptist University.*

PowerPoint Lecture Slides and Clicker Questions Revised for this edition by Michael Cross, *Snow College*.

STUDENT RESOURCES

Student Study Guide and Solutions Manual Authored by David Klein. The fourth edition of the *Student Study Guide and Solutions Manual* to accompany *Organic Chemistry, 4e* contains:

- More detailed explanations within the solutions.
- Concept Review Exercises
- SkillBuilder Review Exercises
- Reaction Review Exercises
- Mechanism 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.

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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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1

A Review of General Chemistry

ELECTRONS, BONDS, AND MOLECULAR PROPERTIES

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 Reading Bond-Line Structures
1.7 Atomic Orbitals
1.8 Valence Bond Theory
1.9 Molecular Orbital Theory
1.10 Hybridized Atomic Orbitals
1.11 Predicting Molecular Geometry: VSEPR Theory
1.12 Dipole Moments and Molecular Polarity
1.13 Intermolecular Forces and Physical Properties
1.14 Solubility

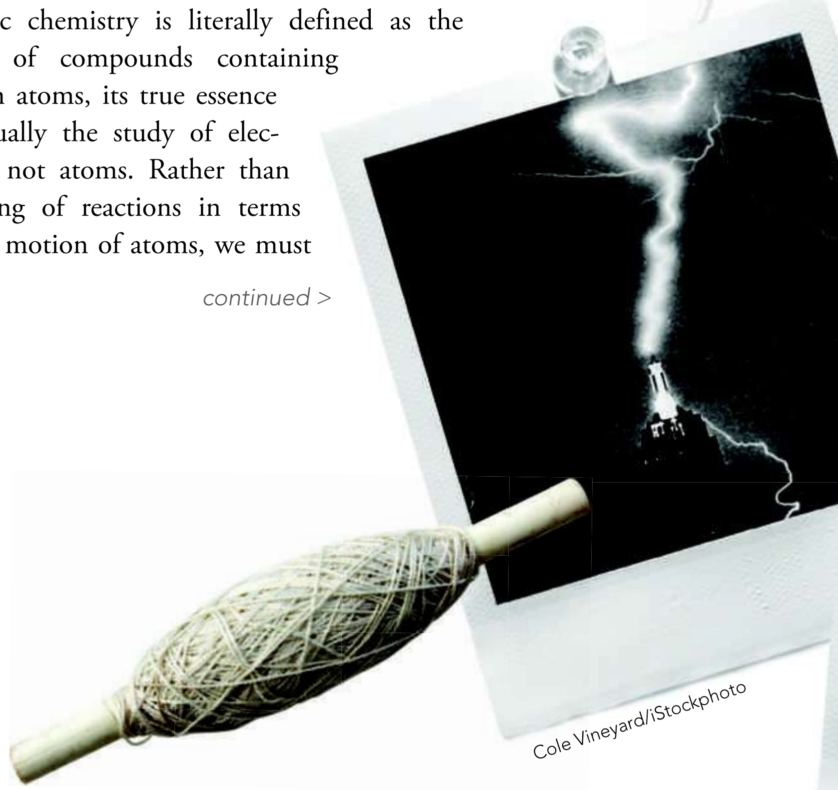
Top (*Key*) Gary S Chapman/Photographer's Choice RF/Getty Images; *Top* (*Lightning*) Justin Horrocks/Getty Images

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

continued >



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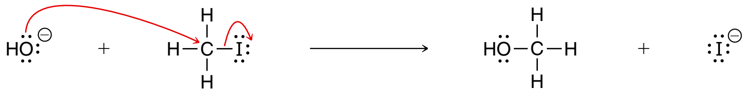
recognize that *reactions occur as a result of the motion of electrons*. For example, in the following reaction the curved arrows represent the motion, or flow, of electrons. This flow of electrons causes the chemical change shown:

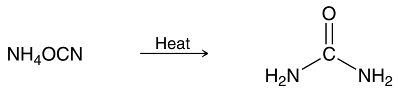


Throughout this course, we will learn how, when, and why electrons flow during reactions. We will learn about the barriers that prevent electrons from flowing, and we will learn how to overcome those barriers. In short, we will study the behavioral patterns of electrons, enabling us to predict, and even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



Ammonium cyanate
(Inorganic)

Urea
(Organic)

BY THE WAY

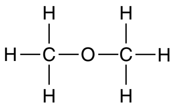
There are some carbon-containing compounds that are traditionally excluded from organic classification. For example, ammonium cyanate (seen on this page) is still classified as inorganic, despite the presence of a carbon atom. Other exceptions include sodium carbonate (Na_2CO_3) and potassium cyanide (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.

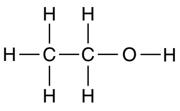
Organic chemistry occupies a central role in the world around us, as we are surrounded by organic compounds. The food that we eat and the clothes that we wear are comprised of organic compounds. Our ability to smell odors or see colors results from the behavior of organic compounds. Pharmaceuticals, 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:



Dimethyl ether
Boiling point = −23°C

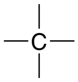
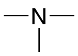


Ethanol
Boiling point = 78.4°C

These compounds have the same molecular formula (C_2H_6O), 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).

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

Tetravalent	*Trivalent*	*Divalent*	*Monovalent*
 Carbon generally forms ***four*** bonds.	 Nitrogen generally forms ***three*** bonds.	—O— Oxygen generally forms ***two*** bonds.	H— X— (where X = F, Cl, Br, or I) Hydrogen and halogens generally form ***one*** bond.

SKILLBUILDER

1.1 DRAWING CONSTITUTIONAL ISOMERS OF SMALL MOLECULES

LEARN the skill

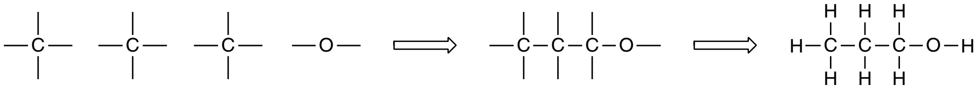
Draw all constitutional isomers that have the molecular formula C_3H_8O.

SOLUTION

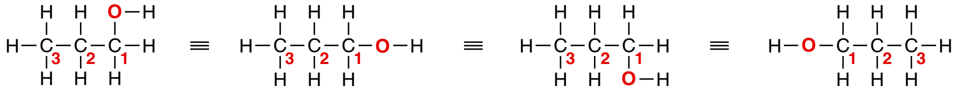
Begin by determining the valency of each atom that appears in the molecular formula. Carbon is tetravalent, hydrogen is monovalent, and oxygen is divalent. The atoms with the highest valency are connected first. So, in this case, we draw our first isomer by connecting the three carbon atoms, as well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

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.



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

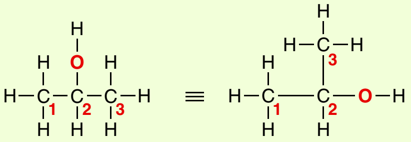


1-Propanol **1-Propanol** **1-Propanol** **1-Propanol**

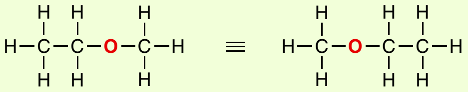
All of these drawings represent the same isomer. If we number the carbon atoms (C1, C2, and C3), with C1 being the carbon atom connected to oxygen, then all of the drawings above show the same connectivity: a three-carbon chain with an oxygen atom attached at one end of the chain.

STEP 3
Consider other ways to connect the atoms.

Thus far, we have drawn just one isomer that has the molecular formula C_3H_8O. 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:

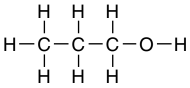


2-Propanol

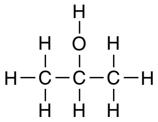


Ethyl methyl ether

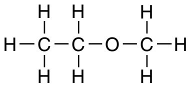
If we continue to search for alternate ways of connecting the three carbon atoms and the oxygen atom, we will not find any other ways of connecting them. So in summary, there are a total of three constitutional isomers with the molecular formula C_3H_8O, shown here:



Oxygen is connected to C1



Oxygen is connected to C2



Oxygen is between two carbon atoms

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) C_3H_7Cl **(b)** C_4H_{10} **(c)** C_5H_{12} **(d)** $C_4H_{10}O$ **(e)** $C_3H_6Cl_2$

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 $C_2Cl_3F_3$.

need more **PRACTICE?** **Try Problems 1.32, 1.42, 1.51**

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:

$$\mathrm{H}^{\bullet} \quad + \quad {}^{\bullet}\mathrm{H} \quad \longrightarrow \quad \mathrm{H{-}H} \qquad \Delta H = -436\ \text{kJ/mol}$$

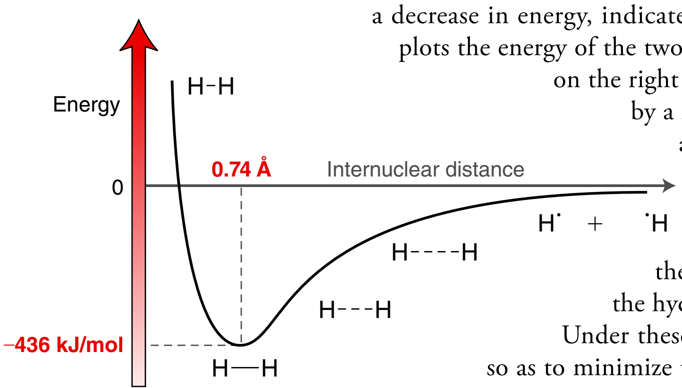


FIGURE 1.2
An energy diagram showing the energy as a function of the internuclear distance between two hydrogen atoms.

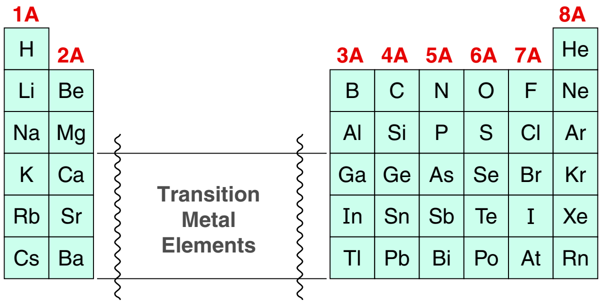
BY THE WAY
1 Å = 10^{-10} meters.

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 Δ*H*. 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 (Å). 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 Å) 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). So, for example, carbon (C) has four valence electrons because it is in group 4A of the periodic table.



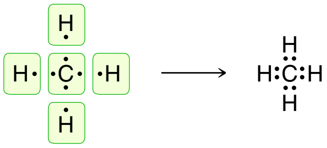
1A	2A		3A	4A	5A	6A	7A	8A
H								He
Li	Be		B	C	N	O	F	Ne
Na	Mg	Transition Metal Elements	Al	Si	P	S	Cl	Ar
K	Ca		Ga	Ge	As	Se	Br	Kr
Rb	Sr		In	Sn	Sb	Te	I	Xe
Cs	Ba		Tl	Pb	Bi	Po	At	Rn

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.). For atoms with four or fewer valence electrons, each valence electron is drawn by itself (unpaired), as seen in the following cases:

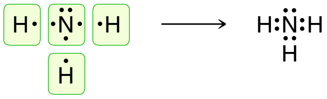
For atoms with more than four valence electrons, the first four valence electrons are drawn unpaired (as seen in the case of carbon above), and then each of the remaining valence electrons is paired up with an electron already drawn:

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 an electron configuration with a full valence shell, just like that 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 Chapter 2, 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

1.2 DRAWING THE LEWIS STRUCTURE OF A SMALL MOLECULE

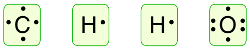
LEARN the skill

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.

STEP 1
Draw all individual atoms.

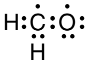


Then, connect any atoms that form more than one bond. Hydrogen atoms only form one bond each, so we will save those for last. In this case, we connect the C and the O.

STEP 2
Connect atoms that form more than one bond.

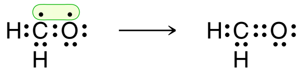
Next, connect all hydrogen atoms. We place the hydrogen atoms next to carbon, because carbon has more unpaired electrons than oxygen.

STEP 3
Connect the hydrogen atoms.



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.

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



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

1.3 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)** CH_3OH

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

1.5 There are four constitutional isomers with the molecular formula C_3H_9N. Draw a Lewis structure for each isomer and determine the number of lone pairs on the nitrogen atom in each case.

APPLY the skill

1.6 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 variety of toxins and carcinogens (cancer-causing compounds) as cigarette smoke.[2] Draw a Lewis structure for each of the following dangerous compounds found in tobacco smoke:

(a) HCN (hydrogen cyanide) **(b)** $CH_2CHCHCH_2$ (1,3-butadiene)

need more **PRACTICE?** **Try Problem 1.35**

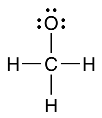
1.4 Identifying Formal Charges

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:

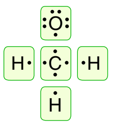
1. Determine the appropriate number of valence electrons for an atom.
2. Determine whether the atom exhibits the appropriate number of electrons.

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.

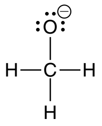
After identifying the appropriate number of electrons for each atom in a Lewis structure, the next task is to determine if any of the atoms exhibit an unexpected number of electrons. For example, consider the structure shown on the right:



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 as shown:

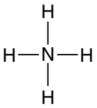


SKILLBUILDER

1.3 CALCULATING FORMAL CHARGE

LEARN the skill

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



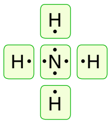
SOLUTION

STEP 1
Determine the appropriate number of valence electrons.

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.

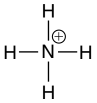
STEP 2
Determine the actual number of valence electrons in this case.

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



STEP 3
Assign a formal charge.

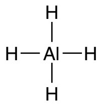
In this case, the nitrogen atom exhibits only four valence electrons. It is missing one electron, so it must bear a positive charge, which is shown like this:



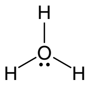
PRACTICE the skill

1.7 Identify any formal charges in the structures below:

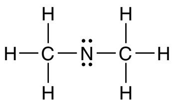
(a)



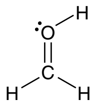
(b)



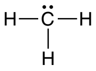
(c)



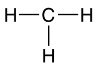
(d)



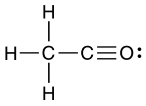
(e)



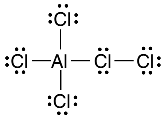
(f)



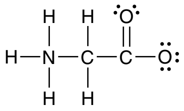
(g)



(h)



(i)

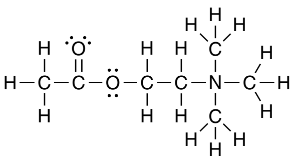


1.8 Draw a structure for each of the following ions; in each case, indicate which atom possesses the formal charge:

(a) BH_4^- **(b)** NH_2^- **(c)** $C_2H_5^+$

APPLY the skill

1.9 If you are having trouble paying attention during a long lecture, your levels of acetylcholine (a neurotransmitter) may be to blame.[3] Identify any formal charges in acetylcholine.



Acetylcholine

need more **PRACTICE?** **Try Problem 1.66, 1.81a**

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 electronegativity values for elements commonly encountered in organic chemistry.

TABLE 1.1 **ELECTRONEGATIVITY VALUES OF SOME COMMON ELEMENTS**

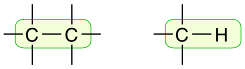
Increasing electronegativity →

		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
K 0.8						**Br** 2.8

↑ Increasing electronegativity

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.

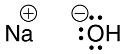
If the difference in electronegativity is between 0.5 and 1.7, the electrons are not shared equally between the atoms, resulting in a **polar covalent bond**. For example, consider a bond between carbon and oxygen (C—O). Oxygen is significantly more electronegative (3.5) than carbon (2.5), and therefore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

$$\overset{+\!\!\!\longrightarrow}{\mathrm{C{-}O}}$$

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.

$$\overset{\delta+}{\mathrm{C}}{-}\overset{\delta-}{\mathrm{O}}$$

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).

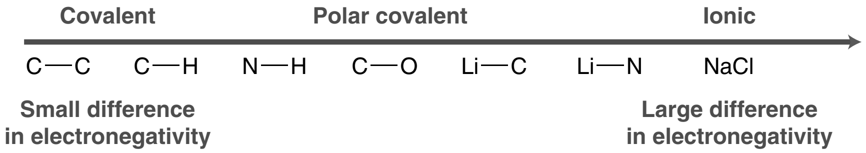
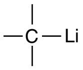
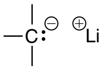


FIGURE 1.4
The nature of various bonds commonly encountered in organic chemistry.

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:



or



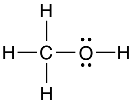
Another reason to avoid absolute cutoff numbers when comparing electronegativity values is that the electronegativity values shown above are obtained via one particular method developed by Linus Pauling. However, there are at least seven other methods for calculating electronegativity values, each of 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

1.4 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:



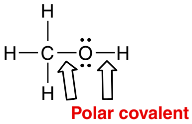
Methanol

SOLUTION

First identify all polar covalent bonds. The C—H bonds are considered to be covalent because the electronegativity values for C and H are fairly close. It is true that carbon is more electronegative than hydrogen, and therefore, there is a small inductive effect for each C—H bond. However, we will generally consider this effect to be negligible for C—H bonds.

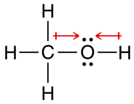
The C—O bond and the O—H bond are both polar covalent bonds:

STEP 1
Identify all polar covalent bonds.



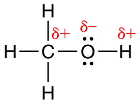
Now determine the direction of the inductive effects. Oxygen is more electronegative than C or H, so the inductive effects are shown like this:

STEP 2
Determine the direction of each dipole.



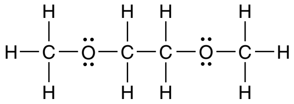
These inductive effects dictate the locations of the partial charges:

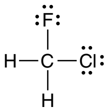
STEP 3
Indicate the location of partial charges.

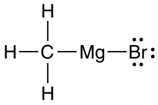


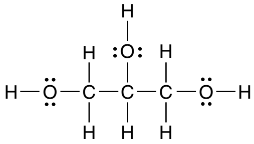
PRACTICE the skill

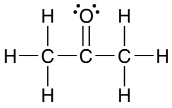
1.10 For each of the following compounds, identify any polar covalent bonds by drawing δ+ and δ− symbols in the appropriate locations:

(a)


(b)


(c)


(d)


(e)


(f)