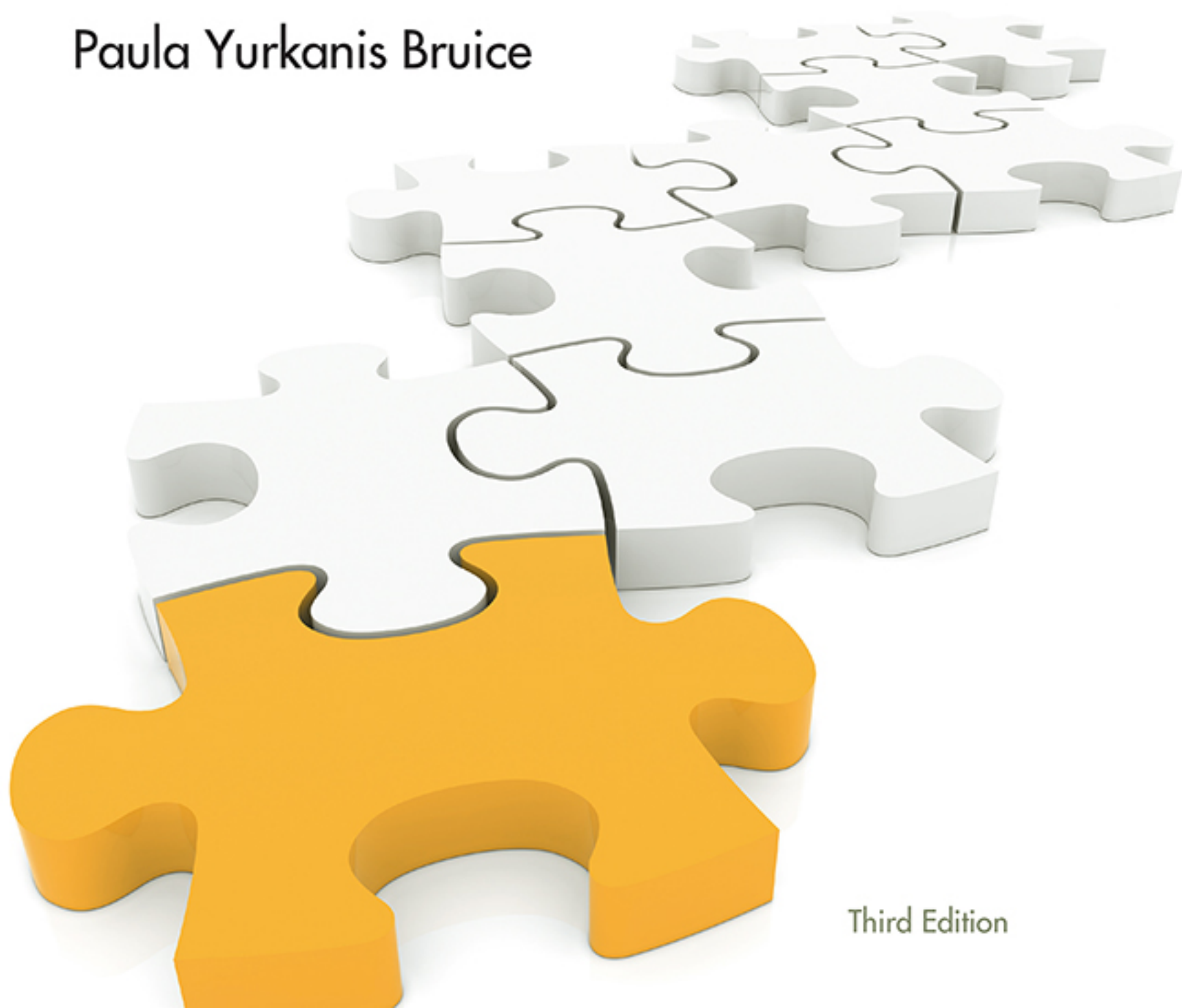


# ESSENTIAL ORGANIC CHEMISTRY

Paula Yurkanis Bruice



Third Edition

# Essential Organic Chemistry

THIRD EDITION

Paula Yurkanis Bruice

UNIVERSITY OF CALIFORNIA  
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- Drawing Resonance Contributors of Substituted Benzenes

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**Organizing What We Know About Organic Chemistry lets students see how families of organic compounds react in similar ways.**

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# Preface

In deciding what constitutes “essential” organic chemistry, I asked myself the following question: What do students need to know if they are not planning to be synthetic organic chemists? In other words, what do they need to know for their careers in medicine, dentistry, applied health professions, nutrition, or engineering?

Based on the answers to that question, I made content and organizational choices with the following goals in mind:

- Students should understand how and why organic compounds react the way they do.
- Students should understand that the reactions they learn in the first part of the course are the same as the reactions that occur in biological systems (that is, that occur in cells).
- Students should appreciate the fun and challenge of designing simple syntheses. (This is also a good way to check if they truly understand reactivity.)
- Students should understand how organic chemistry is integral to biology, to medicine, and to their daily lives.
- In order to achieve the above goals, students need to work as many problems as possible.

To counter the impression that the study of organic chemistry consists primarily of memorizing a diverse collection of molecules and reactions, this book is organized around shared features and unifying concepts, emphasizing principles that can be applied again and again. I want students to learn how to apply what they have learned to new settings, reasoning their way to a solution rather than memorizing a multitude of facts.

A new feature, “**Organizing What We Know about the Reactions of Organic Compounds**,” lets students see where they have been and where they are going as they proceed through the course, encouraging them to keep in mind the fundamental reason behind the reactions of all organic compounds: *electrophiles react with nucleophiles*.

When students see the first reaction of an organic compound (other than an acid–base reaction), they are told that all organic compounds can be divided into families and all members of a family react in the same way. To make things even easier, each family can be put into one of four groups and all the families in a group react in similar ways.

The book then proceeds with each of the four groups (Group I: compounds with carbon–carbon double and triple bonds; Group II: benzene; Group III: compounds with an electronegative group attached to an  $sp^3$  carbon; and Group IV: carbonyl compounds). When the chemistry of all the members of a particular group has been covered, students see a summary of the characteristic reactions of that group (see pages 248, 332, 480) that they can compare with the summary of the characteristic reactions of the group(s) studied previously.

The **margin notes** throughout the book encapsulate key points that students should remember. (For example, “when an acid is added to a reaction, it protonates the most basic atom in the reactant”; “with bases of the same type, the weaker the base, the better it is as a leaving group”; and stable bases are weak bases”.) To simplify mechanistic understanding, common features are pointed out in margin notes (see pages 407, 415, 446, 450).

There are about 140 **application boxes** sprinkled throughout the book. These are designed to show the students the relevance of organic chemistry to medicine (dissolving sutures, mad cow disease, artificial blood, cholesterol and heart disease), to agriculture (acid rain, resisting herbicides, pesticides: natural and synthetic), to nutrition (trans fats, basal metabolic rate, lactose intolerance, omega fatty acids), and to our shared life on this planet (fossil fuels, biodegradable polymers, whales and echolocation).



Success in organic chemistry requires students to work as many problems as possible. Therefore, the book is structured to encourage problem solving. The answers (and explanations, when needed) to all the problems are in the accompanying *Study Guide and Solutions Manual*, which I authored to ensure consistency in language with the text.

New **Tutorials** following relevant chapters give students extra practice so that they can better master important topics: Acids and Bases, Drawing Curved Arrows: Pushing Electrons, and Drawing Resonance Contributors.

The problems within each chapter are primarily drill problems. They appear at the end of each section, so they allow students to test themselves on the material they have just read to see if they are ready to move on to the next section. Selected problems in each chapter are accompanied by worked-out solutions to provide insight into problem-solving techniques. Short answers are provided at the back of the book for problems marked with a diamond to give students immediate feedback concerning their mastery of a skill or concept.

The many **Problem-Solving Strategies** in the book teach students how to approach various kinds of problems. Each Problem-Solving Strategy is followed by an exercise to give the student an opportunity to use the strategy just learned.

The **end-of-chapter problems** vary in difficulty. They begin with drill problems that integrate material from the entire chapter, requiring students to think in terms of all the material in the chapter rather than focusing on individual sections. The problems become more challenging as the student proceeds. The net result for the student is a progressive building of both problem-solving ability and confidence. (I have chosen not to label problems as particularly challenging so as not to intimidate the students before they try to solve the problem.)

Many of the end-of-chapter problems can also be found in MasteringChemistry. Students can master concepts through traditional homework assignments in Mastering that provide hints and answer-specific feedback. Students learn chemistry by practicing chemistry.

Additionally, tutorials in MasteringChemistry, featuring specific wrong-answer feedback, hints, and a wide variety of educationally effective content, guide your students through the course. The hallmark Hints and Feedback offer scaffolded instruction similar to what students would experience in an office hour, allowing them to learn from their mistakes without being given the answer. Organic Chemistry Tutorials in MasteringChemistry pinpoint errors by assessing the logic and accuracy of the student's answers. Individual evaluators written and linked to each problem by organic chemists look at the validity of the student's entry and generate error-specific feedback based on information received from a JChem database.

The book contains **two new chapters**: "Radicals" and "Synthetic Polymers." There is no longer a chapter on the "Organic Chemistry of Drugs." Much of the material that was in that chapter is now in application boxes, so students have the opportunity to learn about that material who may have not had that opportunity if that last chapter were not covered in their course.

Similarly, some of the information on the chemistry of living systems has been integrated into earlier chapters. As examples, noncovalent interactions in biological systems has been added to Chapter 3, the discussion of catalysis in Chapter 5 now includes a discussion of enzymatic catalysis, and acetal formation by glucose has been added to Chapter 12.

The six chapters (Chapters 16–21) that focus primarily on the organic chemistry of living systems have been rewritten to emphasize the connection between the organic reactions that occur in the laboratory and those that occur in cells. Each organic reaction that occurs in a cell is explicitly compared to the organic reaction with which the student is already familiar. Chapter 18 can be found on the Instructor Resource Center.

The chapter on spectroscopy is modular, so it can be covered at any time during the course—at the very beginning, at the very end, somewhere in between, or not covered at all. When I wrote that chapter, I did not want students to be overwhelmed by a topic they may never revisit in their lives, but I did want them to enjoy being able to interpret relatively simple spectra. In addition to the spectroscopy problems in the text, there are over forty new spectroscopy problems in the *Study Guide and Solutions Manual* with worked-out answers. The answers come after the problems, so students have the opportunity to try to solve them on their own first.

New **modern design, streamlined narrative, and bulleted summaries** at the end of each chapter allow students to navigate through the content and study more efficiently with the next.

## ACKNOWLEDGMENTS

It gives me great pleasure to acknowledge the dedicated efforts of Jordan Fantini and Malcolm Forbes, who checked every inch of the book for accuracy; David Yezley, M.D., for his assistance with the section on MRI; Warren Hehre of Wavefunction, Inc., and Alan Shusterman of Reed College for their advice on the electrostatic potential maps that appear in the book; and Jeremy Davis, who created the art that appears on page 119. I am also very grateful to my students, who pointed out sections that needed clarification, worked the problems and suggested new ones, and searched for errors.

The following reviewers have played an enormously important role in the development of this book.

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Malcolm Forbes, *University of North Carolina*

I am deeply grateful to my editor, Jeanne Zalesky, whose talents guided this book and caused it to be as good as it could be, and to Coleen Morrison, whose gentle prodding and attention to detail made the book actually happen. I also want to thank the other talented and dedicated people at Pearson whose contributions made this book a reality. And thank you to Lauren Layn, the creative brains behind the technology that accompanies the book.

I particularly want to thank the many wonderful and talented students I have had over the years, who taught me how to be a teacher. And I want to thank my children, from whom I may have learned the most.

To make this textbook as user friendly as possible, I would appreciate any comments that will help me achieve this goal in future editions. If you find sections that could be clarified or expanded, or examples that could be added, please let me know. Finally, this edition has been painstakingly combed for typographical errors. Any that remain are my responsibility; if you find any, please send me a quick e-mail so that they can be corrected in future printings of this edition.

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# About the Author



Paula Bruice with Zeus, Bacchus, and Abigail

Paula Yurkanis Bruice was raised primarily in Massachusetts. After graduating from the Girls' Latin School in Boston, she earned an A.B. from Mount Holyoke College and a Ph.D. in chemistry from the University of Virginia. She then received an NIH postdoctoral fellowship for study in the Department of Biochemistry at the University of Virginia Medical School and held a postdoctoral appointment in the Department of Pharmacology at the Yale School of Medicine.

Paula has been a member of the faculty at the University of California, Santa Barbara since 1972, where she has received the Associated Students Teacher of the Year Award, the Academic Senate Distinguished Teaching Award, two Mortar Board Professor of the Year Awards, and the UCSB Alumni Association Teaching Award. Her research interests center on the mechanism and catalysis of organic reactions, particularly those of biological significance. Paula has a daughter and a son who are physicians and a son who is a lawyer. Her main hobbies are reading suspense novels, any biographies, and enjoying her pets (three dogs, two cats, and two parrots).



# Essential Skills for Organic Chemistry

New features and major revisions to this third edition focus on developing students' problem solving and analytical reasoning skills. Organized around mechanistic similarities, Bruice encourages students to be mindful of the fundamental reasoning behind the reactions of all organic compounds: electrophiles react with nucleophiles.

**New Tutorials Skill Builders** following select chapters deepen student understanding of key topics while developing their problem solving skills. Tutorials include acid-base chemistry, building molecular models, and drawing curved arrows and are paired with assignable MasteringChemistry® tutorials with wrong answer-specific feedback and coaching.

**TUTORIAL**

Enhanced by  
MasteringChemistry®

### ACIDS AND BASES

This tutorial is designed to give you practice solving problems based on some of the concepts you learned in Chapter 2. Most of the concepts are given here without explanation because full explanations can be found in Chapter 2.

#### An Acid and Its Conjugate Base

An acid is a species that can lose a proton (the Brønsted-Lowry definition). When an acid loses a proton ( $\text{H}^+$ ), it forms its conjugate base. When the proton comes off the acid, the conjugate base retains the electron pair that attached the proton to the acid.

$\text{CH}_3\text{C}(=\text{O})\text{OH}$   
acid

$\text{CH}_3\text{C}(=\text{O})\text{O}^- + \text{H}^+$   
conjugate base + a proton

Often, the lone pairs and bonding electrons are not shown.

$\text{CH}_3\text{COOH}$   
acid

$\text{CH}_3\text{COO}^- + \text{H}^+$   
conjugate base

$\text{CH}_3\text{NH}_2$   
base

$\text{CH}_3\text{NH}_3^+ + \text{H}^+$   
conjugate acid

Notice that a neutral acid forms a negatively charged conjugate base, whereas a positively charged acid forms a neutral conjugate base. (In each case, the charge decreases by one because the acid loses  $\text{H}^+$ .)

**PROBLEM 1** Draw the conjugate base of each of the following acids:  
 a.  $\text{CH}_3\text{OH}$     b.  $\text{CH}_3\text{NH}_2$     c.  $\text{CH}_3\text{NH}_3^+$     d.  $\text{H}_2\text{O}^+$     e.  $\text{H}_2\text{O}$

#### A Base and Its Conjugate Acid

A base is a species that can gain a proton (the Brønsted-Lowry definition). When a base gains a proton ( $\text{H}^+$ ), it forms its conjugate acid. In order to gain a proton, a base must have a lone pair that it can use to form a new bond with the proton.

$\text{CH}_3\text{O}^- + \text{H}^+$   
base

$\text{CH}_3\text{OH}$   
conjugate acid

Often, the lone pairs and bonding electrons are not shown.

$\text{CH}_3\text{O}^- + \text{H}^+$   
base

$\text{CH}_3\text{OH}$   
conjugate acid

$\text{CH}_3\text{NH}_2 + \text{H}^+$   
base

$\text{CH}_3\text{NH}_3^+$   
conjugate acid

$\text{CH}_3\text{COO}^- + \text{H}^+$   
base

$\text{CH}_3\text{COOH}$   
conjugate acid

Notice that a negatively charged base forms a neutral conjugate acid, whereas a neutral base forms a positively charged conjugate acid. (In each case, the charge increases by one because the compound gains  $\text{H}^+$ .)

**PROBLEM 2** Draw the conjugate acid of each of the following bases:  
 a.  $\text{H}_2\text{O}$     b.  $\text{HO}^-$     c.  $\text{CH}_3\text{OH}$     d.  $\text{NH}_3$     e.  $\text{Cl}^-$

#### Acid-Base Reactions

An acid cannot lose a proton unless a base is present to accept the proton. Therefore, an acid always reacts with a base. The reaction of an acid with a base is called an acid-base reaction or a proton-transfer reaction. Acid-base reactions are reversible reactions.

$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$

acid                      base                      conjugate base                      conjugate acid

Notice that an acid reacts with a base in the forward direction (blue labels) and an acid reacts with a base in the reverse direction (red labels).

#### The Products of an Acid-Base Reaction

Both  $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{O}$  in the preceding reaction have protons that can be lost (that is, both can act as acids), and both have lone pairs that can form a bond with a proton (that is, both can act as bases). How do we know which reactant will lose a proton and which will gain a proton? We can determine this by comparing the  $\text{pK}_a$  values of the two reactants; these values are 4.8 for  $\text{CH}_3\text{COOH}$  and 15.7 for  $\text{H}_2\text{O}$ . The stronger acid (the one with the lower  $\text{pK}_a$  value) will be the one that acts as an acid (it will lose a proton). The other reactant will act as a base (it will gain a proton).

$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$

$\text{pK}_a = 4.8$                        $\text{pK}_a = 15.7$

**PROBLEM 3** Draw the products of the following acid-base reactions:  
 a.  $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$     c.  $\text{CH}_3\text{SH} + \text{HO}^-$   
 b.  $\text{HBr} + \text{CH}_3\text{OH}$     d.  $\text{CH}_3\text{NH}_2 + \text{CH}_3\text{OH}$

#### The Position of Equilibrium

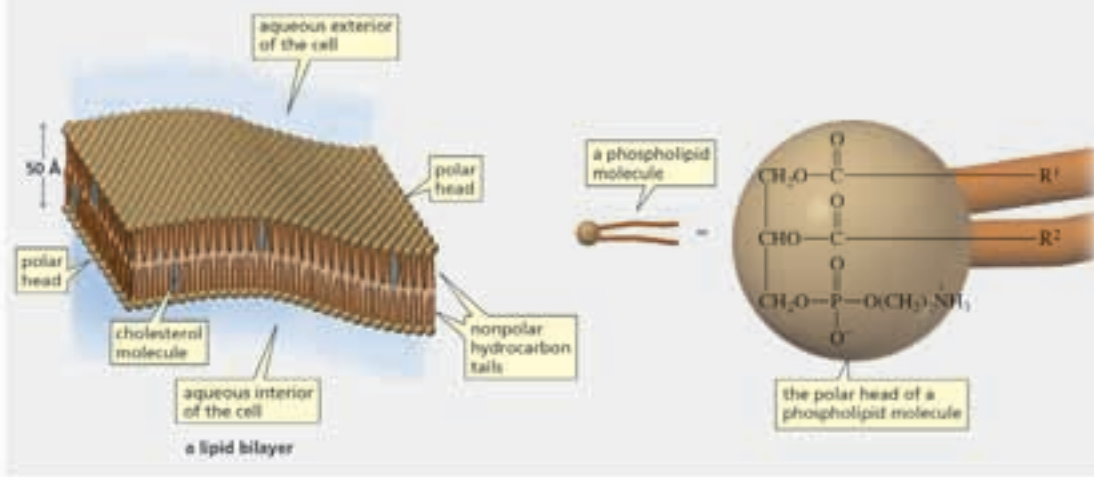
Whether an acid-base reaction favors formation of the products or formation of the reactants can be determined by comparing the  $\text{pK}_a$  value of the acid that loses a proton in the forward direction with the  $\text{pK}_a$  value of the acid that loses a proton in the reverse direction. The equilibrium will favor the reaction of the stronger acid to form the weaker acid. The following reaction favors formation of the reactants, because  $\text{CH}_3\text{OH}_2^+$  is a stronger acid than  $\text{CH}_3\text{COOH}$ .

$\text{CH}_3\text{COOH} + \text{CH}_3\text{OH}_2^+ \rightleftharpoons \text{CH}_3\text{COO}^- + \text{CH}_3\text{OH}$

$\text{pK}_a = 4.8$                        $\text{pK}_a = -1.7$

## Cell Membranes

Cell membranes demonstrate how nonpolar molecules are attracted to other nonpolar molecules, whereas polar molecules are attracted to other polar molecules. All cells are enclosed by a membrane that prevents the aqueous (polar) contents of the cell from pouring out into the aqueous fluid that surrounds the cell. The membrane consists of two layers of phospholipid molecules—called a lipid bilayer. A phospholipid molecule has a polar head and two long nonpolar hydrocarbon tails. The phospholipids are arranged so that the nonpolar tails meet in the center of the membrane. The polar heads are on both the outside surface and the inside surface, where they face the polar solutions on the outside and inside of the cell. Nonpolar cholesterol molecules are found between the tails in order to keep the nonpolar tails from moving around too much. The structure of cholesterol is shown and discussed in Section 3.14.



## New Applications Boxes Throughout!

Numerous new interest boxes throughout each chapter connect chemistry to students' lives and often provide any needed additional explanation on the organic chemistry occurring. New applications include: *Using Genetic Engineering to Treat Ebola, Diseases Caused by a Misfolded Protein, The Inability to Perform an  $S_N2$  Reaction Causes a Severe Clinical Disorder*, and *Electron Delocalization Affects the Three-Dimensional Shape of Proteins*.

23 Elimination Reactions of Alkyl Halides | Substitution and Elimination Reactions

Item type: Tutorial | Difficulty: 3 | Time: 10m | Learning Outcomes: | Contact the Publisher

**Part B**

2-Bromocyclohexane is treated with sodium methoxide in methanol at 323 K. Draw the major product of the reaction. Make sure to consider the stereochemistry of the reaction.

$$\text{Cyclohexane-2-yl-Br} + \text{CH}_3\text{O}^-\text{Na}^+ \xrightarrow[\text{323 K}]{\text{CH}_3\text{OH}}$$

(Draw the molecule on the canvas by choosing buttons from the Tools (for bonds), Atoms, and Advanced Template toolbars. The single bond is active by default.)

**Hint 1.** How to approach the problem

First, identify the substrate (alkyl halide) undergoing the reaction as primary ( $1^\circ$ ), secondary ( $2^\circ$ ), or tertiary ( $3^\circ$ ). Then, identify the nature of the reagent (attacking species) in the reaction. Correlate this with the conditions of substitution or elimination.

Note that for an elimination reaction, both the  $\beta$  hydrogen atom and the leaving group need to be coplanar and anti to each other. The negatively charged base and the leaving group will be pulled from each other, whereas the leaving group and the abstracted  $\beta$  hydrogen atom are anti to each other.

**Hint 2.** Identify the substrate (alkyl halide) as primary, secondary, or tertiary. (see 6.4.1)

**Hint 3.** Identify the nature of the reagent. (see 6.4.1)

**Hint 4.**

This list will be shown after you complete previous hint(s).

## Student Tutorials

MasteringChemistry® provides instant feedback specific to the structure or mechanism each student has drawn. Rather than simply providing feedback of the “right/wrong/try again” variety, Mastering recognizes the individual student error by applying evaluators to each problem that analyze chemical accuracy, employing data gathered from all student entries in Mastering, and providing wrong answer-specific feedback that helps students overcome misconceptions. An updated, mobile compatible drawing tool (java-free), provides wrong-answer feedback and guidance on every mechanism problem.



# Mastering Chemistry<sup>®</sup>

MasteringChemistry<sup>®</sup> from Pearson is the leading online teaching and learning system designed to improve results by engaging students before, during, and after class with powerful content. Ensure that students arrive ready to learn by assigning educationally effective content before class, and encourage critical thinking and retention with in-class resources such as Learning Catalytics. Students can further master concepts after class through traditional homework assignments that provide hints and answer-specific feedback. The Mastering gradebook records scores for all automatically graded assignments while diagnostic tools give instructors access to rich data to assess student understanding and misconceptions.

Mastering brings learning full circle by continuously adapting to each student and making learning more personal than ever—before, during, and after class.

## Before Class

### Reading Quizzes

Mobile-friendly Reading Quizzes give instructors the opportunity to assign reading and test students on their comprehension of chapter content. Wrong answer-specific feedback directs students to the explanation within the eBook while hints support student problem-solving skills.

Part A  
Which of the following structures are chiral?

I: CC[C@H](C)Cl  
II: CC(C)(Br)CC  
III: CC[C@H](O)C(=O)O

only I  
 I, II, and III  
 only II  
 I and II  
 I and III

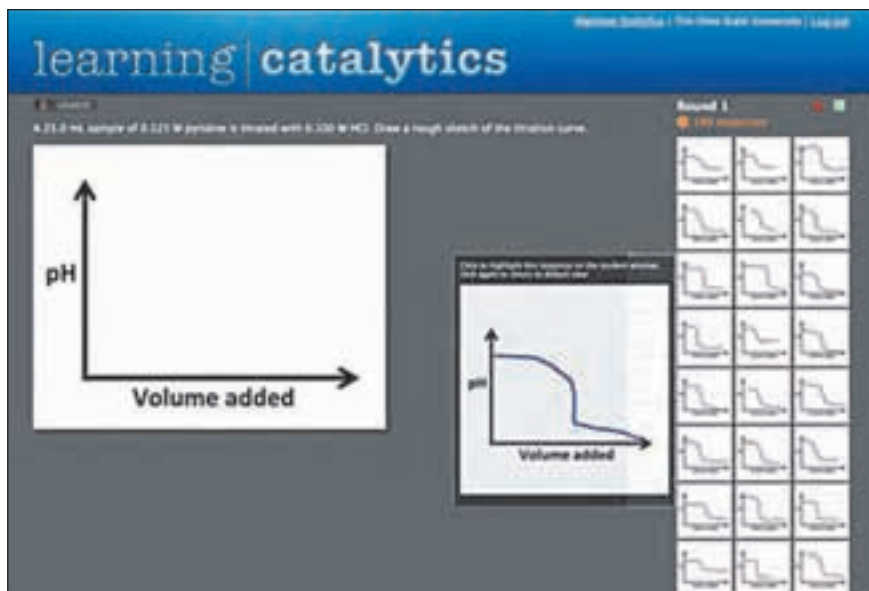
**Incorrect, Try Again**  
If an answer is not the only one, the solution is C.  
(1/10/2015, 11:00)

# During Class

## Learning Catalytics™

Learning Catalytics is a “bring your own device” student engagement, assessment, and classroom intelligence system. With Learning Catalytics you can:

- Assess students in real time, using open-ended tasks to probe student understanding.
- Understand immediately where students are and adjust your lecture accordingly.
- Improve your students’ critical-thinking skills.
- Access rich analytics to understand student performance.
- Add your own questions to make Learning Catalytics fit your course exactly.
- Manage student interactions with intelligent grouping and timing.



# After Class

Students learn chemistry by practicing chemistry.

Tutorials, featuring wrong answer-specific feedback, hints, and a wide variety of educationally effective content, guide your students through the toughest topics in chemistry. The hallmark Hints and Feedback offer instruction similar to what students would experience in an office hour, allowing them to learn from their mistakes without being given the answer.

The screenshot shows a chemistry software interface. On the left, there is a molecular structure editor with a toolbar and a 3D ball-and-stick model of a molecule. On the right, there is a list of questions or tasks. The first question is "Addressing Chemistry: Drawing Tetramine Carbonates II - Organic Chemistry". Below it, there are four numbered tasks: "Task 1: Identify the correct Lewis structure for tetramine carbonate.", "Task 2: Determine the most electronegative atom in the molecule.", "Task 3: Determine the number of lone pairs on the oxygen atom.", and "Task 4: Identify the direction of electron flow." The interface also shows a search bar and various navigation options.

## Digital and Print Resources

*Essential Organic Chemistry* provides an integrated teaching and learning package of support material for both students and professors.

Name of Supplement	Available in Print	Available Online	Instructor or Student Resource	Description
Study Guide and Solutions Manual ISBN: 0133867250	✓		Student	This manual for students, written by Paula Bruice, contains complete and detailed explanations of the solutions to the problems in the text, and definitions of all key terms used in each chapter. In addition, you will find more than 40 new spectroscopy problems, a special topics section on pH, $pK_a$ , and buffers, and 21 practice tests.
MasteringChemistry® www.masteringchemistry.com ISBN: 0133867218		✓	Students & Instructors	MasteringChemistry® from Pearson is the leading online teaching and learning system designed to improve results by engaging students before, during, and after class with powerful content.
Pearson eText ISBN: 0133866890 within Mastering Chemistry® ISBN: 0133858499		✓	Student	<i>Essential Organic Chemistry</i> features a Pearson eText within MasteringChemistry®. The Pearson eText offers students the power to create notes, highlight text in different colors, create bookmarks, zoom, and view single or multiple pages.
TestGen Test Bank ISBN: 0133867234		✓	Instructor	Prepared by Ethan Tsai, this resource includes more than 1200 questions in multiple-choice, matching, true/false, and short answer format. Available for download on the Pearson catalog page for <i>Essential Organic Chemistry</i> at <a href="http://www.pearsonhighered.com">www.pearsonhighered.com</a>
Instructor Resource Materials ISBN: 0133867242		✓	Instructor	Includes all the art, photos, and tables from the book in JPEG format for use in classroom projection or when creating study materials and tests. Available for download on the Pearson catalog page for <i>Essential Organic Chemistry</i> at <a href="http://www.pearsonhighered.com">www.pearsonhighered.com</a>



## 1

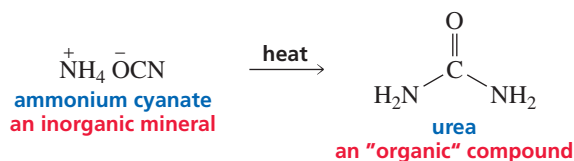
# Remembering General Chemistry: Electronic Structure and Bonding



To stay alive, early humans must have been able to distinguish between the different kinds of materials in their world. “You can live on roots and berries,” they might have said, “but you can’t eat dirt. You can stay warm by burning tree branches, but you can’t burn rocks.”

By the early eighteenth century, scientists thought they had grasped the nature of that difference, and in 1807 Jöns Jakob Berzelius gave names to the two kinds of materials. Compounds derived from living organisms were believed to contain an immeasurable vital force—the essence of life. These he called “organic.” Compounds derived from minerals—those lacking the vital force—were “inorganic.”

Because chemists could not create life in the laboratory, they assumed they could not create compounds that had a vital force. Since this was their mind-set, you can imagine how surprised chemists were in 1828 when Friedrich Wöhler produced urea—a compound known to be excreted by mammals—by heating ammonium cyanate, an inorganic mineral.



For the first time, an “organic” compound had been obtained from something other than a living organism and certainly without the aid of any kind of vital force. Chemists, therefore, needed a new definition for “organic compounds.” **Organic compounds** are now defined as *compounds that contain carbon*.

Organic compounds are  
compounds that contain carbon.

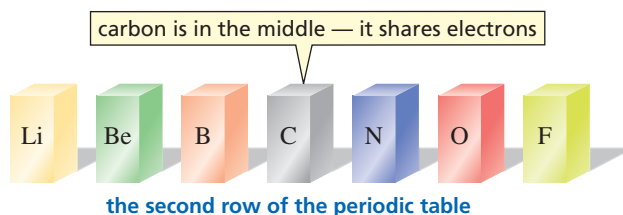
Why is an entire branch of chemistry devoted to the study of carbon-containing compounds? We study organic chemistry because just about all of the molecules that make life possible and that make us who we are—proteins, enzymes, vitamins, lipids, carbohydrates, DNA, RNA—are organic compounds. Thus, the chemical reactions that take

place in living systems, including our own bodies, are reactions of organic compounds. Most of the compounds found in nature—those that we rely on for all of our food, for some of our clothing (cotton, wool, silk), and for energy (natural gas, petroleum)—are organic as well.

Organic compounds are not limited, however, to those found in nature. Chemists have learned how to synthesize millions of organic compounds never found in nature, including synthetic fabrics, plastics, synthetic rubber, and even things like compact discs and Super Glue. And most importantly, almost all of our commonly prescribed drugs are synthetic organic compounds.

Some synthetic organic compounds prevent shortages of naturally occurring products. For example, it has been estimated that if synthetic materials—nylon, polyester, Lycra—were not available for clothing, then all of the arable land in the United States would have to be used for the production of cotton and wool just to provide enough material to clothe us. Other synthetic organic compounds provide us with materials we would not have—Teflon, Plexiglas, Kevlar—if we had only naturally occurring organic compounds. Currently, there are about 16 million known organic compounds, and many more are possible that we cannot even imagine today.

What makes carbon so special? Why are there so many carbon-containing compounds? The answer lies in carbon's position in the periodic table. Carbon is in the center of the second row of elements. We will see that the atoms to the left of carbon have a tendency to give up electrons, whereas the atoms to the right have a tendency to accept electrons (Section 1.3).



Because carbon is in the middle, it neither readily gives up nor readily accepts electrons. Instead, it shares electrons. Carbon can share electrons with several different kinds of atoms, and it can share electrons with other carbon atoms. Consequently, carbon is able to form millions of stable compounds with a wide range of chemical properties simply by sharing electrons.

### Natural Organic Compounds Versus Synthetic Organic Compounds

It is a popular belief that natural substances—those made in nature—are superior to synthetic ones—those made in the laboratory. Yet when a chemist synthesizes a compound, such as penicillin or morphine, the compound is exactly the same in all respects as the compound synthesized in nature. Sometimes chemists can even improve on nature. For example, chemists have synthesized analogues of penicillin that do not produce the allergic responses that a significant fraction of the population experiences from naturally produced penicillin, or that do not have the bacterial resistance of the naturally produced antibiotic (Section 16.15). Chemists have also synthesized analogues of morphine—compounds with structures similar to but not identical to that of morphine—that have the same pain-killing effects but, unlike morphine, are not habit forming.



**A field of poppies growing in Afghanistan.** Most commercial morphine is obtained from opium, the juice extracted from this species of poppy. Morphine is the starting material for the synthesis of heroin. One of the side products formed in the synthesis has an extremely pungent odor; dogs used by drug enforcement agencies are trained to recognize this odor (Section 11.18). Nearly three-quarters of the world's supply of heroin comes from the poppy fields of Afghanistan.

When we study organic chemistry, we learn how organic compounds react. Organic compounds consist of atoms held together by bonds. When an organic compound reacts, some of these bonds break and some new bonds form. *Bonds form when two atoms share electrons, and bonds break when two atoms no longer share electrons.*

How readily a bond forms and how easily it breaks depend on the particular electrons that are shared, which depend, in turn, on the atoms to which the electrons belong. So, if we are going to start our study of organic chemistry at the beginning, we must start with an understanding of the structure of an atom—what electrons an atom has and where they are located.

## 1.1 THE STRUCTURE OF AN ATOM

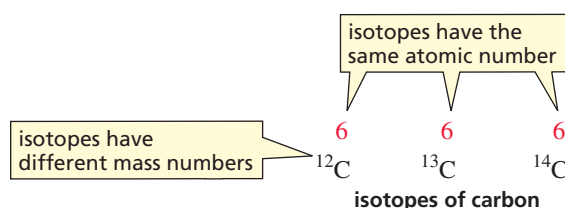
An atom consists of a tiny, dense nucleus surrounded by electrons that are spread throughout a relatively large volume of space around the nucleus called an electron cloud. The nucleus contains **positively charged protons** and **uncharged neutrons**, so it is positively charged. The **electrons are negatively charged**. The amount of positive charge on a proton equals the amount of negative charge on an electron. Therefore, the number of protons and the number of electrons in an uncharged atom must be the same.

Electrons move continuously. Like anything that moves, electrons have kinetic energy, and this energy is what counteracts the attractive force of the positively charged protons that would otherwise pull the negatively charged electrons into the nucleus.

Protons and neutrons have approximately the same mass and are about 1800 times more massive than an electron. Most of the *mass* of an atom, therefore, is in its nucleus. Most of the *volume* of an atom, however, is occupied by its electrons, and this is where our focus will be because it is the electrons that form chemical bonds.

The **atomic number** of an atom is the number of protons in its nucleus. The atomic number is unique to a particular element. For example, the atomic number of carbon is 6, which means that all uncharged carbon atoms have six protons and six electrons. Atoms can gain electrons and thereby become negatively charged, or they can lose electrons and become positively charged, but the number of protons in an atom of a particular element never changes.

Although *all carbon atoms have the same atomic number*, they do not all have the same mass number because they do not all have the same number of neutrons. The **mass number** of an atom is the sum of its protons and neutrons. For example, 98.89% of all carbon atoms have six neutrons—giving them a mass number of 12—and 1.11% have seven neutrons—giving them a mass number of 13. These two different kinds of carbon atoms ( $^{12}\text{C}$  and  $^{13}\text{C}$ ) are called **isotopes**.

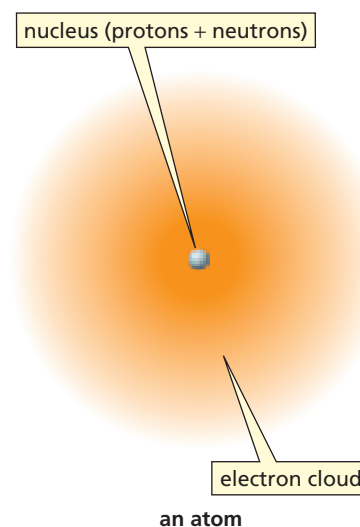


Carbon also contains a trace amount of  $^{14}\text{C}$ , which has six protons and eight neutrons. This isotope of carbon is radioactive, decaying with a half-life of 5730 years. (The *half-life* is the time it takes for one-half of the nuclei to decay.) As long as a plant or animal is alive, it takes in as much  $^{14}\text{C}$  as it excretes or exhales. When it dies, however, it no longer takes in  $^{14}\text{C}$ , so the  $^{14}\text{C}$  in the organism slowly decreases. Therefore, the age of a substance derived from a living organism can be determined by its  $^{14}\text{C}$  content.

The **atomic weight** of an element is the average mass of its atoms. For example, carbon has an atomic number of 12.011 atomic mass units. The **molecular weight** is the *sum of the atomic weights* of all the atoms in a molecule.

The nucleus contains positively charged protons and uncharged neutrons.

The electrons are negatively charged.



atomic number = the number of protons in the nucleus

mass number = the number of protons + the number of neutrons

atomic weight = the average mass of the atoms in the element

molecular weight = the sum of the atomic weights of all the atoms in the molecule



The bronze sculpture of Albert Einstein, on the grounds of the National Academy of Sciences in Washington, D.C., measures 21 feet from the top of the head to the tip of the feet and weighs 7000 pounds. In his left hand, Einstein holds the mathematical equations that represent his three most important contributions to science: the photoelectric effect, the equivalency of energy and matter, and the theory of relativity. At his feet is a map of the sky.

**PROBLEM 1** ♦

Oxygen has three isotopes,  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ . The atomic number of oxygen is 8. How many protons and neutrons does each of the isotopes have? \_\_\_\_\_

## 1.2 HOW THE ELECTRONS IN AN ATOM ARE DISTRIBUTED

The electrons in an atom can be thought of as occupying a set of concentric shells that surround the nucleus. The first shell is the one closest to the nucleus. The second shell lies farther from the nucleus. The third and higher numbered shells lie even farther out.

Each shell contains subshells known as **atomic orbitals**. The first shell has only an *s* atomic orbital; the second shell has *s* and *p* atomic orbitals; the third shell has *s*, *p*, and *d* atomic orbitals; and the fourth and higher shells consist of *s*, *p*, *d*, and *f* atomic orbitals (Table 1.1).

**Table 1.1** Distribution of Electrons in the First Four Shells That Surround the Nucleus

	First shell	Second shell	Third shell	Fourth shell
Atomic orbitals	<i>s</i>	<i>s, p</i>	<i>s, p, d</i>	<i>s, p, d, f</i>
Number of atomic orbitals	1	1, 3	1, 3, 5	1, 3, 5, 7
Maximum number of electrons	2	8	18	32

Each shell contains one *s* orbital. Each second and higher shell—in addition to its *s* orbital—contains three *p* orbitals. The three *p* orbitals have the same energy. The third and higher shells—in addition to their *s* and *p* orbitals—contain five *d* orbitals, and the fourth and higher shells also contain seven *f* orbitals.

Because a maximum of two electrons can coexist in an atomic orbital (see page 5), the first shell, with only one atomic orbital, can contain no more than two electrons (Table 1.1). The second shell, with four atomic orbitals—one *s* and three *p*—can have a total of eight electrons. Eighteen electrons can occupy the nine atomic orbitals—one *s*, three *p*, and five *d*—of the third shell, and 32 electrons can occupy the 16 atomic orbitals of the fourth shell. In studying organic chemistry, we will be concerned primarily with atoms that have electrons only in the first and second shells.

The **electronic configuration** of an atom describes what orbitals the electrons occupy.

The electronic configurations of the smallest atoms are shown in Table 1.2. (Each arrow—whether pointing up or down—represents one electron.)

**Table 1.2** The Electronic Configurations of the Smallest Atoms

Atom	Name of element	Atomic number	1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>	3s
H	Hydrogen	1	↑					
He	Helium	2	↑↓					
Li	Lithium	3	↑↓	↑				
Be	Beryllium	4	↑↓	↑↓				
B	Boron	5	↑↓	↑↓	↑			
C	Carbon	6	↑↓	↑↓	↑	↑		
N	Nitrogen	7	↑↓	↑↓	↑	↑	↑	
O	Oxygen	8	↑↓	↑↓	↑↓	↑	↑	
F	Fluorine	9	↑↓	↑↓	↑↓	↑↓	↑	
Ne	Neon	10	↑↓	↑↓	↑↓	↑↓	↑↓	
Na	Sodium	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑

The following three rules specify which orbitals an atom's electrons occupy:

**1. An electron always goes into the available orbital with the lowest energy.**

*It is important to remember that the closer the atomic orbital is to the nucleus, the lower is its energy.* Because a  $1s$  orbital is closer to the nucleus, it is lower in energy than a  $2s$  orbital, which is lower in energy—and closer to the nucleus—than a  $3s$  orbital. When comparing atomic orbitals in the same shell, we see that an  $s$  orbital is lower in energy than a  $p$  orbital, and a  $p$  orbital is lower in energy than a  $d$  orbital.

**Relative energies of atomic orbitals:**



**2. No more than two electrons can occupy each atomic orbital, and the two electrons must be of opposite spin.** (Notice in Table 1.2 that spin in one direction is designated by  $\uparrow$ , and spin in the opposite direction is designated by  $\downarrow$ .)

From these first two rules, we can assign electrons to atomic orbitals for atoms that contain one, two, three, four, or five electrons. The single electron of a hydrogen atom occupies a  $1s$  orbital, the second electron of a helium atom fills the  $1s$  orbital, the third electron of a lithium atom occupies a  $2s$  orbital, the fourth electron of a beryllium atom fills the  $2s$  orbital, and the fifth electron of a boron atom occupies one of the  $2p$  orbitals. (The subscripts  $x$ ,  $y$ , and  $z$  distinguish the three  $2p$  orbitals.) Because the three  $p$  orbitals have the same energy, the electron can be put into any one of them. Before we can discuss atoms containing six or more electrons, we need the third rule.

**3. When there are two or more atomic orbitals with the same energy, an electron will occupy an empty orbital before it will pair up with another electron.** In this way, electron repulsion is minimized.

The sixth electron of a carbon atom, therefore, goes into an empty  $2p$  orbital, rather than pairing up with the electron already occupying a  $2p$  orbital (see Table 1.2). There is one more empty  $2p$  orbital, so that is where nitrogen's seventh electron goes. The eighth electron of an oxygen atom pairs up with an electron occupying a  $2p$  orbital rather than going into the higher-energy  $3s$  orbital.

The locations of the electrons in the remaining elements can be assigned using these three rules.

The electrons in inner shells (those below the outermost shell) are called **core electrons**. The electrons in the outermost shell are called **valence electrons**.

Carbon has two core electrons and four valence electrons (Table 1.2). Lithium and sodium each have one valence electron. If you examine the periodic table inside the back cover of this book, you will see that lithium and sodium are in the same column. Elements in the same column of the periodic table have the same number of valence electrons. Because the number of valence electrons is the major factor determining an element's chemical properties, elements in the same column of the periodic table have similar chemical properties. Thus, the chemical behavior of an element depends on its electronic configuration.

Core electrons are electrons in inner shells.

Valence electrons are electrons in the outermost shell.

The chemical behavior of an element depends on its electronic configuration.

**PROBLEM 2** ♦

How many valence electrons do the following atoms have?

- a. boron    b. nitrogen    c. oxygen    d. fluorine

**PROBLEM 3** ♦

How many valence electrons do chlorine, bromine, and iodine have?

**PROBLEM 4** ♦

Look at the relative positions of each pair of atoms listed here in the periodic table. How many core electrons does each have? How many valence electrons does each have?

- a. carbon and silicon    b. oxygen and sulfur    c. nitrogen and phosphorus

## 1.3 IONIC AND COVALENT BONDS

Now that you know about the electronic configuration of atoms, let's look at why atoms come together to form bonds. In explaining why atoms form bonds, G. N. Lewis proposed that

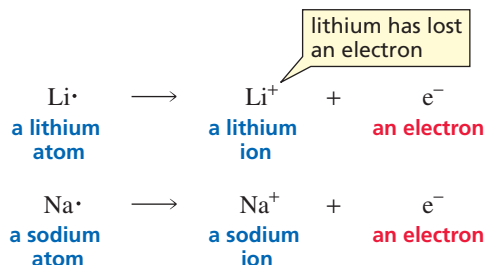
*An atom is most stable if its outer shell is either filled or contains eight electrons, and it has no electrons of higher energy.*

According to Lewis's theory, an atom will give up, accept, or share electrons in order to achieve a filled outer shell or an outer shell that contains eight electrons. This theory has come to be called the **octet rule** (even though hydrogen needs only two electrons to achieve a filled outer shell).

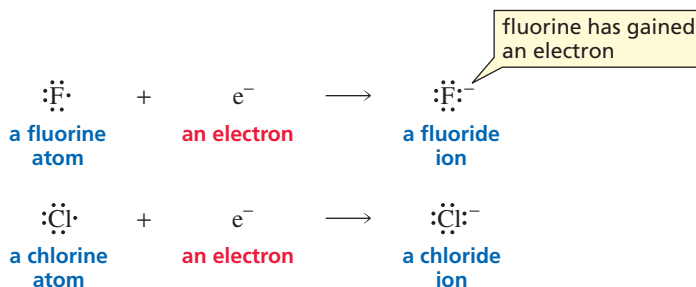
Lithium (Li) has a single electron in its  $2s$  orbital. If it loses this electron, the lithium atom ends up with a filled outer shell—a stable configuration. Lithium, therefore, loses an electron relatively easily. Sodium (Na) has a single electron in its  $3s$  orbital, so it too loses an electron easily.

Each of the elements in the first column of the periodic table readily loses an electron because each has a single electron in its outermost shell.

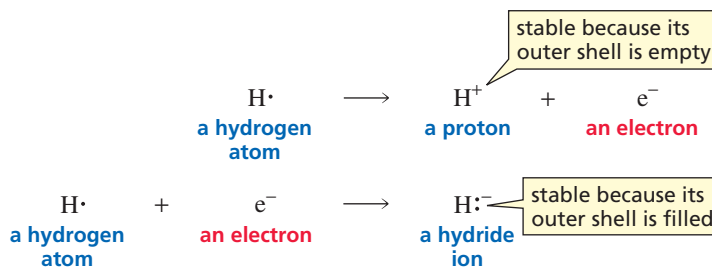
When we draw the electrons around an atom, as in the following equations, core electrons are not shown. Only valence electrons are shown because core electrons are not used in bonding; only valence electrons are used in bonding. Each valence electron is shown as a dot. When the single valence electron of lithium or sodium is removed, the species that is formed is called an ion because it carries a charge.



Fluorine and chlorine each have seven valence electrons. Consequently, each readily acquires an electron in order to have an outer shell of eight electrons, thereby forming  $\text{F}^-$ , a fluoride ion, and  $\text{Cl}^-$ , a chloride ion.



A hydrogen atom has one valence electron. Therefore, it can achieve a completely empty shell by losing an electron or a filled outer shell by gaining an electron.



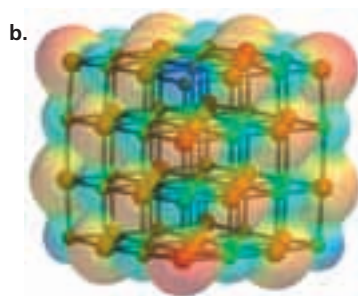
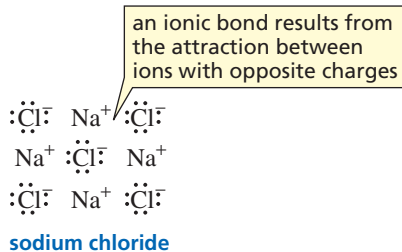
Loss of its sole electron results in a positively charged **hydrogen ion**. A positively charged hydrogen ion is called a **proton** because when a hydrogen atom loses its valence electron, only the hydrogen nucleus—which consists of a single proton—remains. When a hydrogen atom gains an electron, a negatively charged hydrogen ion—called a **hydride ion**—is formed.

#### PROBLEM 5♦

- Find potassium (K) in the periodic table and predict how many valence electrons it has.
- What orbital does the unpaired electron occupy?

## Ionic Bonds Are Formed by the Attraction Between Ions of Opposite Charge

We have just seen that sodium gives up an electron easily and chlorine readily acquires an electron, both in order to achieve a filled outer shell. Therefore, when sodium metal and chlorine gas are mixed, each sodium atom transfers an electron to a chlorine atom, and crystalline sodium chloride (table salt) is formed as a result. The positively charged sodium ions and negatively charged chloride ions are held together by the attraction of opposite charges (Figure 1.1).



An ionic bond results from the attraction between ions of opposite charge.

▲ **Figure 1.1**

- Crystalline sodium chloride.
- The electron-rich chloride ions are red, and the electron-poor sodium ions are blue. Each chloride ion is surrounded by six sodium ions, and each sodium ion is surrounded by six chloride ions. Ignore the sticks holding the balls together; they are there only to keep the model from falling apart.

A **bond** is an attractive force between two ions or between two atoms. A bond that results from the attraction between ions of opposite charge is called an **ionic bond**.

Sodium chloride is an example of an ionic compound. **Ionic compounds** are formed when an element on the left side of the periodic table *transfers* one or more electrons to an element on the right side of the periodic table.

## Covalent Bonds Are Formed by Sharing a Pair of Electrons

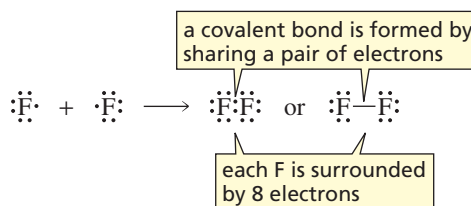
Instead of giving up or acquiring electrons to achieve a filled outer shell, an atom can achieve a filled outer shell by sharing a pair of electrons. For example, two fluorine atoms can each attain a filled second shell by sharing their unpaired valence electrons.



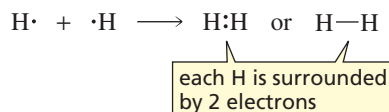
Salar de Uyuni in Bolivia—the largest deposit of natural lithium in the world. Lithium salts are used clinically. Lithium chloride ( $\text{Li}^+\text{Cl}^-$ ) is an anti-depressant, lithium bromide ( $\text{Li}^+\text{Br}^-$ ) is a sedative, and lithium carbonate ( $\text{Li}_2^+\text{CO}_3^{2-}$ ) is used to stabilize mood swings in people who suffer from bipolar disorder. Scientists do not yet know why lithium salts have these therapeutic effects.

A bond formed as a result of sharing electrons is called a **covalent bond**. A covalent bond is commonly shown by a solid line rather than as a pair of dots.

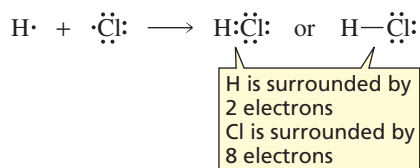
A covalent bond is formed when two atoms share a pair of electrons.



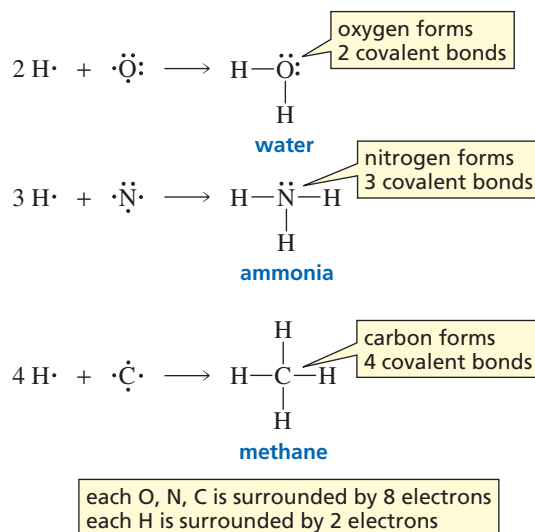
Two hydrogen atoms can form a covalent bond by sharing electrons. As a result of covalent bonding, each hydrogen acquires a stable, filled first shell.



Similarly, hydrogen and chlorine can form a covalent bond by sharing electrons. In doing so, hydrogen fills its only shell, and chlorine achieves an outer shell of eight electrons.



We just saw that because hydrogen has one valence electron and chlorine has seven valence electrons, each can achieve a filled outer shell by forming one covalent bond. Oxygen, however, has six valence electrons, so it needs to form two covalent bonds to achieve an outer shell of eight electrons. Nitrogen, with five valence electrons, must form three covalent bonds, and carbon, with four valence electrons, must form four covalent bonds to achieve a filled outer shell. Notice that all the atoms in water, ammonia, and methane have filled outer shells.



## Nonpolar Covalent Bonds and Polar Covalent Bonds

The atoms that share the bonding electrons in the F—F and H—H covalent bonds are identical. Therefore, they share the electrons equally; that is, each electron spends as much time in the vicinity of one atom as in that of the other. Such a bond is called a **nonpolar covalent bond**.

A nonpolar covalent bond is a covalent bond between atoms with the same electronegativity.



In contrast, the bonding electrons in hydrogen chloride, water, and ammonia are more attracted to one atom than to another because the atoms that share the electrons in these molecules are different and have different electronegativities.

**Electronegativity** is a measure of the ability of an atom to pull the bonding electrons toward itself. The bonding electrons in hydrogen chloride, water, and ammonia are more attracted to the atom with the greater electronegativity. The bonds in these compounds are **polar covalent bonds**.

The electronegativities of some of the elements are shown in Table 1.3. Notice that electronegativity increases from left to right across a row of the periodic table and from bottom to top in any of the columns.

A polar covalent bond is a covalent bond between atoms with different electronegativities.

**Table 1.3** The Electronegativities of Selected Elements<sup>a</sup>

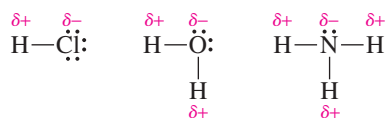
1A	2A		3A	4A	5A	6A	7A
H 2.1							
Li 1.0	Be 1.5		B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0						Br 2.8
							I 2.5

increasing electronegativity (horizontal arrow pointing right)

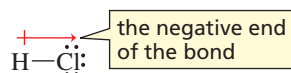
increasing electronegativity (vertical arrow pointing up)

<sup>a</sup>Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.

A polar covalent bond has a slight positive charge on one end and a slight negative charge on the other. Polarity in a covalent bond is indicated by the symbols  $\delta^+$  and  $\delta^-$ , which denote partial positive and partial negative charges. The negative end of the bond is the end that has the more electronegative atom. The greater the difference in electronegativity between the bonded atoms, the more polar the bond will be.



The direction of bond polarity can be indicated with an arrow. By convention, chemists draw the arrow so that it points in the direction in which the electrons are pulled. Thus, the head of the arrow is at the negative end of the bond; a short perpendicular line near the tail of the arrow marks the positive end of the bond. (Physicists draw the arrow in the opposite direction.)



You can think of ionic bonds and nonpolar covalent bonds as being at the opposite ends of a continuum of bond types. All bonds fall somewhere on this line. At one end is an ionic bond—a bond in which no electrons are shared. At the other end is a nonpolar covalent bond—a bond in which the electrons are shared equally. Polar covalent bonds fall somewhere in between.