

GLOBAL
EDITION



Organic Chemistry

EIGHTH EDITION

Paula Yurkanis Bruice



ALWAYS LEARNING

PEARSON

To the Student

Welcome to the fascinating world of organic chemistry. You are about to embark on an exciting journey. This book has been written with students like you in mind—those who are encountering the subject for the first time. The book's central goal is to make this journey through organic chemistry both stimulating and enjoyable by helping you understand central principles and asking you to apply them as you progress through the pages. You will be reminded about these principles at frequent intervals in references back to sections you have already mastered.

You should start by familiarizing yourself with the book. At the back of the book is information you may want to refer to often during the course. The list of Some Important Things to Remember and the Reaction Summary at each chapter's end provide helpful checklists of the concepts you should understand after studying the chapter. The Glossary at the end of the book can also be a useful study aid, as can the Appendices, which consolidate useful categories of information. The molecular models and electrostatic potential maps that you will find throughout the book are provided to give you an appreciation of what molecules look like in three dimensions and to show how charge is distributed within a molecule. Think of the margin notes as the author's opportunity to inject personal reminders of ideas and facts that are important to remember. Be sure to read them.

Work all the problems *within* each chapter. These are drill problems that you will find at the end of each section that allow you to check whether you have mastered the skills and concepts the particular section is teaching before you go on to the next section. Some of these problems are solved for you in the text. Short answers to some of the others—those marked with a diamond—are provided at the end of the book. Do not overlook the “Problem-Solving Strategies” that are also sprinkled throughout the text; they provide practical suggestions on the best way to approach important types of problems.

In addition to the *within-chapter* problems, work as many *end-of-chapter* problems as you can. The more problems you work, the more comfortable you will be with the subject matter and the better prepared you will be for the material in subsequent chapters. Do not let any problem frustrate you. Be sure to visit www.MasteringChemistry.com, where you can explore study tools including Exercise Sets, an Interactive Molecular Gallery, and Biographical Sketches of historically important chemists, and where you can access content on many important topics.

The most important advice to remember (and follow) in studying organic chemistry is DO NOT FALL BEHIND! The individual steps to learning organic chemistry are quite simple; each by itself is relatively easy to master. But they are numerous, and the subject can quickly become overwhelming if you do not keep up.

The key to succeeding in this course is paying attention to unifying principles. Before many of the theories and mechanisms were figured out, organic chemistry was a discipline that could be mastered only through memorization. Fortunately, that is no longer true. You will find many unifying principles that allow you to use what you have learned in one situation to predict what will happen in other situations. So, as you read the book and study your notes, always make sure that you understand *why* each chemical event or behavior happens. For example, when the reasons behind reactivity are understood, most reactions can be predicted. Approaching the course with the misconception that to succeed you must memorize hundreds of unrelated reactions could be your downfall. There is simply too much material to memorize. Understanding and reasoning, not memorization, provide the necessary foundation on which to lay subsequent learning. Nevertheless, from time to time some memorization will be required: some fundamental rules will have to be memorized, and you will need to learn the common names of a number of organic compounds. But that should not be a problem; after all, your friends have common names that you have been able to learn and remember.

Students who study organic chemistry to gain entrance into medical school sometimes wonder why medical schools pay so much attention to this topic. The importance of organic chemistry is not in the subject matter alone, however. Mastering organic chemistry requires a thorough understanding of certain fundamental principles and the ability to use those fundamentals to analyze, classify, and predict. The study of medicine makes similar demands: a physician uses an understanding of certain fundamental principles to analyze, classify, and diagnose.

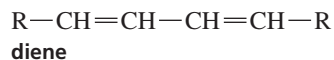
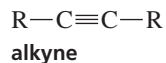
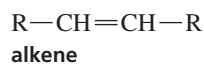
Good luck in your study. I hope you will enjoy studying organic chemistry and learn to appreciate the logic of this fascinating discipline. If you have any comments about the book or any suggestions for improving it, I would love to hear from you. Remember, positive comments are the most fun, but negative comments are the most useful.

Paula Yurkanis Bruice

Organizing What We Know About The Reactions of Organic Chemistry

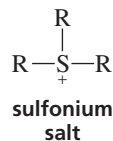
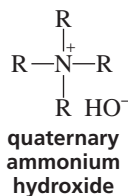
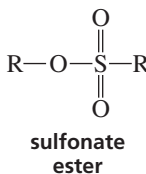
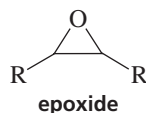
(See pages 408, 535, 878, and 979.)

Group I



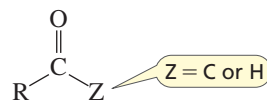
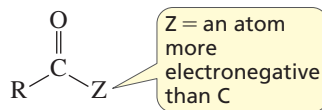
These are nucleophiles.
They undergo electrophilic addition reactions.

Group II



These are electrophiles.
They undergo nucleophilic substitution and/or elimination reactions.

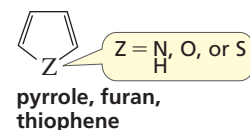
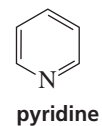
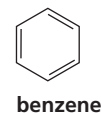
Group III



These are electrophiles.
They undergo nucleophilic acyl substitution reactions, nucleophilic addition reactions, or nucleophilic addition-elimination reactions.

Removal of a hydrogen from an α -carbon forms a nucleophile that can react with electrophiles.

Group IV



These are nucleophiles.
They undergo electrophilic aromatic substitution reactions.

Halo-substituted benzenes and halo-substituted pyridines are electrophiles.
They undergo nucleophilic aromatic substitution reactions.

Organic Chemistry

EIGHTH EDITION

GLOBAL EDITION

Paula Yurkanis Bruice

University Of California
Santa Barbara

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*To Meghan, Kenton, and Alec
with love and immense respect
and to Tom, my best friend*

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- Basics of Model Building
- Building and Recognizing Chiral Molecules
- Recognizing Chirality in Cyclic Molecules

Using the *E,Z* system to name alkenes was moved to Chapter 4, so now it appears immediately after using *cis* and *trans* to distinguish alkene stereoisomers.

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- Interconverting Fischer Projections and Perspective Formulas
- Interconverting Perspective Formulas, Fischer Projections, and Skeletal Structures
- Interconverting Perspective Formulas, Fischer Projections, and Newman Projections

Catalytic hydrogenation and relative stabilities of alkenes were moved from Chapter 6 to Chapter 5 (thermodynamics), so they can be used to illustrate how ΔH° values can be used to determine relative stabilities.

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- An Exercise in Drawing Curved Arrows: Pushing Electrons
- An Exercise in Drawing Curved Arrows: Predicting Electron Movement
- An Exercise in Drawing Curved Arrows: Interpreting Electron Movement

All the reactions in Chapter 6 follow the same mechanism the first step is always addition of the electrophile to the sp^2 carbon bonded to the most hydrogens.

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Chapter 8 starts by discussing the structure of benzene because it is the ideal compound to use to explain delocalized electrons. This chapter also includes a discussion of aromaticity, so a short introduction to electrophilic aromatic substitution reactions is now included. This allows students to see how aromaticity causes benzene to undergo electrophilic substitution rather than electrophilic addition—the reactions they have just finished studying.

Traditionally, electronic effects are taught so students can understand the directing effects of substituents on benzene rings. Now that most of the chemistry of benzene follows carbonyl chemistry, students need to know about electronic effects before they get to benzene chemistry (so they are better prepared for spectroscopy and carbonyl chemistry). Therefore, electronic effects are now discussed in Chapter 8 and used to teach students how substituents affect the pK_a values of phenols, benzoic acids, and anilinium ions. Electronic effects are then reviewed in the chapter on benzene.

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- Drawing Resonance Contributors: Moving π Electrons
- Drawing Resonance Contributors: Predicting Aromaticity
- Drawing Resonance Contributors: Substituted Benzene Rings

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The two chapters in the previous edition on substitution and elimination reactions of alkenes have been combined into one chapter. The recent compelling evidence showing that secondary alkyl halides do not undergo S_N1 solvolysis reactions has allowed this material to be greatly simplified, so now it fits nicely into one chapter.

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- Curved Arrows in Radical Systems: Interpreting Curved Arrows
- Curved Arrows in Radical Systems: Drawing Curved Arrows
- Curved Arrows in Radical Systems: Drawing Resonance Contributors

PART FOUR Identification of Organic Compounds 602

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PART FIVE Carbonyl Compounds 721

The focus of the first chapter on carbonyl chemistry is all about how a tetrahedral intermediate partitions. If students understand this, then carbonyl chemistry becomes pretty straightforward. I found that the lipid material that had been put into this chapter in the last edition detracted from the main message of the chapter. Therefore, the lipid material was removed and put into a new chapter exclusively about lipids.

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This chapter was reorganized and rewritten for ease of understanding.

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The lipid material previously in the chapter on carboxylic acids and their derivatives has been moved into this new chapter. The discussion of terpenes from the metabolism chapter has also been moved into this chapter, along with some new material.

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Preface

The guiding principle behind this book is to present organic chemistry as an exciting and vitally important science. To counter the impression that the study of organic chemistry consists primarily of memorizing a multitude of facts, I have organized this book around shared features and unifying concepts, while emphasizing principles that can be applied again and again. I want students to apply what they have learned to new settings and to learn how to reason their way to solutions. I also want them to see that organic chemistry is a fascinating discipline that is integral to their daily lives.

Preparing Students for Future Study in a Variety of Scientific Disciplines

This book organizes the functional groups around mechanistic similarities. When students see their first reaction (other than an acid–base reaction), they are told that all organic compounds can be divided into families and that all members of a family react *in the same way*. And 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*.

“Organizing What We Know About Organic Chemistry” is a feature based on these statements. It lets students see where they have been and where they are going as they proceed through each of the four groups. It also encourages them to remember the fundamental reason behind the reactions of all organic compounds: *electrophiles react with nucleophiles*. When students finish studying a particular group, they are given the opportunity to review the group and understand why the families came to be members of that particular group. The four groups are covered in the following order. (However, the book is written to be modular, so they could be covered in any order.)

- **Group I: Compounds with carbon-carbon double and triple bonds.** These compounds are nucleophiles and, therefore, react with electrophiles—undergoing electrophilic addition reactions.
- **Group II: Compounds with electron-withdrawing atoms or groups attached to sp^3 carbons.** These compounds are electrophiles and, therefore, react with nucleophiles—undergoing nucleophilic substitution and elimination reactions.
- **Group III: Carbonyl compounds.** These compounds are electrophiles and, therefore, react with nucleophiles—undergoing nucleophilic acyl substitution, nucleophilic addition, and nucleophilic addition-elimination reactions. Because of the “acidity” of the α -carbon, a carbonyl compound can become a nucleophile and, therefore, react with electrophiles.
- **Group IV: Aromatic compounds.** Some aromatic compounds are nucleophiles and, therefore, react with electrophiles—undergoing electrophilic aromatic substitution reactions. Other aromatic compounds are electrophiles and, therefore, react with nucleophiles—undergoing nucleophilic aromatic substitution reactions.

The organization discourages rote memorization and allows students to learn reactions based on their pattern of reactivity. It is only after these patterns of reactivity are understood that a deep understanding of organic chemistry can begin. As a result, students achieve the predictive capacity that is the beauty of studying science. A course that teaches students to analyze, classify, explain, and predict gives them a strong foundation to bring to their subsequent study of science, regardless of the discipline.

As students proceed through the book, they come across ~200 interest boxes that connect what they are studying to real life. Students don’t have to be preparing for a career in medicine to appreciate a box on the experimental drug used to treat Ebola, and they don’t have to be preparing for a career in engineering to appreciate a box on the properties that a polymer used for dental impressions must have.

The Organization Ties Together Reactivity and Synthesis

Many organic chemistry textbooks discuss the synthesis of a functional group and the reactivity of that group sequentially, but these two groups of reactions generally have little to do with one another. Instead, when I discuss a functional group's reactivity, I cover the synthesis of compounds that are formed as a result of that reactivity, often by having students design syntheses. In Chapter 6, for example, students learn about the *reactions* of alkenes, but they *do not* learn about the *synthesis* of alkenes. Instead, they learn about the synthesis of alkyl halides, alcohols, ethers, epoxides, alkanes, etc.—the compounds formed when alkenes react. The synthesis of alkenes is not covered until the reactions of alkyl halides and alcohols are discussed—compounds whose reactions lead to the synthesis of alkenes.

This strategy of tying together the reactivity of a functional group and the synthesis of compounds resulting from its reactivity prevents the student from having to memorize lists of unrelated reactions. It also results in a certain economy of presentation, allowing more material to be covered in less time.

Although memorizing different ways a particular functional group can be prepared can be counterproductive to enjoying organic chemistry, it is useful to have such a compilation of reactions when designing multistep syntheses. For this reason, lists of reactions that yield a particular functional group are compiled in Appendix III. In the course of learning how to design syntheses, students come to appreciate the importance of reactions that change the carbon skeleton of a molecule; these reactions are compiled in Appendix IV.

Helping Students Learn and Study Organic Chemistry

As each student generation evolves and becomes increasingly diverse, we are challenged as teachers to support the unique ways students acquire knowledge, study, practice, and master a subject. In order to support contemporary students who are often visual learners, with preferences for interactivity and small “bites” of information, I have revisited this edition to make it more compatible with their learning style by streamlining the narrative and using organizing bullets and subheads. This will allow them to study more efficiently with the text.

The book is written much like a tutorial. Each section ends with a set of problems that students need to work through to find out if they are ready to go on to the next section, or if they need to review the section they thought they had just mastered. This allows the book to work well in a “flipped classroom.”

For those who teach organic chemistry after one semester of general chemistry, Chapter 5 and Appendix II contain material on thermodynamics and kinetics, so those topics can be taught in the organic course.

An enhanced art program with new and expanded annotations provides key information to students so that they can review important parts of the chapter with the support of the visual program. Margin notes throughout the book succinctly repeat key points and help students review important material at a glance.

Tutorials follow relevant chapters to help students master essential skills:

- Acids and Bases
- Using Molecular Models
- Interconverting Structural Representations
- Drawing Curved Arrows
- Drawing Resonance Contributors
- Drawing Curved Arrows in Radical Systems
- Synthesis and Retrosynthetic analysis

MasteringChemistry includes additional online tutorials on each of these topics that can be assigned as homework or for test preparation.

Organizational Changes

Using the *E,Z* system to distinguish alkene stereoisomers was moved to Chapter 4, so now it appears immediately after using *cis* and *trans* to distinguish alkene stereoisomers.

Catalytic hydrogenation and the relative stabilities of alkenes was moved from Chapter 6 to Chapter 5 (thermodynamics), so it can be used to illustrate how ΔH° values can be used to determine relative stabilities. Moving this has another advantage—because catalytic hydrogenation is the only reaction of alkenes that does not have a well-defined mechanism, all the remaining reactions

in Chapter 6 now have well-defined mechanisms, all following the general rule that applies to all electrophilic addition reactions: the first step is always the addition of the electrophile to the sp^2 carbon bonded to the most hydrogens.

Chapter 8 starts by discussing the structure of benzene because it is the ideal compound to use to explain delocalized electrons. This chapter also includes a discussion on aromaticity, so a short introduction to electrophilic aromatic substitution reactions is now included. This allows students to see how aromaticity causes benzene to undergo electrophilic substitution rather than electrophilic addition—the reactions they just finished studying.

Traditionally, electronic effects are taught so students can understand the activating and directing effects of substituents on benzene rings. Now that most of the chemistry of benzene follows carbonyl chemistry, students need to know about electronic effects before they get to benzene chemistry (so they are better prepared for spectroscopy and carbonyl chemistry). Therefore, in this edition electronic effects are discussed in Chapter 8 and used to teach students how substituents affect the pK_a values of phenols, benzoic acids, and anilinium ions. Electronic effects are then reviewed in the chapter on benzene.

The two chapters in the previous edition that covered the substitution and elimination reactions of alkyl halides have been combined into one chapter (Chapter 9). The recent compelling evidence showing that alkyl halides do not undergo S_N1 solvolysis reactions has allowed this material to be greatly simplified, so now it fits nicely into one chapter.

I have found that teaching carbonyl chemistry before the chemistry of aromatic compounds (a change made in the last edition) has worked well for my students. Carbonyl compounds are probably the most important organic compounds, and moving them forward gives them the prominence they should have. In addition, the current location of the chemistry of benzene allows it and the chemistry of aromatic heterocyclic compounds to be taught sequentially.

The focus of the first chapter on carbonyl chemistry should be all about how a tetrahedral intermediate partitions. If students understand this, then carbonyl chemistry becomes relatively easy. I found that the lipid material that had been put into this chapter detracted from the main message of the chapter. Therefore, the lipid material was removed and put into a new chapter: The Organic Chemistry of Lipids. The discussion of terpenes from the metabolism chapter has also been moved into this chapter, and some new material has been included.

Modularity/Spectroscopy

The book is designed to be modular, so the four groups (Group I—Chapters 6, 7, 8; Group II—Chapters 9 and 10; Group III—Chapters 15, 16, 17; Group IV—Chapters 18 and 19) can be covered in any order.

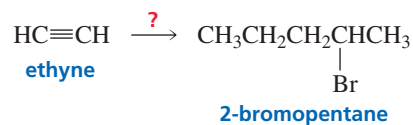
The spectroscopy chapters (Chapters 13 and 14) are written so that they can be covered at any time during the course. For those who prefer to teach spectroscopy before all the functional groups have been introduced—or in a separate laboratory course—there is a table of functional groups at the beginning of Chapter 13.

An Early and Consistent Emphasis on Organic Synthesis

Students are introduced to synthetic chemistry and retrosynthetic analysis early in the book (Chapters 6 and 7, respectively), so they can start designing multistep syntheses early in the course. Seven special sections on synthesis design, each with a different focus, are introduced at appropriate intervals. There is also a tutorial on synthesis and retrosynthetic analysis that includes some examples of complicated multistep syntheses from the literature.

Example 2

Starting with ethyne, how could you make 2-bromopentane?



2-Bromopentane can be prepared from 1-pentene, which can be prepared from 1-pentyne. 1-Pentyne can be prepared from ethyne and an alkyl halide with three carbons.

Problems, Solved Problems, and Problem-Solving Strategies

The book contains more than 2,000 problems, many with multiple parts. This edition has many new problems, both in-chapter and end-of-chapter. They include new solved problems, new problem-solving strategies, and new problems incorporating information from more than one chapter. I keep a list of questions my students have when they come to office hours. Many of the new problems were created as a result of these questions.

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 material just covered before moving on to the next section. Short answers provided at the end of the book for problems marked with a diamond give students immediate feedback concerning their mastery of a skill or concept.

Selected problems are accompanied by worked-out solutions to provide insight into problem-solving techniques, and the many Problem-Solving Strategies teach students how to approach various kinds of problems. These skill-teaching problems are indicated by LEARN THE STRATEGY in the margin. These strategies are followed by one or more problems that give students the opportunity to use the strategy just learned. These problems, or the first of a group of such problems, are indicated in the margin by USE THE STRATEGY.

Powerpoint

All the art in the text is available on PowerPoint slides. I created the PowerPoint lectures so they would be consistent with the language and philosophy of the text.

Students Interested in The Biological Sciences and MCAT²⁰¹⁵

I have long believed that students who take organic chemistry also should be exposed to bioorganic chemistry—the organic chemistry that occurs in biological systems. Students leave their organic chemistry course with a solid appreciation of organic mechanism and synthesis. But when they take biochemistry, they will never hear about Claisen condensations, S_N2 reactions, nucleophilic acyl substitution reactions, etc., although these are extremely important reactions in cells. Why are students required to take organic chemistry if they are not going to be taught how the organic chemistry they learn repeats itself in the biological world?

Now that the MCAT is focusing almost exclusively on the organic chemistry of living systems, it is even more important that we provide our students with the “bioorganic bridge”—the material that provides the bridge between organic chemistry and biochemistry. Students should see that the organic reactions that chemists carry out in the laboratory are in many ways the same as those performed by nature inside a cell.

The seven chapters (Chapters 20–26) that focus primarily on the organic chemistry of living systems 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.

For example, the first step in glycolysis is an S_N2 reaction, the second step is identical to the enediol rearrangement that students learn when they study carbohydrate chemistry, the third step is another S_N2 reaction, the fourth step is a reverse aldol addition, and so on. The first step in the citric acid cycle is an aldol addition followed by a nucleophilic acyl substitution reaction, the second step is an E2 dehydration followed by the conjugate addition of water, the third step is oxidation of a secondary alcohol followed by decarboxylation of a 3-oxocarboxylate ion, and so on.

We teach students about halide and sulfonate leaving groups. Adding phosphate leaving groups takes little additional time but introduces the students to valuable information if they are going on to study biochemistry.

Students who study organic chemistry learn about tautomerization and imine hydrolysis, and students who study biochemistry learn that DNA has thymine bases in place of the uracil bases in RNA. But how many of these students are ever told that the reason for the difference in the bases in DNA and RNA is tautomerization and imine hydrolysis?

Colleagues have asked how they can find time to fit the “bioorganic bridge” into their organic chemistry courses. I found that tying together reactivity and synthesis (see p. 23) frees up a lot of time. (This is the organization I adopted many years ago when I was trying to figure out how to incorporate the bioorganic bridge into my course.) And if you find that this still does not give you enough time, I have organized the book in a way that allows some “traditional” chapters to be omitted (Chapters 12, 18, 19, and 28), so students can be prepared for biochemistry and/or the MCAT without sacrificing the rigor of the organic course.

The Bioorganic Bridge

Bioorganic chemistry is found throughout the text to show students that organic chemistry and biochemistry are not separate entities but rather are closely related on a continuum of knowledge. Once students learn how, for example, electron delocalization, leaving-group propensity, electrophilicity, and nucleophilicity affect the reactions of simple organic compounds, they can appreciate how these same factors influence the reactions of organic compounds in cells.

In Chapters 1–19, the bioorganic material is limited mostly to “interest boxes” and to the last sections of the chapters. Thus, the material is available to the curious student without requiring the instructor to introduce bioorganic topics into the course. For example, after hydrogen bonding is introduced in Chapter 3, hydrogen bonding in proteins in DNA is discussed; after catalysis is introduced in Chapter 5, catalysis by enzymes is discussed; after the stereochemistry of organic reactions is presented in Chapter 6, the stereochemistry of enzyme-catalyzed reactions is discussed; after sulfonium ions are discussed in Chapter 10, a biological methylation reaction using a sulfonium ion is examined and the reason for the use of different methylating agents by chemists and cells is explained; after the methods chemists use to activate carboxylic acids are presented (by giving them halide or anhydride leaving groups) in Chapter 15, the methods cells use to activate these same acids are explained (by giving them phosphoanhydride, pyrophosphate, or thiol leaving groups); and after condensation reactions are discussed in Chapter 17, the mechanisms of some biological condensation reactions are shown.

In addition, seven chapters in the last part of the book (Chapters 20–26) focus on the organic chemistry of living systems. These chapters have the unique distinction of containing more chemistry than is typically found in the corresponding parts of a biochemistry text. Chapter 22 (Catalysis in Organic Reactions and in Enzymatic Reactions), for example, explains the various modes of catalysis employed in organic reactions and then shows that they are identical to the modes of catalysis found in reactions catalyzed by enzymes. All of this is presented in a way that allows students to understand the lightning-fast rates of enzymatic reactions. Chapter 23 (The Organic Chemistry of the Coenzymes, Compounds Derived from Vitamins) emphasizes the role of vitamin B₁ in electron delocalization, vitamin K as a strong base, vitamin B₁₂ as a radical initiator, biotin as a compound that transfers a carboxyl group by means of a nucleophilic acyl substitution reaction, and describes how the many different reactions of vitamin B₆ have common mechanisms—with the first step always being imine formation. Chapter 24 (The Organic Chemistry of Metabolic Pathways) explains the chemical function of ATP and shows students that the reactions encountered in metabolism are just additional examples of reactions that they already have mastered. In Chapter 26 (The Chemistry of the Nucleic Acids), students learn that 2'-OH group on the ribose molecules in RNA catalyzes its hydrolysis and that is why DNA, which has to stay intact for the life of the cell, does not have 2'-OH groups. Students also see that the synthesis of proteins in cells is just another example of a nucleophilic acyl substitution reaction. Thus, these chapters do not replicate what will be covered in a biochemistry course; they provide a bridge between the two disciplines, allowing students to see how the organic chemistry that they have learned is repeated in the biological world.

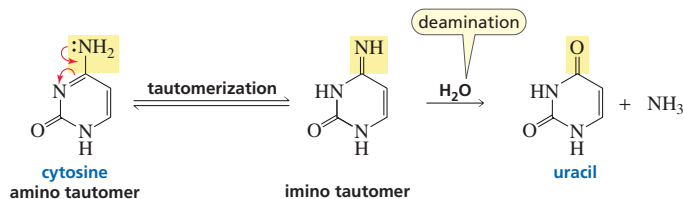
ENGAGING MIXED SCIENCE MAJORS IN ORGANIC CHEMISTRY

Students better understand the relevance of what they're studying by seeing the connections between the reactions of organic compounds that occur in the laboratory and those that occur in a cell. Changes throughout this edition provide students with this much-needed "bioorganic bridge," while maintaining the rigor of the traditional organic course.

For example, we teach students about halide and sulfonate leaving groups. Adding phosphate leaving groups takes little additional time, but it introduces students to valuable information, particularly if they are taking organic chemistry because of an interest in the biological sciences. Students who are studying organic chemistry learn about tautomerization and imine hydrolysis, and students studying biochemistry learn that DNA has thymine bases in place of the uracil bases in RNA. But how many of these students are ever told that the reason for the difference in the bases in DNA and RNA is tautomerization and imine hydrolysis?

The NADP⁺ formed in this reaction has to be reduced back to NADPH by NADH. Every NADH formed in a cell can result in the formation of 2.5 ATPs (Section 24.10). Therefore, reducing dihydrofolate comes at the expense of ATP. This means that the synthesis of thymine is energetically expensive, so there must be a good reason for DNA to contain thymine instead of uracil.

The presence of thymine instead of uracil in DNA prevents potentially lethal mutations. Cytosine can tautomerize to form an imine (Section 17.2), which can be hydrolyzed to uracil (Section 16.8). The overall reaction is called a **deamination** because it removes an amino group.



More Applications Than Any Other Organic Text

NEW! and Updated Application boxes connect the discussion to medical, environmental, biological, pharmaceutical, nutritional, chemical, industrial, historical, and general applications and allow students to relate the material to real life and to potential future careers.

Using Genetic Engineering to Treat the Ebola Virus

Plants have long been a source of drugs—morphine, ephedrine, and codeine are just a few examples (Section 10.9). Now scientists are attempting to obtain drugs from plants by biopharming. Biopharming uses genetic engineering techniques to produce drugs in crops such as corn, rice, tomatoes, and tobacco. To date, the only biopharmed drug approved by the Food and Drug Administration (FDA) is one that is manufactured in carrots and used to treat Gaucher's disease.

An experimental drug that was used to treat a handful of patients with Ebola, the virus that was spreading throughout West Africa, was obtained from genetically engineered tobacco plants. The tobacco plants were infected with three genetically engineered plant viruses that are harmless to humans and animals but have structures similar to that of the Ebola virus. As a result of being infected, the plants produced antibodies to the viruses. The antibodies were isolated from the plants, purified, and then used to treat the patients with Ebola.

The experimental drug had been tested in 18 monkeys who had been exposed to a lethal dose of Ebola. All 18 monkeys survived, whereas the three monkeys in the control group died. Typically, drugs go through rigorous testing on healthy humans prior to being administered to infected patients (see page 326). In the Ebola case, the FDA made an exception because it feared that the drug might be these patients' only hope. Five of the seven people given the drug survived. Currently, it takes about 50 kilograms of tobacco leaves and about 4 to 6 months to produce enough drug to treat one patient.



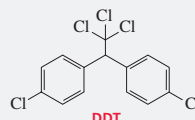
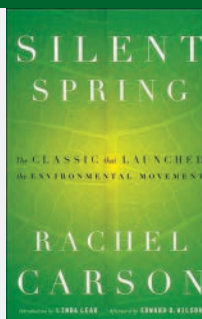
tobacco plants

The Birth of the Environmental Movement

Alkyl halides have been used as insecticides since 1939, when it was discovered that DDT (first synthesized in 1874) has a high toxicity to insects and a relatively low toxicity to mammals. DDT was used widely in World War II to control typhus and malaria in both the military and civilian populations. It saved millions of lives, but no one realized at that time that, because it is a very stable compound, it is resistant to biodegradation. In addition, DDT and DDE, a compound formed as a result of elimination of HCl from DDT, are not water soluble. Therefore, they accumulate in the fatty tissues of birds and fish and can be passed up the food chain. Most older adults have a low concentration of DDT or DDE in their bodies.

In 1962, Rachel Carson, a marine biologist, published *Silent Spring*, where she pointed out the environmental impacts of the widespread use of DDT. The book was widely read, so it brought the problem of environmental pollution to the attention of the general public for the first time. Consequently, its publication was an important event in the birth of the environmental movement. Because of the concern it raised, DDT was banned in the United States in 1972. In 2004, the Stockholm Convention banned the worldwide use of DDT except for the control of malaria in countries where the disease is a major health problem.

In Section 12.12, we will look at the environmental effects caused by synthetic alkyl halides known as chlorofluorocarbons (CFCs).



GUIDED APPROACH TO PROBLEM SOLVING

Essential Skill Tutorials

These tutorials guide students through some of the topics in organic chemistry that they typically find to be the most challenging. They provide concise explanations, related problem-solving opportunities, and answers for self-check. The print tutorials are paired with MasteringChemistry online tutorials. These are additional problem sets that can be assigned as homework or as test preparation.

DRAWING CURVED ARROWS

This is an extension of what you learned about drawing curved arrows on pp. 235–237. Working through these problems will take only a little of your time. It will be time well spent, however, because curved arrows are used throughout the book and it is important that you are comfortable with them. (You will not encounter some of the reaction steps shown in this exercise for weeks or even months, so don't worry about why the chemical changes take place.)

Chemists use curved arrows to show how electrons move as covalent bonds break and/or new covalent bonds form.

- Each arrow represents the simultaneous movement of two electrons (an electron pair) from a nucleophile (at the tail of the arrow) toward an electrophile (at the point of the arrow).
- The tail of the arrow is positioned where the electrons are in the reactant; the tail always starts at a lone pair or at a bond.
- The head of the arrow points to where these same electrons end up in the product; the arrow always points at an atom or at a bond.

In the following reaction step, the bond between bromine and a carbon of the cyclohexane ring breaks and both electrons in the bond end up with bromine. Thus, the **arrow starts at the electrons that carbon and bromine share in the reactant, and the head of the arrow points at bromine** because this is where the two electrons end up in the product.

Notice that the carbon of the cyclohexane ring is positively charged in the product. This is because it has lost the two electrons it was sharing with bromine. The bromine is negatively charged in the product because it has gained the electrons that it shared with carbon in the reactant. The fact that two electrons move in this example is indicated by the two barbs on the arrowhead.

Notice that the arrow *always* starts at a bond or at a lone pair. It does *not* start at a negative charge.

In the following reaction step, a bond is being formed between the oxygen of water and a carbon of the other reactant. The arrow starts at one of the lone pairs of the oxygen and points at the atom (the carbon) that will share the electrons in the product. The oxygen in the product is positively charged, because the electrons that oxygen had to itself in the reactant are now being shared with carbon. The carbon that was positively charged in the reactant is not charged in the product, because it has gained a share in a pair of electrons.

PROBLEM 1 Draw curved arrows to show the movement of the electrons in the following reaction steps. (The answers to all problems appear immediately after Problem 10.)

a.

b.

ESSENTIAL SKILL TUTORIAL

Enhanced by MasteringChemistry®

Organizing What We Know About the Reactivity of Organic Compounds

This organization emphasizes the unifying principles of reactivity and offers an economy of presentation while discouraging memorization. Students learn that

- organic compounds can be classified into *families* and that all members of a family react in the same way.
- the families can be put into one of four *groups* and that all the family members in a group react in similar ways.

The Organizing What We Know table builds as students work sequentially through the four groups.

- Group I: electrophilic addition reactions
- Group II: nucleophilic substitution reactions and elimination reactions
- Group III: nucleophilic acyl substitution reactions, nucleophilic addition reactions, and nucleophilic addition–elimination reactions
- Group IV: electrophilic (and nucleophilic) aromatic substitution reactions

19.8

ORGANIZING WHAT WE KNOW ABOUT THE REACTIONS OF ORGANIC COMPOUNDS

Group I	Group II	Group III	Group IV
$R-CH=CH-R$ alkene $R-C\equiv C-R$ alkyne $R-CH=CH-CH=CH-R$ diene These are nucleophiles. They undergo electrophilic addition reactions.	$R-X$ alkyl halide $X = F, Cl, Br, I$ $R-OH$ alcohol $R-OR$ ether epoxide $R-O-S(=O)_2-R$ sulfonate ester $R-N^+(R)_3-O^-$ quaternary ammonium hydroxide $R-S(=O)_2-R$ sulfonium salt These are electrophiles. They undergo nucleophilic substitution and/or elimination reactions.	$R-C(=O)-Z$ $Z = \text{an atom more electronegative than C}$ $R-C(=O)-Z$ $Z = C \text{ or } H$ These are electrophiles. They undergo nucleophilic acyl substitution reactions, nucleophilic addition reactions, or nucleophilic addition–elimination reactions. Removal of a hydrogen from an α-carbon forms a nucleophile that can react with electrophiles.	 benzene pyridine $Z = N, O, \text{ or } S$ pyrrole, furan, thiophene $Z = N, O, \text{ or } S$ These are nucleophiles. They undergo electrophilic aromatic substitution reactions. Halo-substituted benzenes and halo-substituted pyridines are electrophiles. They undergo nucleophilic aromatic substitution reactions.

Emphasis on the Strategies Needed to Solve Problems and Master Content

Passages explaining important problem-solving strategies are clearly labeled with a LEARN THE STRATEGY label. Follow-up problems that require students to apply the just-learned strategy are labeled with a USE THE STRATEGY label. These labels, which are implemented throughout the text, allow students to easily find important content and practice its use.

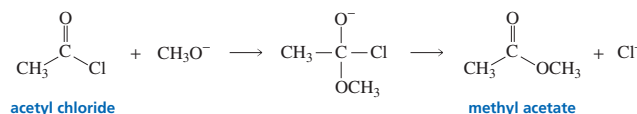
LEARN THE STRATEGY

PROBLEM-SOLVING STRATEGY

Using Basicity to Predict the Outcome of a Nucleophilic Acyl Substitution Reaction

What is the product of the reaction of acetyl chloride with CH_3O^- ? The $\text{p}K_{\text{a}}$ of HCl is -7 ; the $\text{p}K_{\text{a}}$ of CH_3OH is 15.5 .

To identify the product of the reaction, we need to compare the basicities of the two groups in the tetrahedral intermediate so we can determine which one will be eliminated. Because HCl is a stronger acid than CH_3OH , Cl^- is a weaker base than CH_3O^- . Therefore, Cl^- is eliminated from the tetrahedral intermediate and methyl acetate is the product of the reaction.



USE THE STRATEGY

PROBLEM 7 ♦

- What is the product of the reaction of acetyl chloride with HO^- ? The $\text{p}K_{\text{a}}$ of HCl is -7 ; the $\text{p}K_{\text{a}}$ of H_2O is 15.7 .
- What is the product of the reaction of acetamide with HO^- ? The $\text{p}K_{\text{a}}$ of NH_3 is 36 ; the $\text{p}K_{\text{a}}$ of H_2O is 15.7 .

PROBLEM 8 ♦

What is the product of an acyl substitution reaction—a new carboxylic acid derivative, a mixture of two carboxylic acid derivatives, or no reaction—if the new group in the tetrahedral intermediate is the following?

- a stronger base than the substituent that is attached to the acyl group
- a weaker base than the substituent that is attached to the acyl group
- similar in basicity to the substituent that is attached to the acyl group

Designing a Synthesis

This recurring feature helps students learn to design multi-step syntheses and facilitates the development of complex problem-solving skills. Many problems include the synthesis of well-known compounds such as Novocain[®], Valium[®], and Ketoprofen[®].

DESIGNING A SYNTHESIS V

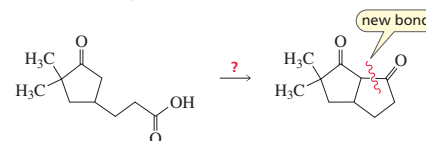
17.20 MAKING NEW CARBON–CARBON BONDS

When planning the synthesis of a compound that requires the formation of a new carbon–carbon bond:

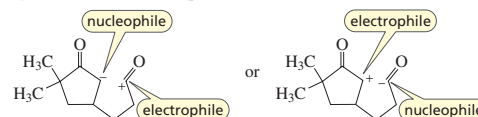
- locate the new bond that needs to be made and perform a disconnection—that is, break the bond to produce two fragments.
- determine which of the atoms that will form the new bond should be the electrophile and which should be the nucleophile.
- choose a compound with the desired electrophilic and nucleophilic groups.

Example 1

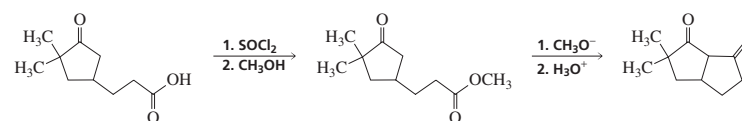
The new bond that needs to be made in the synthesis of the following β -diketone is the one that makes the second five-membered ring:



It is easy to choose between the two possibilities for the electrophile and nucleophile because we know that a carbonyl carbon is an electrophile.



If we know what the starting material is, we can use it as a clue to arrive at the desired compound. For example, an ester carbonyl group would be a good electrophile for this synthesis because it has a group that would be eliminated. Moreover, the α -hydrogens of the ketone are more acidic than the α -hydrogens of the ester, so the desired nucleophile would be easy to obtain. Thus, converting the starting material to an ester (Section 15.18), followed by an intramolecular condensation, forms the target molecule.



MasteringChemistry® www.masteringchemistry.com

MasteringChemistry motivates student to learn outside of class and arrive prepared for lecture. The text works with MasteringChemistry to guide students on what they need to know before testing them on the content. The third edition continually engages students through pre-lecture, during-lecture, and post-lecture activities that all include real-life applications.

DYNAMIC STUDY MODULES

Help Students Learn Chemistry Quickly!

Now assignable, Dynamic Study Modules enable your students to study on their own and be better prepared for class. The modules cover content and skills needed to succeed in organic chemistry: fundamental concepts from general chemistry; practice with nomenclature, functional groups, and key mechanisms; and problem-solving skills. For students who want to study on the go, a mobile app that records student results to the MasteringChemistry gradebook is available for iOS and Android devices.



The screenshot shows a web browser window displaying a Pearson MyLab Chemistry question. The page title is "Organometallic Reactions". The question asks: "Which of the following is a Grignard reagent?". There are five answer choices, each with a radio button:

- ☐ C1CCCCC1[Mg]Br
- ☒ BrCC1CCCCC1
- ☐ c1ccccc1[Mg]Br
- ☒ [Li+].[Cu-](c1ccccc1)2
- ☐ I DON'T KNOW YET

Below the choices, it says "ONE IS CORRECT". To the right of the question area, there is a section titled "ANSWER" which is currently blank.

To the right of the main screenshot, there is a smaller inset showing the feedback after selecting the correct answer. It indicates that the second choice was correct and provides the following information:

- THE CORRECT ANSWER: c1ccccc1[Mg]Br
- YOU WERE SURE AND INCORRECT: CCC[Li]
- I DON'T KNOW YET: c1ccccc1Br

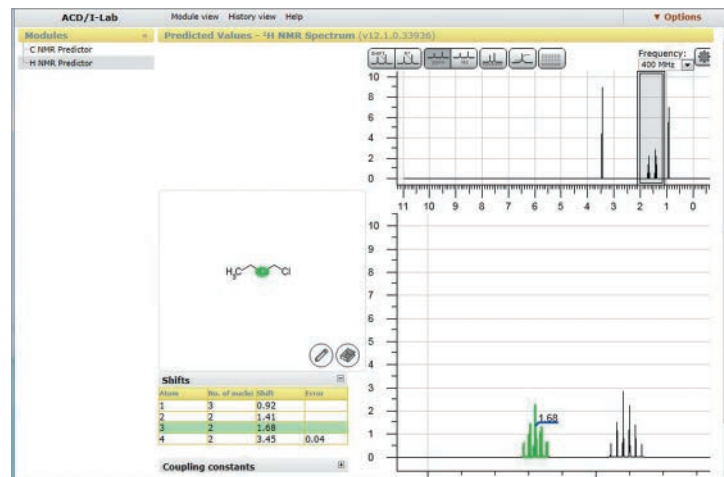
At the bottom right, there is a section titled "WHAT YOU NEED TO KNOW" explaining why the correct answer is a Grignard reagent:

c1ccccc1[Mg]Br is a Grignard reagent because it contains a carbon-magnesium halide bond.

The other answer choices are incorrect because they are alkyl lithium compounds, halides where a halogen is directly bonded to a carbon, or an ether where oxygen is single bonded to two separate carbons.

Spectroscopy Simulations

NEW! Six NMR/IR Spectroscopy simulations (a partnership with ACD labs) allow professors and students access to limitless spectral analysis with guided activities that can be used in the lab, in the classroom, or after class to study and explore spectra virtually. Activities authored by Mike Huggins, University of West Florida, prompt students to utilize the spectral simulator and walk them through different analyses and possible conclusions.



RESOURCES IN PRINT AND ONLINE

Supplement	Available in Print?	Available Online?	Instructor or Student Supplement	Description
MasteringChemistry®		✓	Instructor and Student Supplement	MasteringChemistry® from Pearson has been designed and refined with a single purpose in mind: to help educators create that moment of understanding with their students. The Mastering platform delivers engaging, dynamic learning opportunities—focused on your course objectives and responsive to each student’s progress—that are proven to help students absorb course material and understand difficult concepts.
Test Bank		✓	Instructor Supplement	This test bank contains over 2500 multiple-choice, true/false, and matching questions. It is available in print format, in the TestGen program, and in Word format, and is included in the item library of MasteringChemistry®.
Instructor Resource Materials		✓	Instructor Supplement	This provides an integrated collection of online resources to help instructors make efficient and effective use of their time. It includes all artwork from the text, including figures and tables in PDF format for high-resolution printing, as well as pre-built PowerPoint™ presentations. The first presentation contains the images embedded within PowerPoint slides. The second includes a complete lecture outline that is modifiable by the user. Powerpoints of the in-chapter worked examples are also included.

ACKNOWLEDGMENTS

It gives me great pleasure to acknowledge the dedicated efforts of many good friends who made this book a reality. In particular, a loud thanks goes to Richard Morrison of the University of Georgia, who read every page, made critically important suggestions, checked every answer in the *Solutions Manual*, and created many new end-of-chapter problems—and to Jordan Fantini of Dennison University, who created the interactive digital modules designed to engage students in the fundamental principles of reactivity while advancing their visualization skills. I am also deeply grateful to Laura Sessions of Valencia College who checked every inch of the book for accuracy; David Yertzley, 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; and to my student, Jeremy Davis, who created the dog cartoons that appear on page 180. I also thank my many students, who pointed out sections that needed clarification, searched for errors, and whose questions guided the creation of new problems.

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

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Stephen Miller, *University of Florida*
Christopher Roy, *Duke University*
Chad Snyder, *Western Kentucky University*

Many people made this book possible, but at the top of the list is my editor, Jeanne Zalesky, who has been involved and supportive at every stage of its creation and whose many talents guided the book to make it as good as it could be. I am also extremely grateful to have had the opportunity to work with Matt Walker, the development editor. His insights into how today's students learn and his creative art development skills have had a huge effect on this edition. I am also grateful to Elisa Mandelbaum, the project editor, whose attention to detail and creation of manageable deadlines made the book actually happen. And I want to thank the other talented and dedicated people at Pearson whose contributions made this book a reality:

I particularly want to thank the many wonderful and talented students I have had over the years, who inspired me, challenged me, and 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 email so they can be corrected in future printings of this edition.

Paula Yurkanis Bruice
University of California, Santa Barbara

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Reviewers

Vinh Nguyen, *The University of New South Wales*

Prasanna Ghalsasi, *The MS University of Baroda*

Pauline Chiu, *The University of Hong Kong*

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 mysteries and biographies and enjoying her pets (three dogs, two cats, and two parrots).

PART ONE

An Introduction to the Study of Organic Chemistry

The first three chapters of this textbook cover a variety of topics with which you need to be familiar to start your study of the reactions and synthesis of organic compounds.

Chapter 1 Remembering General Chemistry: Electronic Structure and Bonding

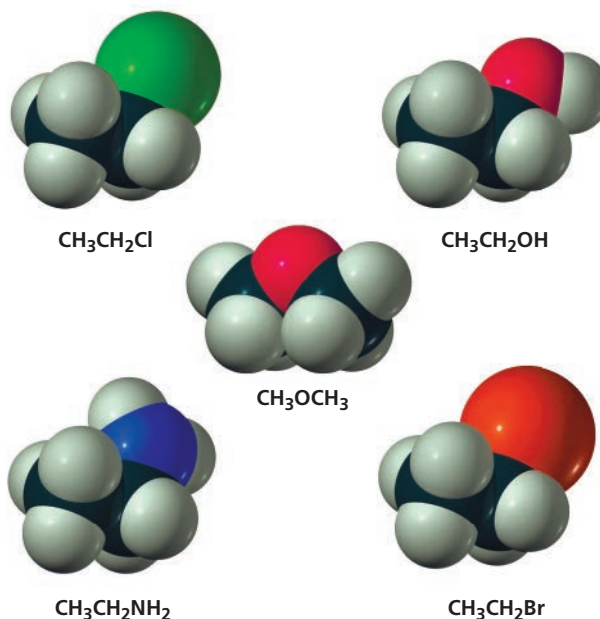
Chapter 1 reviews the topics from general chemistry that are important to your study of organic chemistry. The chapter starts with a description of the structure of atoms and then proceeds to a description of the structure of molecules. Molecular orbital theory is introduced.

Chapter 2 Acids and Bases: Central to Understanding Organic Chemistry

Chapter 2 discusses acid–base chemistry, a topic that is central to understanding many organic reactions. You will see how the structure of a molecule affects its acidity and how the acidity of a solution affects molecular structure.

Chapter 3 An Introduction to Organic Compounds: Nomenclature, Physical Properties, and Representation of Structure

To discuss organic compounds, you must know how to name them and be able to visualize their structures when you read or hear their names. In **Chapter 3**, you will learn how to name five different families of organic compounds. This will give you a good understanding of the basic rules for naming compounds. Because the compounds examined in the chapter are the reactants or the products of many of the reactions presented in the first third of the book, you will have numerous opportunities to review the nomenclature of these compounds as you proceed through these chapters. Chapter 3 also compares and contrasts the structures and physical properties of these compounds, which makes learning about them a little easier than if the structure and physical properties of each family were presented separately. Because organic chemistry is a study of compounds that contain carbon, the last part of Chapter 3 discusses the spatial arrangement of the atoms in both chains and rings of carbon atoms.



1

Remembering General Chemistry: Electronic Structure and Bonding



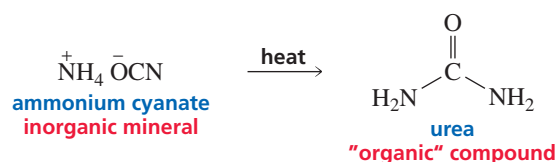
NOTE TO THE STUDENT

- Biographies of the scientists mentioned in this text book can be found on the book's Website.

To stay alive, early humans must have been able to distinguish between 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 have a vital force. You can imagine their surprise when, in 1828, Friedrich Wöhler produced urea—a compound 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, therefore, did not contain a vital force. Thus, chemists needed a new definition for “organic compounds.” **Organic compounds** are now defined as *compounds that are based on 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 compounds 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

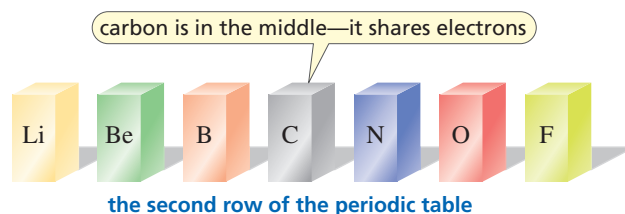
Organic compounds are compounds that are based on carbon.

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

Organic compounds are not limited to those found in nature. Chemists have learned how to synthesize millions of organic compounds not found in nature, including synthetic fabrics, plastics, synthetic rubber, and even things such as compact discs and Super Glue. And most importantly, almost all commonly prescribed drugs are synthetic organic compounds.

Some synthetic organic compounds prevent shortages of naturally occurring compounds. For example, it has been estimated that if synthetic materials—nylon, polyester, Lycra—were not available for clothing, 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.

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 kinds of atoms as well as with other carbon atoms. Consequently, carbon forms millions of stable compounds with a wide range of chemical properties simply by sharing electrons.

Natural 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 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—compounds with structures similar to that 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 15.11).

Chemists have also synthesized analogues of morphine that have the same pain-killing effects but, unlike morphine, are not habit-forming. Most commercial morphine is obtained from opium, the juice extracted from the species of poppy shown in the photo. 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 15.16). Nearly three-quarters of the world's supply of heroin comes from the poppy fields of Afghanistan.



a field of poppies in Afghanistan

When we study organic chemistry, we learn how organic compounds react. Organic compounds consist of atoms held together by covalent bonds. When an organic compound reacts, some of these covalent bonds break and some new covalent bonds form.

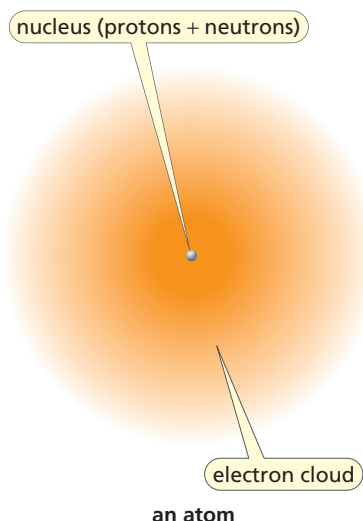
*Covalent bonds form when two atoms share electrons,
and they break when two atoms no longer share electrons.*

How easily a covalent bond forms or breaks depends on the electrons that are shared, which, in turn, depends 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

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 mass = the weighted average mass of the isotopes in the element

molecular mass = the sum of the atomic masses of all the atoms in the molecule

A molecule is a group of two or more atoms held together by bonds.

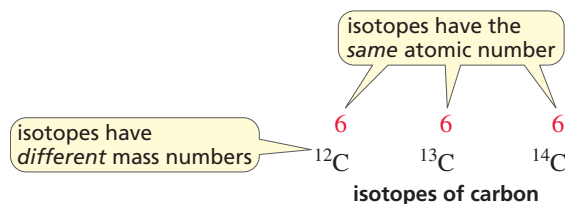
An atom consists of a tiny dense nucleus surrounded by electrons that are spread throughout a relatively large volume of space around the nucleus called an electron cloud. The nucleus contains **positively charged protons** and **uncharged neutrons**, so it is positively charged. The **electrons** are **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 counteracts the attractive force of the positively charged protons that pull the negatively charged electrons toward 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 electron cloud. 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. Although atoms can gain electrons and become negatively charged or lose electrons and become positively charged, the number of protons in an atom of a particular element never changes.

The **mass number** of an atom is the sum of its protons and neutrons. Although all carbon atoms have the same *atomic number*, they do not all have the same *mass number*. Why? Because carbon atoms can have varying numbers of 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}C and ^{13}C) are called **isotopes**.



Carbon also contains a trace amount of ^{14}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 an animal is alive, the ^{14}C that is lost through exhalation or excretion is constantly replenished. When it dies, however, it no longer ingests ^{14}C . Consequently, its ^{14}C is slowly lost through radioactive decay. Therefore, the age of a substance derived from a living organism can be determined by its ^{14}C content.

The **atomic mass** is the weighted average of the isotopes in the element. Because an *atomic mass unit (amu)* is defined as exactly 1/12 of the mass of ^{12}C , the mass of ^{12}C is 12.0000 amu; the mass of ^{13}C is 13.0035 amu. Therefore, the atomic mass of carbon is 12.011 amu because $(0.9889 \times 12.0000) + (0.0111 \times 13.0035) = 12.011$. The **molecular mass** is the sum of the atomic masses of all the atoms in the molecule.

PROBLEM 1 ♦

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

PROBLEM 2 ♦

- a. How many protons do the following species have? (See the periodic table on p. 1337.)
 b. How many electrons does each have?
 1. Na^+ 2. Ar 3. Cl^-

PROBLEM 3 ♦

Chlorine has two isotopes, ^{35}Cl and ^{37}Cl ; 75.77% of chlorine is ^{35}Cl , and 24.23% is ^{37}Cl . The atomic mass of ^{35}Cl is 34.969 amu, and the atomic mass of ^{37}Cl is 36.966 amu. What is the atomic weight of chlorine?



Albert Einstein

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.

1.2 HOW THE ELECTRONS IN AN ATOM ARE DISTRIBUTED

For a long time, electrons were perceived to be particles—infinitesimal “planets” that orbit the nucleus of an atom. In 1924, however, Louis de Broglie, a French physicist, showed that electrons also have wave-like properties. He did this by combining a formula developed by Albert Einstein relating mass and energy with a formula developed by Max Planck relating frequency and energy. The realization that electrons have wave-like properties spurred physicists to propose a mathematical concept known as quantum mechanics to describe the motion of an electron around a nucleus.

Quantum mechanics uses the same mathematical equations that describe the wave motion of a guitar string to characterize the motion of an electron around a nucleus. The version of quantum mechanics most useful to chemists was proposed by Erwin Schrödinger in 1926.

According to Schrödinger, the electrons in an atom can be thought of as occupying a set of concentric shells that surround the nucleus (Table 1.1).

Table 1.1 Distribution of Electrons in the First Four Shells

	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

- 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.
- The shells contain subshells known as **atomic orbitals**. We will see that an atomic orbital has a characteristic shape and energy and occupies a characteristic volume of space (Section 1.5).
- Each shell contains one *s* atomic orbital. Each second and higher shell—in addition to its *s* atomic orbital—contains three *degenerate p* atomic orbitals. **Degenerate orbitals** are orbitals that have the same energy. The third and higher shells—in addition to their *s* and *p* atomic orbitals—contain five degenerate *d* atomic orbitals, and the fourth and higher shells also contain seven degenerate *f* atomic orbitals.
- A maximum of two electrons can coexist in an atomic orbital. (See the Pauli exclusion principle on p. 42.) Therefore, the first four shells, with 1, 4, 9, and 16 atomic orbitals, respectively, can contain a maximum of 2, 8, 18, and 32 electrons.

In our study of organic chemistry, we will be concerned primarily with atoms that have electrons only in the first two shells.

Degenerate orbitals are orbitals that have the same energy.

Ground-State Electronic Configuration

The **ground-state electronic configuration** of an atom describes the atomic orbitals occupied by the atom's electrons when they are all in the available orbitals with the lowest energy. If energy is applied to an atom in the ground state, one or more electrons can jump into a higher-energy orbital. The atom then would be in an excited state and have an **excited-state electronic configuration**.

The ground-state 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 _x	2p _y	2p _z	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	↑↓	↑↓	↑↓	↑↓	↑↓	↑

Three rules specify which atomic orbitals an atom's electrons occupy:

1. The **aufbau principle** (*aufbau* is German for “building up”) states that

an electron always goes into the available orbital with the lowest energy.

When using the aufbau principle rule, it is important to remember that the closer the atomic orbital is to the nucleus, the lower is its energy. Because the 1s orbital is closer to the nucleus, it is lower in energy than the 2s orbital, which is lower in energy—and closer to the nucleus—than the 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

lowest energy $\rightarrow$ 1s < 2s < 2p < 3s < 3p < 3d $\rightarrow$ highest energy

2. The **Pauli exclusion principle** states that

no more than two electrons can occupy each atomic orbital, and the two electrons must be of opposite spin.

This is called an exclusion principle because it limits the number of electrons that can occupy an atomic orbital and, therefore, any particular shell. (Notice in Table 1.2 that opposite spins are designated by ↑ and ↓.)

These first two rules allow us to 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.
- 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 are degenerate, 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. Hund's rule states that

*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.

- Therefore, the sixth electron of a carbon atom 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.

Valence and Core Electrons

The major factor that determines the chemical behavior of an element is the number of valence electrons it has. **Valence electrons** are electrons in an atom's outermost shell. Electrons in inner shells (below the outermost shell) are called **core electrons**. For example, carbon has four valence electrons and two core electrons (Table 1.2). Valence electrons participate in chemical bonding; core electrons do not.

Elements in the same column of the periodic table have similar chemical properties because they have the same number of valence electrons. If you examine the periodic table on p.1337, you will see that lithium and sodium, which have similar chemical properties, are in the same column because each has one valence electron.

Valence electrons are electrons in the outermost shell.

Core electrons are electrons in inner shells.

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

PROBLEM 4 ♦

How many valence electrons do the following atoms have?

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

PROBLEM 5 ♦

- a. Write the ground-state electronic configuration for chlorine (atomic number 17), bromine (atomic number 35), and iodine (atomic number 53).
b. How many valence electrons do chlorine, bromine, and iodine have?

PROBLEM 6

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 c. nitrogen and phosphorus
b. oxygen and sulfur d. magnesium and calcium

1.3 COVALENT BONDS

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

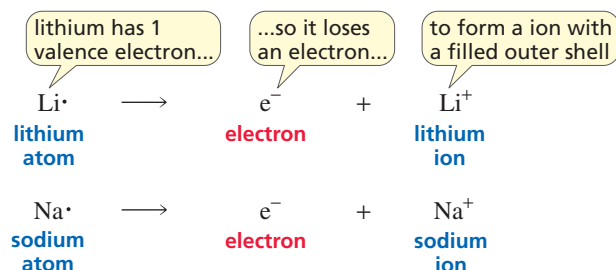
*an atom is most stable if its outer shell is either filled or contains eight electrons,
and it has no electrons of higher energy.*

According to Lewis's theory, an atom will give up, accept, or share electrons 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).

Achieving a Filled Outer Shell by Losing or Gaining Electrons

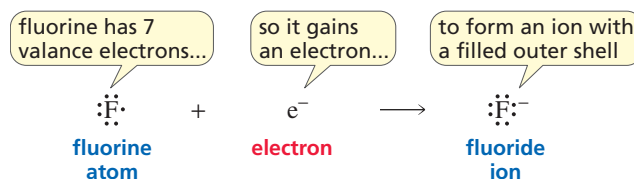
Lithium (Li) has a single electron in its $2s$ orbital. If it loses this electron, lithium ends up with a filled outer shell—a stable configuration. Lithium, therefore, loses an electron relatively easily. Sodium (Na) has a single electron in its $3s$ orbital; so it, too, loses an electron easily.

Because only valence electrons are used in bonding, only valence electrons are shown in the following equations. (The symbol for the element represents the protons, neutrons, and core electrons.) 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.

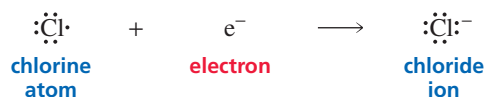


Each of the elements in the first column of the periodic table readily loses an electron because each has a single electron in its outermost shell.

Fluorine has seven valence electrons (Table 1.2). Therefore, it readily acquires an electron to fill its outer shell. Gaining the electron forms F^- , a fluoride ion.

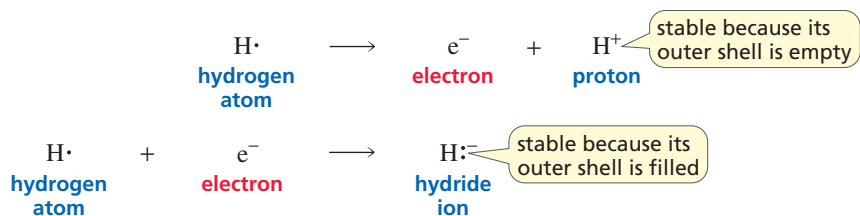


Elements in the same column of the periodic table as fluorine (such as chlorine, bromine, and iodine) also need only one electron to have an outer shell of eight; so they, too, readily acquire an electron.



Elements (such as fluorine and chlorine) that readily acquire an electron are said to be **electronegative**.

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.



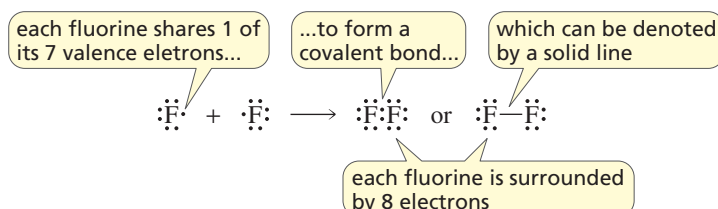
Loss of its sole electron results in a positively charged **hydrogen ion**. A positively charged hydrogen ion is called a **proton** because when a hydrogen atom loses its valence electron, only the hydrogen nucleus—which consists of a single proton—remains. When a hydrogen atom gains an electron, a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

PROBLEM 7 ♦

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

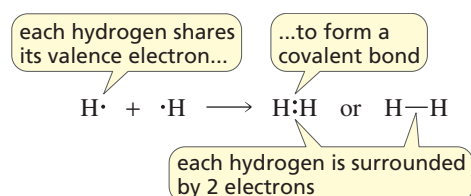
Achieving a Filled Outer Shell by Sharing Electrons

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

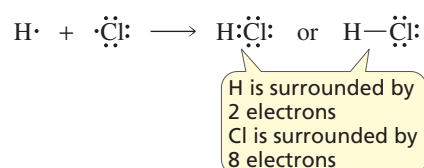


A covalent bond is formed when two atoms share a pair of electrons.

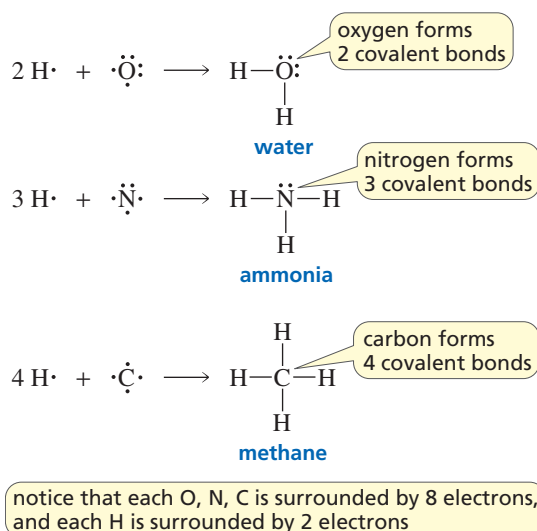
Two hydrogen atoms can form a covalent bond by sharing electrons. As a result of covalent bonding, each hydrogen acquires a stable, filled first shell.



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.



Let's now look at the bonds formed by oxygen, nitrogen, and carbon. Oxygen 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. Notice that all the atoms in water, ammonia, and methane have filled outer shells.



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

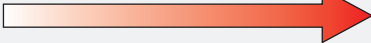
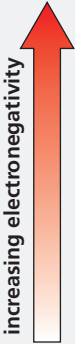
A **polar covalent bond** is a covalent bond between atoms with different electronegativities.

Nonpolar and Polar Covalent Bonds

Covalent bonds are classified as nonpolar or polar depending on the difference in the electronegativities of the atoms that share the electrons. **Electronegativity** is a measure of the ability of an atom to pull electrons toward itself. 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.

Table 1.3 The Electronegativities of Selected Elements^a

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
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5
K 0.8	Ca 1.0						F 4.0
							Cl 3.0
							Br 2.8
							I 2.5

^aElectronegativity 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.



sodium chloride crystals (table salt)



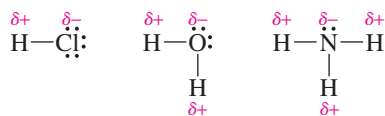
Salar de Uyuni in Bolivia—the largest deposit of natural lithium in the world

Lithium salts are used clinically. Lithium chloride (LiCl) is an antidepressant, lithium bromide (LiBr) is a sedative, and lithium carbonate (Li₂CO₃) 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.

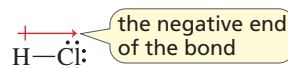
If the electronegativity difference between the bonded atoms is *less than 0.5*, then the bond is a **nonpolar covalent bond**. That is, the atoms share the bonding electrons equally—the electrons represented by the bond are symmetrically distributed around each atom. Examples of nonpolar covalent bonds are shown below.



If the electronegativity difference between the bonded atoms is *between 0.5 and about 1.9*, then the bond is a **polar covalent bond**. The bonding electrons are unsymmetrically distributed because the bonding atoms have sufficiently different electronegativities; one end of a polar covalent bond has a partial negative charge (δ^-), and one end has a partial positive charge (δ^+). The negative end of the bond is the end with the more electronegative atom. The greater the difference in electronegativity between the bonded atoms, the more polar the bond.

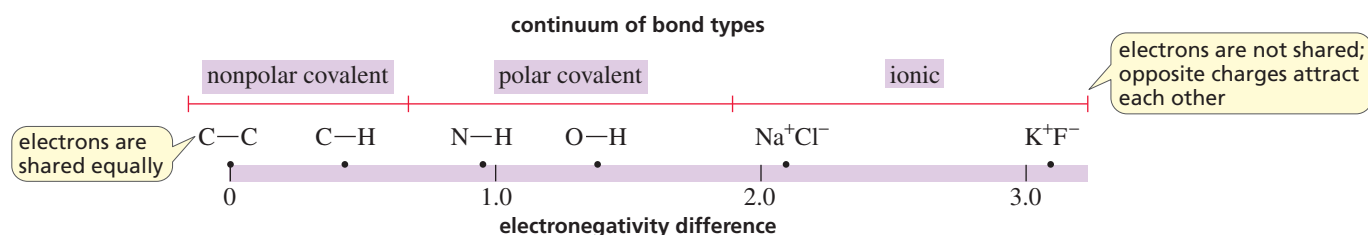


The direction of bond polarity can be indicated with an arrow. By convention, chemists draw the arrow in the direction the electrons are pulled. Thus, the head of the arrow is at the negative end of the bond; a short perpendicular line near the tail of the arrow marks the positive end of the bond. (Physicists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



If the electronegativity difference between the atoms is *greater than 1.9*, the atoms do not share their electrons. One of the atoms transfers an electron to the other, and the resulting ions (for example, Na⁺ and Cl⁻) are held together by **electrostatic attraction**—an attractive force between opposite charges. Sodium chloride is an example of an **ionic compound** (also known as a **salt**). 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.

You can think of nonpolar covalent bonds—where the electrons are shared equally—being at one end of the continuum of bond types and ionic compounds—where no electrons are shared—at the other end. Polar covalent bonds fall somewhere in between.



PROBLEM 8 ♦

Which bond is more polar?

- a. $\text{H}-\text{CH}_3$ or $:\ddot{\text{Cl}}-\text{CH}_3$ c. $\text{H}-\ddot{\text{Cl}}:$ or $\text{H}-\ddot{\text{F}}:$
 b. $\text{H}-\ddot{\text{O}}\text{H}$ or $\text{H}-\text{H}$ d. $:\ddot{\text{Cl}}-\ddot{\text{Cl}}:$ or $:\ddot{\text{Cl}}-\text{CH}_3$

PROBLEM 9 ♦

Which of the following has

- a. the most polar bond? b. the least polar bond?
 NaI LiBr Cl_2 KCl

Dipole Moments of Bonds

A polar covalent bond has a **dipole**—that is, it has a negative end and a positive end. The size of the dipole is indicated by the dipole moment. The **dipole moment** of a bond is equal to the magnitude of the charge on either atom (because the partial positive charge and the partial negative charge have the same magnitude) times the distance between the two charges:

$$\text{dipole moment of a bond} = \text{size of the charge} \times \text{the distance between the charges}$$

A dipole moment is reported in a unit called a **debye (D)** (pronounced de-bye). Because the charge on an electron is 4.80×10^{-10} electrostatic units (esu) and the distance between charges in a polar covalent bond has units of 10^{-8} cm, the product of charge and distance has units of 10^{-18} esu cm; so $1.0 \text{ D} = 1.0 \times 10^{-18}$ esu cm. Thus, a dipole moment of 1.5×10^{-18} esu cm is simply stated as 1.5 D. The dipole moments of bonds commonly found in organic compounds are listed in Table 1.4.

Table 1.4 The Dipole Moments of Some Common Bonds

Bond	Dipole moment (D)	Bond	Dipole moment (D)
H—C	0.4	C—C	0
H—N	1.3	C—N	0.2
H—O	1.5	C—O	0.7
H—F	1.7	C—F	1.6
H—Cl	1.1	C—Cl	1.5
H—Br	0.8	C—Br	1.4
H—I	0.4	C—I	1.2

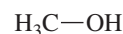
When a molecule has only one covalent bond, its dipole moment is identical to the dipole moment of the bond. For example, the dipole moment of hydrogen chloride (HCl) is 1.1 D because the dipole moment of the H—Cl bond is 1.1 D.

The dipole moment of a molecule with more than one covalent bond depends on the dipole moments of all the bonds in the molecule and the geometry of the molecule. We will look at this in Section 1.16, after you learn about the geometry of molecules.

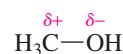
LEARN THE STRATEGY

PROBLEM 10 SOLVED

Use the symbols δ^+ and δ^- to show the direction of the polarity of the bond between carbon and oxygen.



According to Table 1.3, the electronegativity of carbon is 2.5 and the electronegativity of oxygen is 3.5. Because oxygen is more electronegative than carbon, oxygen has a partial negative charge and carbon has a partial positive charge.



USE THE STRATEGY

PROBLEM 11 ♦

Use the symbols δ^+ and δ^- to show the direction of the polarity of the indicated bond in each of the following compounds:

- | | | | |
|---------|-------------------------------------|------------------------|------------------------|
| a. HO—H | c. H ₃ C—NH ₂ | e. HO—Br | g. I—Cl |
| b. F—Br | d. H ₃ C—Cl | f. H ₃ C—Li | h. H ₂ N—OH |

PROBLEM 12 SOLVED

Determine the partial negative charge on the fluorine atom in a C—F bond. The bond length is 1.39 Å*, and the bond dipole moment is 1.60 D. The charge on an electron is 4.80×10^{-10} esu.

SOLUTION If fluorine had a full negative charge, the dipole moment would be

$$(4.80 \times 10^{-10} \text{ esu})(1.39 \times 10^{-8} \text{ cm}) = 6.67 \times 10^{-18} \text{ esu cm} = 6.67 \text{ D}$$

Knowing that the dipole moment is 1.60 D and that the dipole moment would be 6.67 D if fluorine had a full negative charge, we can calculate that the partial negative charge on the fluorine atom is 0.24 of a full charge:

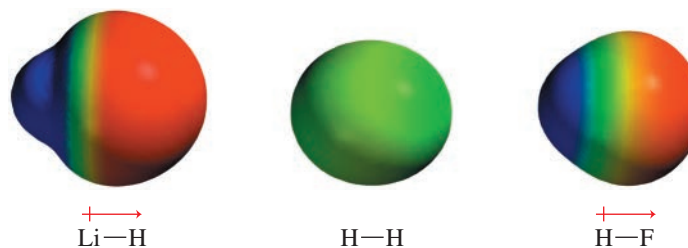
$$\frac{1.60 \text{ D}}{6.67 \text{ D}} = 0.24$$

PROBLEM 13

Explain why HCl has a smaller dipole moment than HF, even though the H—Cl bond is longer than the H—F bond.

Electrostatic Potential Maps

Understanding bond polarity is critical to understanding how organic reactions occur, because a central rule governing the reactivity of organic compounds is that *electron-rich atoms or molecules are attracted to electron-deficient atoms or molecules* (Section 5.5). **Electrostatic potential maps** (often called simply potential maps) are models that show how charge is distributed in the molecule under the map. The potential maps for LiH, H₂, and HF are shown here.



The colors on a potential map indicate the relative charge distribution in the molecule and, therefore, the degree to which the molecule (or an atom in the molecule) attracts other species. Red, signifying the most negative electrostatic potential, is used for regions that attract electron-deficient species most strongly. Blue is used for areas with the most positive electrostatic

*The angstrom (Å) is not a Système International (SI) unit. Those who prefer SI units can convert Å into picometers (pm): 1 Å = 100 pm. Because the angstrom continues to be used by many organic chemists, we will use angstroms in this text book. Dipole moment calculations require the bond length to be in centimeters: 1 Å = 10^{-8} cm.

potential—regions that attract electron-rich species most strongly. Other colors indicate intermediate levels of attraction.



The potential map for LiH shows that the hydrogen atom (red) is more electron-rich than the lithium atom (blue). By comparing the three maps, we can tell that the hydrogen in LiH is more electron-rich than a hydrogen in H₂, whereas the hydrogen in HF is less electron-rich than a hydrogen in H₂.

Because a potential map roughly marks the “edge” of the molecule’s electron cloud, the map tells us something about the relative size and shape of the molecule. A particular atom can have different sizes in different molecules, because the size of an atom in a potential map depends on its electron density. For example, the negatively charged hydrogen in LiH is bigger than a neutral hydrogen in H₂, which is bigger than the positively charged hydrogen in HF.

PROBLEM 14 ♦

After examining the potential maps for LiH, HF, and H₂, answer the following questions:

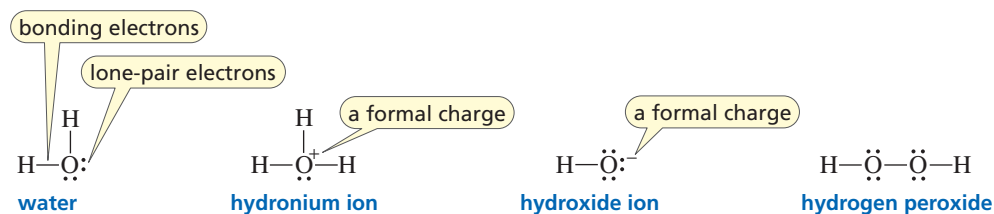
- Which compounds are polar?
- Why does LiH have the largest hydrogen?
- Which compound has the hydrogen that would be most apt to attract a negatively charged molecule?

1.4 HOW THE STRUCTURE OF A COMPOUND IS REPRESENTED

First, we will see how compounds are represented using Lewis structures. Then we will look at the kinds of structures that are used more commonly for organic compounds.

Lewis Structures

The chemical symbols we have been using, in which the valence electrons are represented as dots or solid lines, are called **Lewis structures**. Lewis structures show us which atoms are bonded together and tell us whether any atoms possess *lone-pair electrons* or have a *formal charge*, two concepts described below. The Lewis structures for H₂O, H₃O⁺, HO[−], and H₂O₂ are shown here.



Notice that the atoms in Lewis structures are always lined up linearly or at right angles. Therefore, they do not tell us anything about the bond angles in the actual molecule.

Lone-Pair Electrons

When you draw a Lewis structure, make sure hydrogen atoms are surrounded by two electrons and C, O, N, and halogen (F, Cl, Br, I) atoms are surrounded by eight electrons, in accordance with the octet rule. Valence electrons not used in bonding are called **nonbonding electrons**, **lone-pair electrons**, or simply, **lone pairs**.

Lone-pair electrons are valence electrons that do not form bonds.

Formal Charge

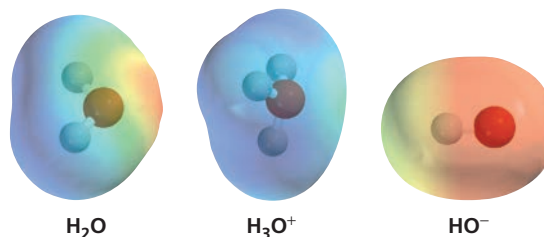
Once the atoms and the electrons are in place, you must examine each atom to see whether a formal charge should be assigned to it. A **formal charge** is the *difference* between the number of valence electrons an atom has when it is not bonded to other atoms and the number it “owns” when it is bonded. An atom “owns” all of its lone-pair electrons and half of its bonding (shared) electrons. (Notice that half the bonding electrons is the same as the number of bonds.)

$$\text{formal charge} = \text{the number of valence electrons} - \left(\text{the number of lone-pair electrons} + \text{the number of bonds} \right)$$

Now we will see how to apply the equation for formal charge to three of the oxygen-containing species on p. 49. An oxygen atom has six valence electrons (Table 1.2). In water (H_2O), oxygen “owns” six electrons—four lone-pair electrons and half of the four bonding electrons. (Notice that one-half of the bonding electrons is the same as the number of bonds.) Because the number of electrons it “owns” is equal to the number of its valence electrons ($6 - 6 = 0$), the oxygen atom in water does not have a formal charge.

The oxygen atom in the hydronium ion (H_3O^+) “owns” five electrons: two lone-pair electrons plus three (half of six) bonding electrons. Because the number of electrons oxygen “owns” is one less than the number of its valence electrons ($6 - 5 = 1$), its formal charge is +1.

The oxygen atom in the hydroxide ion (HO^-) “owns” seven electrons: six lone-pair electrons plus one (half of two) bonding electron. Because oxygen “owns” one more electron than the number of its valence electrons ($6 - 7 = -1$), its formal charge is -1.



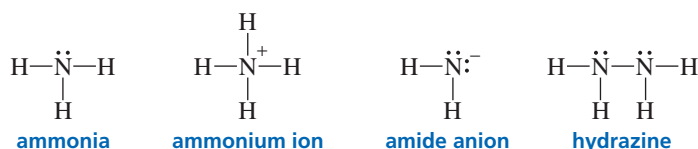
PROBLEM 15 ♦

An atom with a formal charge does not necessarily have more or less electron density than the atoms in the molecule without formal charges. We can see this by examining the potential maps for H_2O , H_3O^+ , and HO^- .

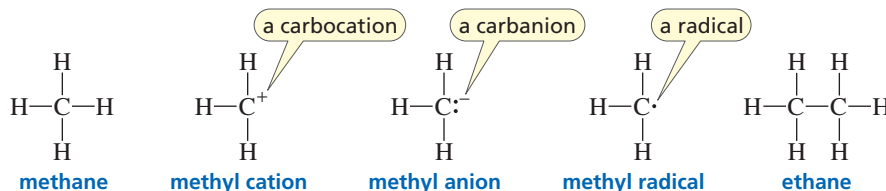
- Which atom bears the formal negative charge in the hydroxide ion?
- Which atom has the greater electron density in the hydroxide ion?
- Which atom bears the formal positive charge in the hydronium ion?
- Which atom has the least electron density in the hydronium ion?

Drawing Lewis Structures

Nitrogen has five valence electrons (Table 1.2). Prove to yourself that the appropriate formal charges have been assigned to the nitrogen atoms in the following Lewis structures:



Carbon has four valence electrons. Take a moment to make sure you understand why the carbon atoms in the following Lewis structures have the indicated formal charges:



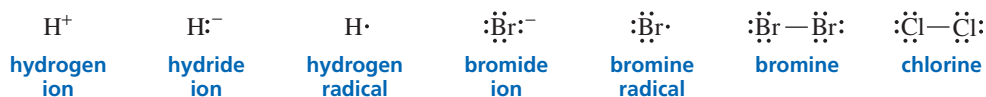
A carbocation is a species that contains a positively charged carbon.

A carbanion is a species that contains a negatively charged carbon.

A radical is a species that contains an atom with an unpaired electron.

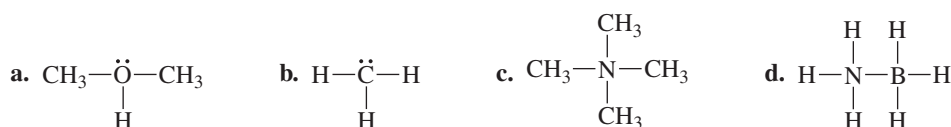
A species containing a positively charged carbon is called a **carbocation**, and a species containing a negatively charged carbon is called a **carbanion**. (Recall that a *cation* is a positively charged ion and an *anion* is a negatively charged ion.) A species containing an atom with a single unpaired electron is called a **radical** (often called a **free radical**).

Hydrogen has one valence electron, and each halogen (F, Cl, Br, I) has seven valence electrons; so the following species have the indicated formal charges:



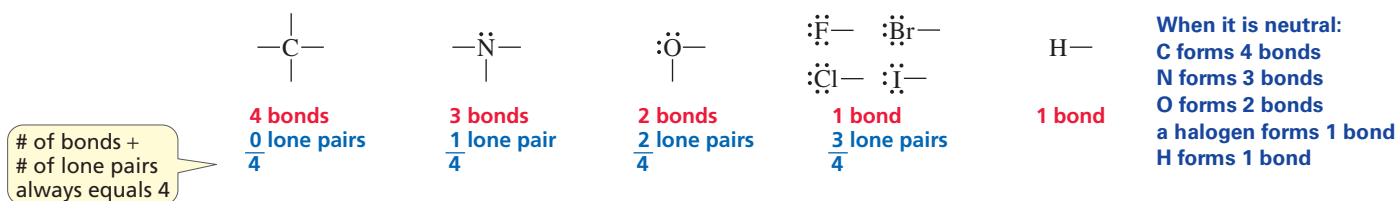
PROBLEM 16

Give each atom the appropriate formal charge:



While studying the molecules in this section notice that when the atoms do not bear a formal charge or an unpaired electron,

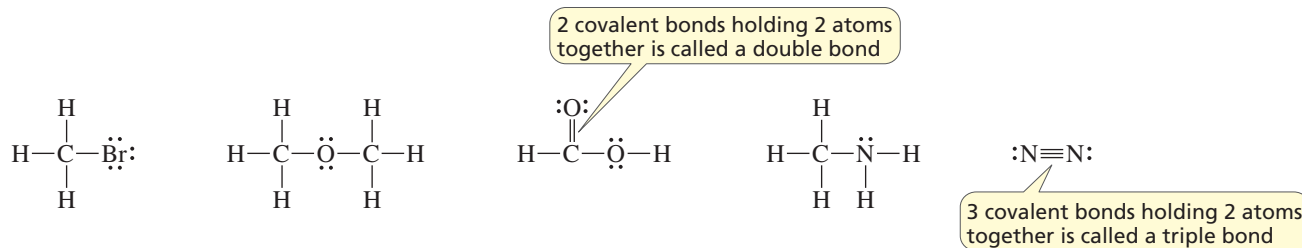
- carbon always forms 4 covalent bonds and has no lone pairs.
- nitrogen always forms 3 covalent bonds and has 1 lone pair.
- oxygen always forms 2 covalent bonds and has 2 lone pairs.
- a halogen always forms 1 covalent bond and has 3 lone pairs.
- hydrogen always forms 1 covalent bond and has no lone pairs.



Notice that to have a complete octet, the number of bonds and the number of lone pairs must total four (except for hydrogen, which requires only two electrons to fill its shell).

These numbers are very important to remember when you are drawing structures of organic compounds because they provide a quick way to recognize when you have made a mistake. Atoms with more bonds or fewer bonds than is required for a neutral atom must have either a formal charge or an unpaired electron.

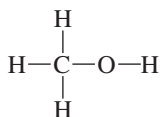
Each atom in the following Lewis structures has a filled outer shell. Notice that because none of the molecules has a formal charge or an unpaired electron, H forms 1 bond, C forms 4 bonds, N forms 3 bonds, O forms 2 bonds, and Br forms 1 bond. Notice, too, that each N has 1 lone pair, each O has 2 lone pairs, and Br has 3 lone pairs.



PROBLEM-SOLVING STRATEGY

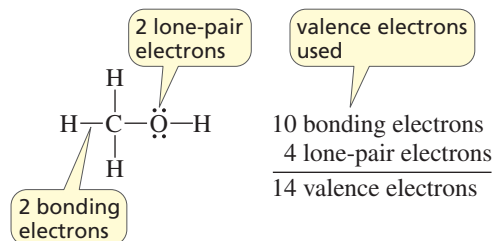
Drawing Lewis Structures

- a. Draw the Lewis structure for CH_4O . b. Draw the Lewis structure for HNO_2 .
- a. **1. Determine the total number of valence electrons** (4 for C, 1 for each H, and 6 for O adds up to $4 + 4 + 6 = 14$ valence electrons).
- 2. Distribute the atoms**, remembering that C forms 4 bonds, O forms 2 bonds, and each H forms 1 bond. Always put the hydrogens on the outside of the molecule because H can form only 1 bond.



LEARN THE STRATEGY

3. **Form bonds and fill octets with lone-pair electrons**, using the number of valence electrons determined in 1.



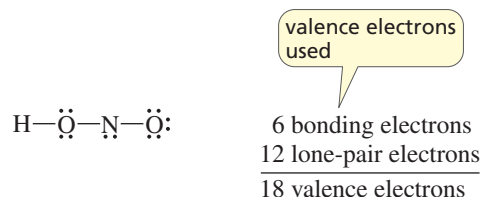
4. **Assign a formal charge** to any atom whose number of valence electrons is not equal to the number of its lone-pair electrons plus the number of bonds. (None of the atoms in CH_4O has a formal charge.)

- b. 1. **Determine the total number of valence electrons** (1 for H, 5 for N, and 6 for each O adds up to $1 + 5 + 12 = 18$ valence electrons).

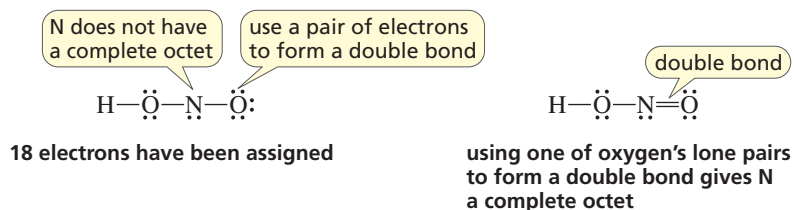
2. **Distribute the atoms**, putting the hydrogen on the outside of the molecule. If a species has two or more oxygen atoms, avoid oxygen–oxygen single bonds. These are weak bonds, and few compounds have them.



3. **Form bonds and fill octets with lone-pair electrons**, using the number of valence electrons determined in 1.



If after all the electrons have been assigned, an atom (other than hydrogen) does not have a complete octet, use a lone pair on an adjacent atom to form a double bond to the electron-deficient atom.



4. **Assign a formal charge** to any atom whose number of valence electrons is not equal to the number of its lone-pair electrons plus the number of bonds. (None of the atoms in HNO_2 has a formal charge.)

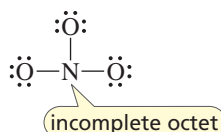
USE THE STRATEGY

PROBLEM 17 SOLVED

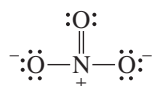
Draw the Lewis structure for each of the following:

- | | | | |
|--------------------|-----------------------------|-------------------------------|---------------------|
| a. NO_3^- | c. C_2H_5^- | e. CH_3NH_3^+ | g. HCO_3^- |
| b. NO_2^+ | d. C_2H_5^+ | f. NaOH | h. HCO_2^- |

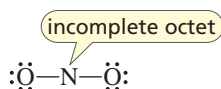
SOLUTION TO 17 a. The total number of valence electrons is 23 (5 for N and 6 for each of the three Os). Because the species has one negative charge, we must add 1 to the number of valence electrons, for a total of 24. The only way we can arrange one N and three Os and avoid O—O single bonds is to place the three Os around the N. We then use the 24 electrons to form bonds and fill octets with lone-pair electrons.



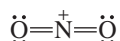
All 24 electrons have been assigned, but N does not have a complete octet. We complete N's octet by using one of oxygen's lone pairs to form a double bond. (It does not make a difference which oxygen atom we choose.) When we check each atom to see whether it has a formal charge, we find that two of the Os are negatively charged and that the N is positively charged, for an overall charge of -1 .



SOLUTION TO 17 b. The total number of valence electrons is 17 (5 for N and 6 for each of the two Os). Because the species has one positive charge, we must subtract 1 from the number of valence electrons, for a total of 16. The 16 electrons are used to form bonds and fill octets with lone-pair electrons.



Two double bonds are necessary to complete N's octet. We find that the N has a formal charge of $+1$.



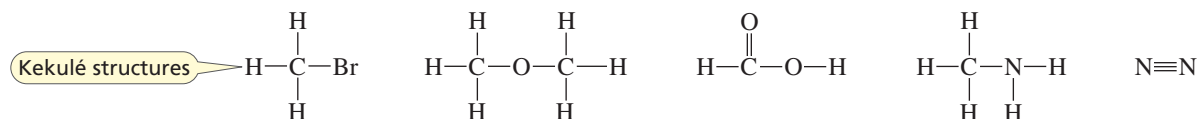
PROBLEM 18 ♦

a. Draw two Lewis structures for $\text{C}_2\text{H}_6\text{O}$. **b.** Draw three Lewis structures for $\text{C}_3\text{H}_8\text{O}$.

(Hint: The two Lewis structures in part **a** are **constitutional isomers**—molecules that have the same atoms but differ in the way the atoms are connected. The three Lewis structures in part **b** are also constitutional isomers.)

Kekulé Structures

Kekulé structures are like Lewis structures except that lone pairs are normally omitted.



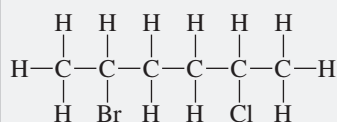
Condensed Structures

Condensed structures omit some (or all) of the covalent bonds and list atoms bonded to a particular carbon (or nitrogen or oxygen) next to it (with a subscript if there is more than one of a particular atom). Lone pairs are usually not shown, unless they are needed to draw attention to some chemical property of the molecule.



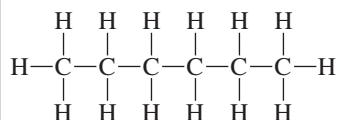
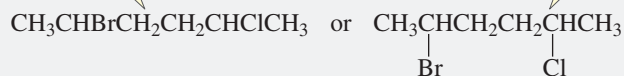
(Although lone pairs are not shown, you should remember that neutral nitrogen, oxygen, and halogen atoms always have them: one pair for nitrogen, two pairs for oxygen, and three pairs for a halogen.)

You can find examples of Kekulé and condensed structures and the conventions commonly used to create condensed structures in Table 1.5. Notice that because none of the molecules in Table 1.5 has a formal charge or an unpaired electron, each C has four bonds, each N has three bonds, each O has two bonds, and each H or halogen has one bond.

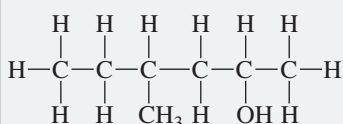
Table 1.5 Kekulé Structures and Condensed Structures**Kekulé Structures****Condensed Structures**

atoms bonded to a carbon are shown to the right of the carbon...

...or connected to a carbon by a line bond above or below the carbon

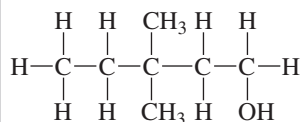


repeating CH_2 groups can be shown in parentheses

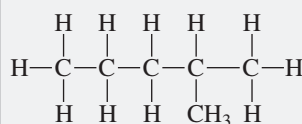
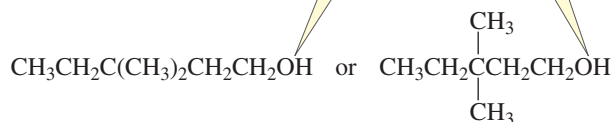


groups bonded to a carbon can be shown in parentheses to the right of the carbon...

...or connected to the carbon by a line bond above or below the carbon

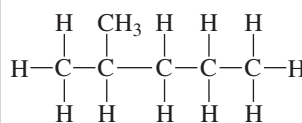
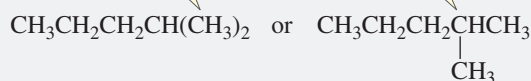


a single group bonded to the terminal carbon of a chain is not put in parentheses



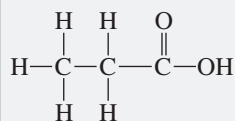
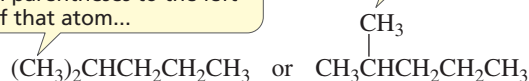
2 or more identical groups on the terminal carbon of a chain can be shown in parentheses...

...or connected to a carbon by a line bond above or below the carbon



2 or more identical groups bonded to the "first" atom on the left can be shown in parentheses to the left of that atom...

...or connected to that atom by a line bond above or below the carbon



an oxygen doubly bonded to a carbon...

...can also be shown to the right of the carbon

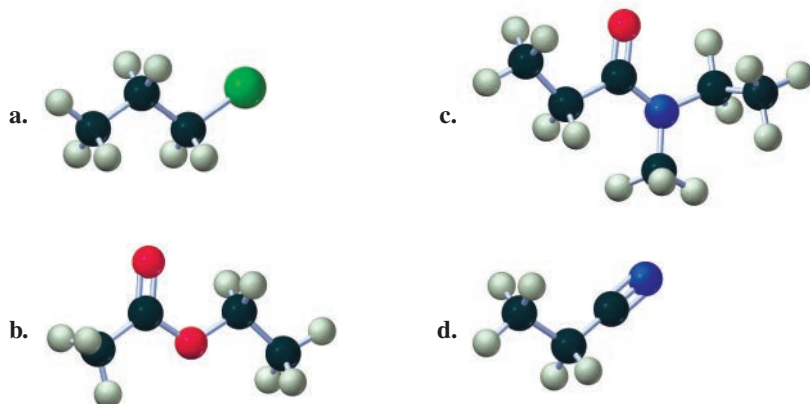
**PROBLEM 19** ♦

Draw the lone-pair electrons that are not shown in the following condensed structures:

- | | | |
|--|--------------------------------------|--------------------------------------|
| a. $\text{CH}_3\text{CH}_2\text{NH}_2$ | c. $\text{CH}_3\text{CH}_2\text{OH}$ | e. $\text{CH}_3\text{CH}_2\text{Cl}$ |
| b. CH_3NHCH_3 | d. CH_3OCH_3 | f. HONH_2 |

PROBLEM 20 ♦

Draw condensed structures for the compounds represented by the following models (black = C, gray = H, red = O, blue = N, and green = Cl):



PROBLEM 21 ♦

Which of the atoms in the molecular models in Problem 20 have

- a. three lone pairs? b. two lone pairs? c. one lone pair? d. no lone pairs?

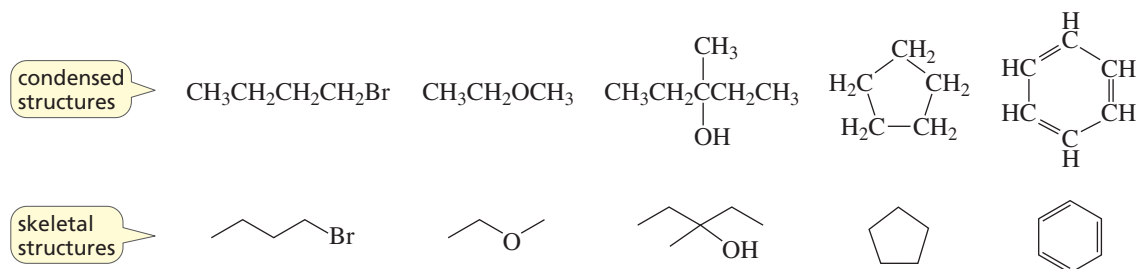
PROBLEM 22

Change the following condensed structures to Kekulé structures:

- a. $\text{CH}_3\text{NH}(\text{CH}_2)_2\text{CH}_3$ b. $(\text{CH}_3)_2\text{CHCl}$ c. $(\text{CH}_3)_3\text{CBr}$ d. $(\text{CH}_3)_3\text{C}(\text{CH}_2)_3\text{CHO}$

Skeletal Structures

Skeletal structures show the carbon–carbon bonds as lines, but do not show the carbons or the hydrogens that are bonded to the carbons. Each vertex in a skeletal structure represents a carbon, and each carbon is understood to be bonded to the appropriate number of hydrogens to give the carbon four bonds. Atoms other than carbons are shown, and hydrogens bonded to atoms other than carbon are also shown.



PROBLEM 23

Convert the models in Problem 20 to skeletal structures.

1.5 ATOMIC ORBITALS

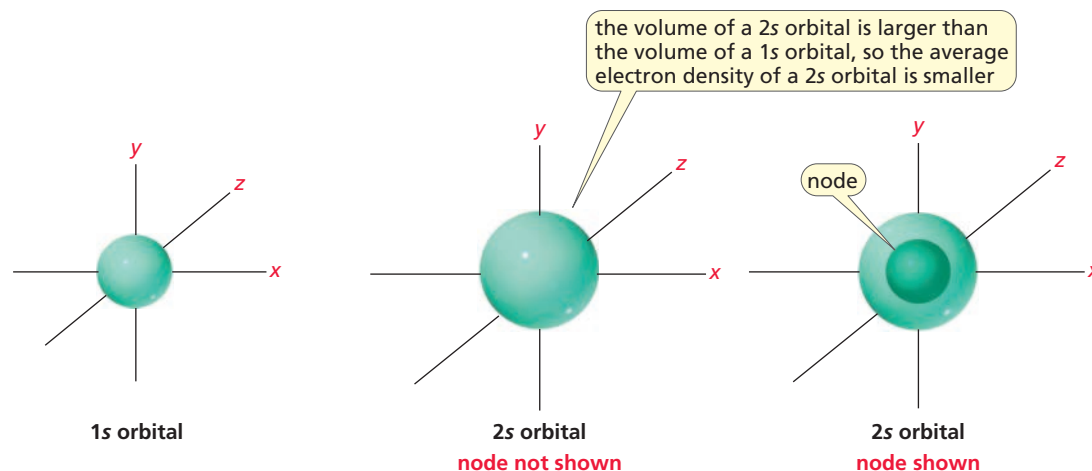
We saw that electrons are distributed into different atomic orbitals (Table 1.2). An atomic orbital is a three-dimensional region around the nucleus where an electron is most likely to be found. Because the **Heisenberg uncertainty principle** states that both the precise location and the exact momentum of an atomic particle cannot be simultaneously determined, we can never say precisely where an electron is—we can only describe its probable location.

An atomic orbital is the three-dimensional region around the nucleus where an electron is most likely to be found.

s Atomic Orbitals

Mathematical calculations indicate that an s atomic orbital is a sphere with the nucleus at its center, and experimental evidence supports this theory. Thus, when we say that an electron occupies a $1s$ orbital, we mean that there is a greater than 90% probability that the electron is in the space defined by the sphere.

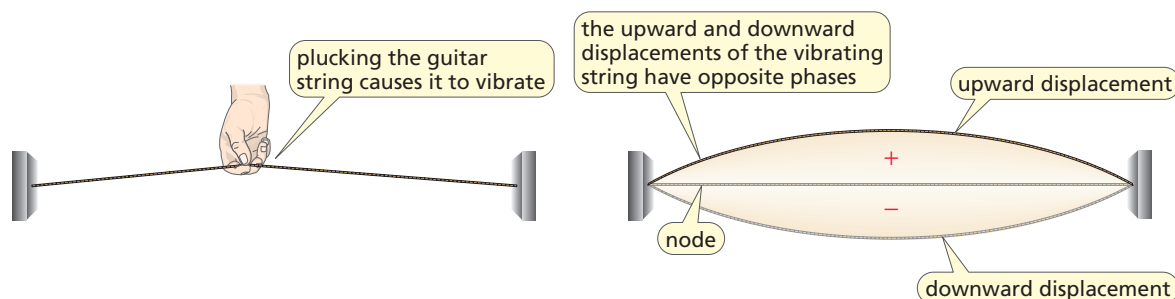
Because the second shell lies farther from the nucleus than does the first shell (Section 1.2), the average distance from the nucleus is greater for an electron in a $2s$ orbital than it is for an electron in a $1s$ orbital. A $2s$ orbital, therefore, is represented by a larger sphere. Because of the greater size of a $2s$ orbital, its average electron density is less than the average electron density of a $1s$ orbital.



Electrons have particle-like and wave-like properties.

An electron in a $1s$ orbital can be anywhere within the orbital, but a $2s$ orbital has a region where the probability of finding an electron falls to zero. This is called a **node**. Nodes occur because electrons have both particle-like and wave-like properties. A node is a consequence of the wave-like properties of an electron.

There are two types of waves: traveling waves and standing waves. Traveling waves move through space. Light is an example of a traveling wave. A standing wave, on the other hand, is confined to a limited space. The vibrating string of a guitar is a standing wave—the string moves up and down but does not travel through space. The amplitude is (+) in the region above where the guitar string is at rest, and it is (–) in the region below where the guitar string is at rest—the two regions are said to have opposite phases. The region where the guitar string has no transverse displacement (zero amplitude) is a node.



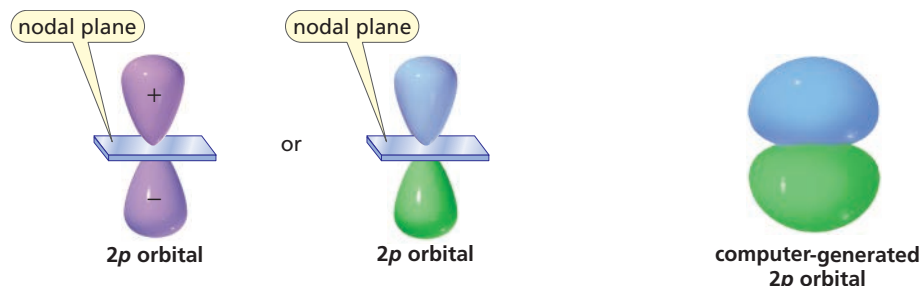
There is zero probability of finding an electron at a node.

An electron behaves like a standing wave, but unlike the wave created by a vibrating guitar string, it is three-dimensional. This means that the node of a $2s$ orbital is actually a spherical surface within the $2s$ orbital. Because the electron wave has zero amplitude at the node, there is zero probability of finding an electron at the node.

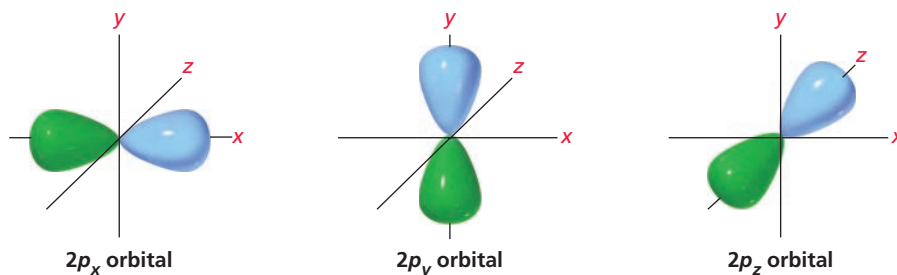
p Atomic Orbitals

Unlike s orbitals that resemble spheres, p orbitals have two lobes. Generally, the lobes are depicted as teardrop shaped, but computer-generated representations reveal that they are shaped more like doorknobs (as shown on the right on the top of p. 57). Like the vibrating guitar string, the lobes have opposite phases, which can be designated by plus (+) and minus (–) or by two different colors.

(Notice that in this context, + and – indicate the phase of the orbital; they do not indicate charge.) The node of the p orbital is a plane—called a **nodal plane**—that passes through the center of the nucleus, between its two lobes. There is zero probability of finding an electron in the nodal plane of the p orbital.



In Section 1.2, we saw that the second and higher numbered shells each contain three degenerate p atomic orbitals. The p_x orbital is symmetrical about the x -axis, the p_y orbital is symmetrical about the y -axis, and the p_z orbital is symmetrical about the z -axis. This means that each p orbital is perpendicular to the other two p orbitals. The energy of a $2p$ orbital is slightly greater than that of a $2s$ orbital because the average location of an electron in a $2p$ orbital is farther away from the nucleus.



PROBLEM 24

Draw the following orbitals:

a. $3s$ orbital

b. $4s$ orbital

c. $3p$ orbital

1.6 AN INTRODUCTION TO MOLECULAR ORBITAL THEORY

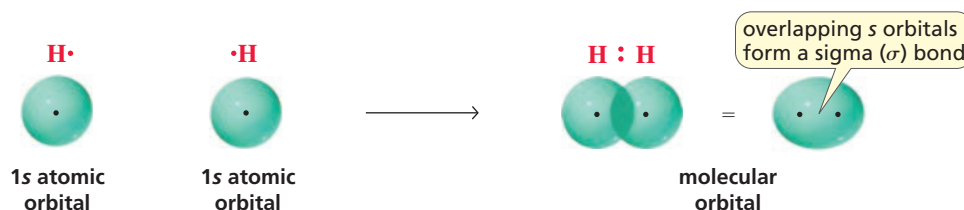
How do atoms form covalent bonds in order to form molecules? The Lewis model, which shows atoms attaining a complete octet by sharing electrons, tells only part of the story. A drawback of the model is that it treats electrons like particles and does not take into account their wave-like properties.

Molecular orbital (MO) theory combines the tendency of atoms to fill their octets by sharing electrons (the Lewis model) with their wave-like properties, assigning electrons to a volume of space called an orbital. According to MO theory, covalent bonds result when atomic orbitals combine to form *molecular orbitals*. Like an atomic orbital, which describes the volume of space around an atom's nucleus where an electron is likely to be found, a **molecular orbital** describes the volume of space around a molecule where an electron is likely to be found. And like atomic orbitals, molecular orbitals, too, have specific sizes, shapes, and energies.

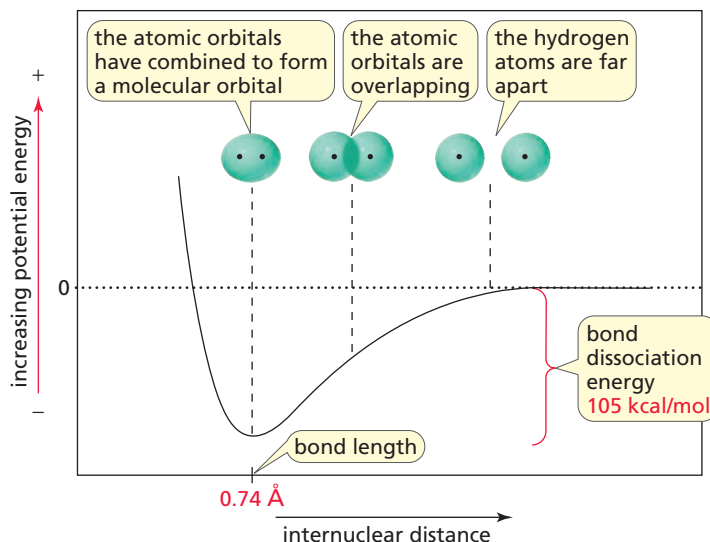
*An atomic orbital surrounds an atom.
A molecular orbital surrounds a molecule.*

Forming a sigma (σ) Bond

Let's look first at the bonding in a hydrogen molecule (H_2). Imagine a meeting of two separate H atoms. As the $1s$ atomic orbital of one hydrogen atom approaches the $1s$ atomic orbital of the other hydrogen atom, the orbitals begin to overlap. The atoms continue to move closer, and the amount of overlap increases until the orbitals combine to form a molecular orbital. The covalent bond that is formed when the two s orbitals overlap is called a **sigma (σ) bond**. A σ bond is cylindrically symmetrical—the electrons in the bond are symmetrically distributed about an imaginary line connecting the nuclei of the two atoms joined by the bond.



As the two orbitals begin to overlap, energy is released because the electron in each atom is attracted to its own nucleus *and* to the nucleus of the other atom (Figure 1.1).



► **Figure 1.1**
The change in energy that occurs as two hydrogen atoms approach each other. The internuclear distance at minimum potential energy is the length of the H—H covalent bond.

Minimum energy corresponds to maximum stability.

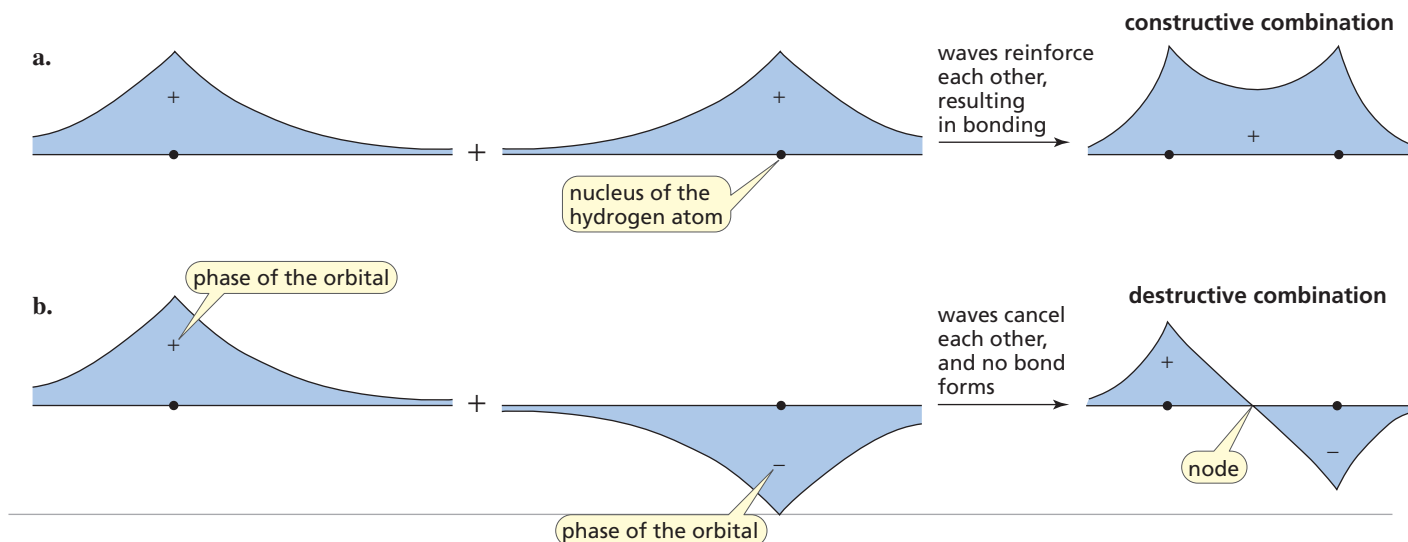
The attraction of the two negatively charged electrons for the two positively charged nuclei is what holds the two H atoms together. The more the orbitals overlap, the more the energy decreases, until the atoms are so close that their positively charged nuclei begin to repel each other. This repulsion causes a large increase in energy. Figure 1.1 shows that minimum energy (maximum stability) is achieved when the nuclei are a particular distance apart. This distance is the **bond length** of the new covalent bond; the bond length of the H—H bond is 0.74 Å.

As Figure 1.1 shows, energy is released when a covalent bond forms. We see that when the H—H bond forms, 105 kcal/mol of energy is released. Breaking the bond requires precisely the same amount of energy. Thus, the **bond dissociation energy**—a measure of bond strength—is the energy required to break a bond or the energy released when a bond is formed. Every covalent bond has a characteristic bond length and bond dissociation energy.

Bonding and Antibonding Molecular Orbitals

Orbitals are conserved. In other words, the number of molecular orbitals formed must equal the number of atomic orbitals combined. In describing the formation of an H—H bond, we combined two atomic orbitals but discussed only one molecular orbital. Where is the other molecular orbital? As you will see shortly, it is there; it just doesn't contain any electrons.

It is the wave-like properties of the electrons that cause two atomic orbitals to form two molecular orbitals. The two atomic orbitals can combine in an additive (constructive) manner, just as two light waves or two sound waves can reinforce each other (Figure 1.2a). The constructive combination of two s atomic orbitals is called a σ (**sigma**) **bonding molecular orbital**.



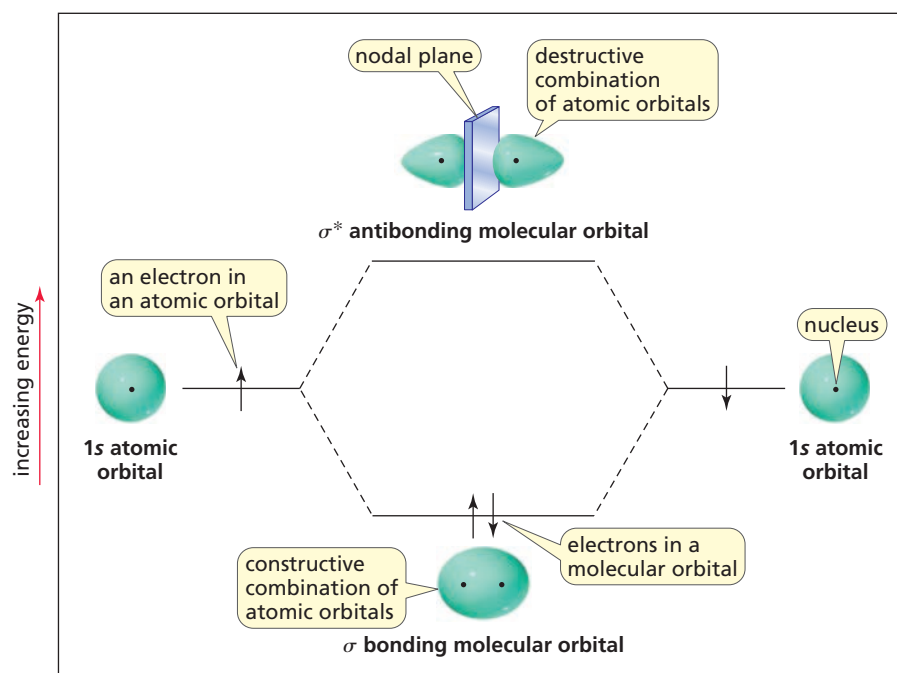
▲ Figure 1.2

- (a) Waves with the same phase (+/+) overlap constructively, reinforcing each other and resulting in bonding.
 (b) Waves with opposite phases (+/-) overlap destructively, canceling each other and forming a node.

The two atomic orbitals can also combine in a destructive way, canceling each other. The cancellation is similar to the darkness that results when two light waves cancel each other or to the silence that results when two sound waves cancel each other (Figure 1.2b). The destructive combination of two *s* atomic orbitals is called a **σ^* antibonding molecular orbital**. An antibonding orbital is indicated by an asterisk (*), which chemists read as “star.” Thus, σ^* is read as “sigma star.”

The σ bonding molecular orbital and the σ^* antibonding molecular orbital are shown in the molecular orbital (MO) diagram in Figure 1.3. In an MO diagram, the energies of both the atomic orbitals and the molecular orbitals are represented as horizontal lines, with the bottom line being the lowest energy level and the top line the highest energy level.

When two atomic orbitals overlap, two molecular orbitals are formed—one lower in energy and one higher in energy than the atomic orbitals.



◀ Figure 1.3

Atomic orbitals of $H\cdot$ and molecular orbitals of H_2 . Before covalent bond formation, each electron is in an atomic orbital. After covalent bond formation, both electrons are in the bonding MO. The antibonding MO is empty.

The electrons in the bonding molecular orbital are most likely to be found between the nuclei, where they can more easily attract both nuclei simultaneously. This increased electron density between the nuclei is what binds the atoms together (Figure 1.2a). Electrons in the antibonding molecular orbital, however, are most likely to be found anywhere except between the nuclei, because a nodal plane lies between the nuclei (Figure 1.2b). As a result, electrons in the antibonding orbital leave the positively charged nuclei more exposed to one another. Therefore, electrons in the antibonding orbital detract from, rather than assist in, the formation of a bond.

Electrons in a bonding MO assist in bonding.

Electrons in an antibonding MO detract from bonding.

The MO diagram shows that the bonding molecular orbital is lower in energy and is, therefore, more stable than the individual atomic orbitals. This is because the more nuclei an electron senses, the more stable it is. The antibonding molecular orbital, with less electron density between the nuclei, is less stable—and, therefore, higher in energy—than the atomic orbitals.

Electrons are assigned to the molecular orbitals using the same rules used to assign electrons to atomic orbitals:

- electrons always occupy available orbitals with the lowest energy (the aufbau principle).
- no more than two electrons can occupy a molecular orbital (the Pauli exclusion principle).

Thus, the two electrons of the H—H bond occupy the lower-energy bonding molecular orbital (the σ bonding MO in Figure 1.3), where they are attracted to both positively charged nuclei. It is this electrostatic attraction that gives a covalent bond its strength. We can conclude, therefore, that the strength of the covalent bond increases as the overlap of the atomic orbitals increases.

Covalent bond strength increases as atomic orbital overlap increases.

The MO diagram in Figure 1.3 allows us to predict that H_2^+ would not be as stable as H_2 because H_2^+ has only one electron in the bonding molecular orbital. Using the same diagram, we can also predict that He_2 does not exist, because the four electrons of He_2 (two from each He atom) would fill the lower energy bonding MO and the higher energy antibonding MO. *The two electrons in the antibonding MO would cancel the advantage to bonding that is gained by the two electrons in the bonding MO.*

PROBLEM 25 ♦

Predict whether He_2^+ exists.

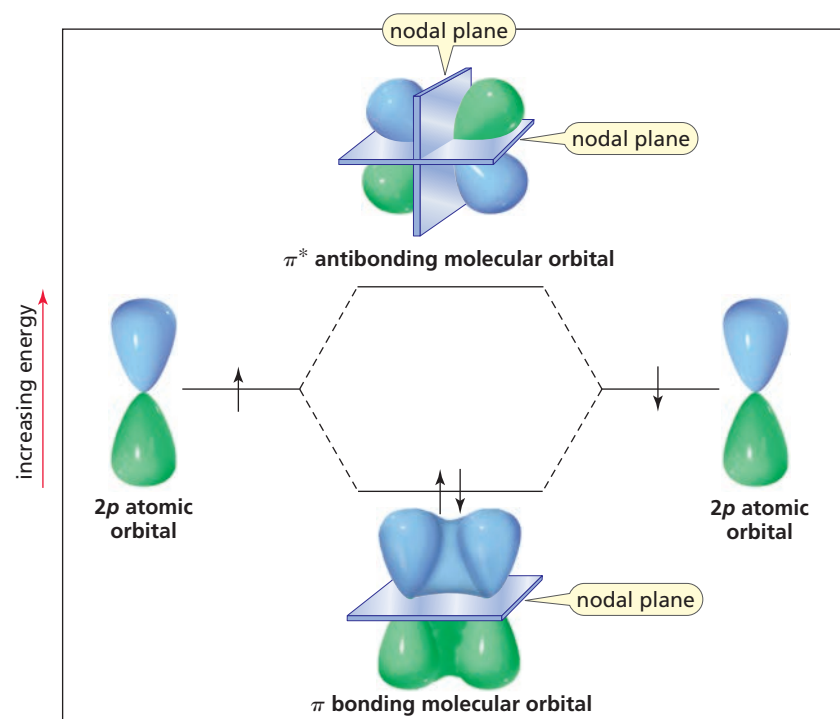
Forming a pi (π) Bond

When two p atomic orbitals overlap, the side of one orbital overlaps the side of the other. The side-to-side overlap of two parallel p orbitals forms a bond that is called a **pi (π) bond**.

Side-to-side overlap of two in-phase p atomic orbitals (blue lobes overlap blue lobes and green lobes overlap green lobes) is a constructive overlap and forms a π bonding molecular orbital, whereas side-to-side overlap of two out-of-phase p orbitals (blue lobes overlap green lobes) is a destructive overlap and forms a π^* (read “pi star”) antibonding molecular orbital (Figure 1.4). The π bonding MO has one node—a nodal plane that passes through both nuclei. The π^* antibonding MO has two nodal planes.

The VSEPR Model

To learn even more about the bonds in a molecule, organic chemists turn to the **valence-shell electron-pair repulsion (VSEPR) model**—a model for predicting molecular geometry based on the minimization of electron repulsion between regions of electron density around an atom. In other words, atoms share electrons by overlapping their atomic orbitals and, because electron pairs repel each other, the bonding electrons and lone-pair electrons around an atom are positioned as far apart as possible. Thus, a Lewis structure gives us a first approximation of the structure of a simple molecule, and VSEPR gives us a first glance at the shape of the molecule.



Side-to-side overlap of two p orbitals forms a π bond. All other covalent bonds in organic molecules are σ bonds.

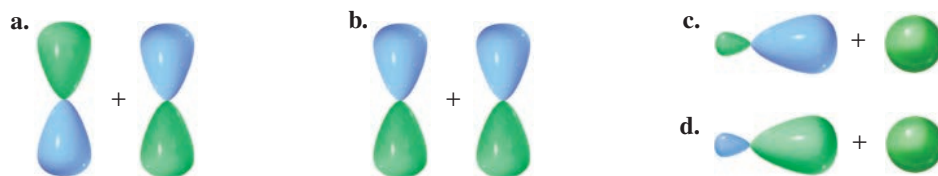
In-phase overlap forms a bonding MO; out-of-phase overlap forms an antibonding MO.

◀ **Figure 1.4**
Side-to-side overlap of two parallel p atomic orbitals forms a π bonding molecular orbital and a π^* antibonding molecular orbital.

Because organic chemists generally think of chemical reactions in terms of the changes that occur in the bonds of the reacting molecules, the VSEPR model often provides the easiest way to visualize chemical change. However, the model is inadequate for some molecules because it does not allow for antibonding molecular orbitals. We will use both the MO and the VSEPR models in this book. Our choice will depend on which model provides the best description of the molecule under discussion. We will use the VSEPR model in Sections 1.7–1.13.

PROBLEM 26 ♦

Indicate the kind of molecular orbital (σ , σ^* , π , or π^*) that results when the two atomic orbitals are combined:

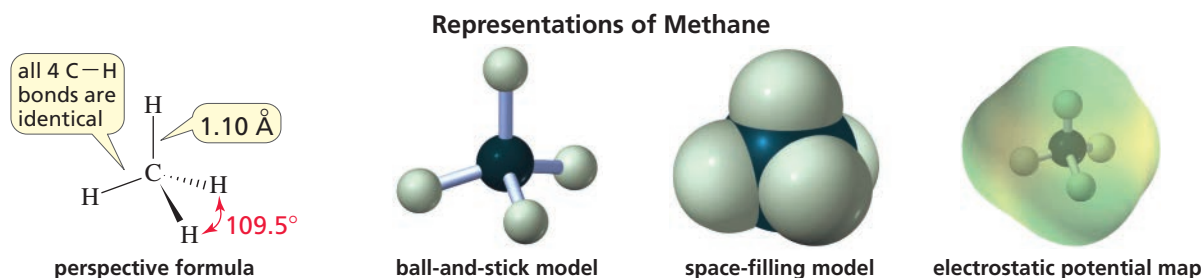


1.7 HOW SINGLE BONDS ARE FORMED IN ORGANIC COMPOUNDS

We will begin our discussion of bonding in organic compounds by looking at the bonding in methane, a compound with only one carbon. Then we will examine the bonding in ethane, a compound with two carbons attached by a carbon–carbon single bond.

The Bonds in Methane

Methane (CH_4) has four covalent C—H bonds. Because all four bonds have the same length (1.10 Å) and all the bond angles are the same (109.5°), we can conclude that the four C—H bonds in methane are identical. Four different ways to represent a methane molecule are shown here.



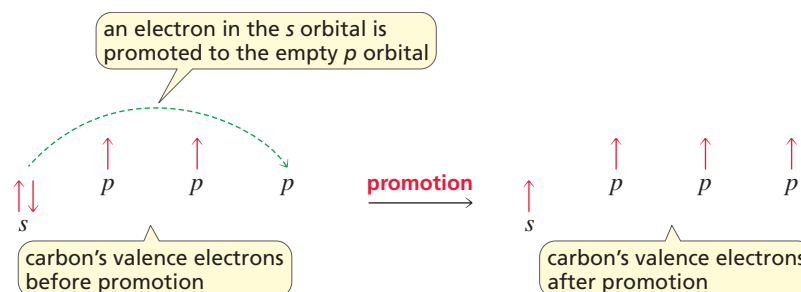
The blue colors of Uranus and Neptune are caused by the presence of methane, a colorless and odorless gas, in their atmospheres. Natural gas—called a fossil fuel because it is formed from the decomposition of plant and animal material in the Earth's crust—is approximately 75% methane.

In a **perspective formula**, bonds in the plane of the paper are drawn as solid lines (and they must be adjacent to one another), a bond protruding out of the plane of the paper toward the viewer is drawn as a solid wedge, and one projecting back from the plane of the paper away from the viewer is drawn as a hatched wedge.

The potential map of methane shows that neither carbon nor hydrogen carries much of a charge: there are neither red areas, representing partially negatively charged atoms, nor blue areas, representing partially positively charged atoms. (Compare this map with the potential map for water on p. 73.) The absence of partially charged atoms can be explained by the similar electronegativities of carbon and hydrogen, which cause them to share their bonding electrons relatively equally (see p. 47). Methane, therefore, is a **nonpolar molecule**.

You might be wondering how carbon can form four covalent bonds when it has only two unpaired valence electrons (Table 1.2). Carbon has to form four covalent bonds otherwise it would not complete its octet. We need, therefore, to come up with an explanation that accounts for the fact that carbon forms four covalent bonds when it has only two valence electrons.

If one of the electrons in carbon's $2s$ orbital is promoted into its empty $2p$ orbital, then carbon will have four unpaired valence electrons (and then four covalent bonds can be formed).



However, we know that the four C—H bonds in methane are identical. How can they be identical if carbon uses an s orbital and three p orbitals to form these four bonds? Wouldn't the bond formed with the s orbital be different from the three bonds formed with p orbitals? The four C—H bonds are identical because carbon uses hybrid atomic orbitals.

Hybrid Orbitals

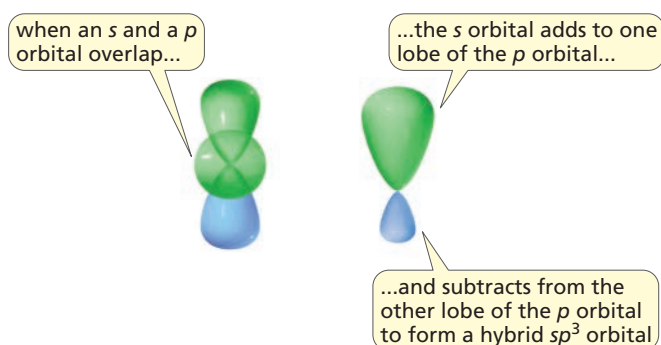
Hybrid orbitals are mixed orbitals that result from combining atomic orbitals. The concept of combining atomic orbitals, called **hybridization**, was first proposed by Linus Pauling in 1931.

If the one s and three p orbitals of the second shell are all combined and then apportioned into four equal orbitals, each of the four resulting orbitals will be one part s and three parts p . This type of mixed orbital is called an sp^3 (read “ s - p -three,” not “ s - p -cubed”) orbital. The superscript 3 means that three p orbitals were mixed with one s orbital—the superscript 1 on the s is implied—to form the four hybrid orbitals. Each sp^3 orbital has 25% s character and 75% p character. The four sp^3 orbitals are degenerate—that is, they all have the same energy.



Hybrid orbitals result from combining atomic orbitals.

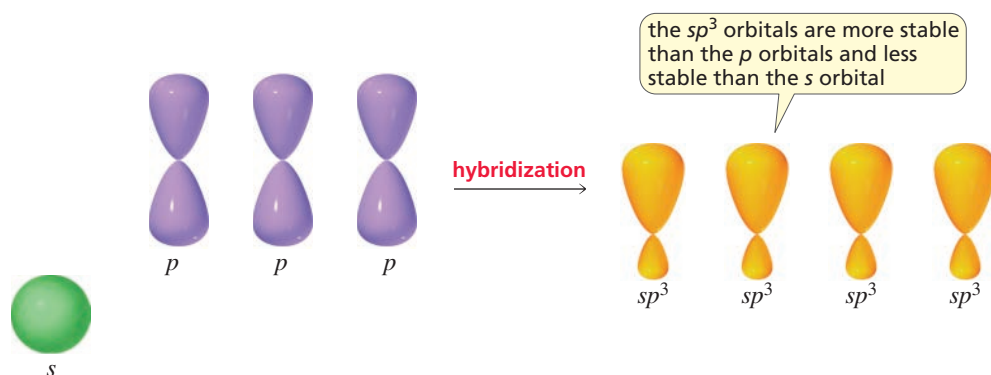
Like a p orbital, an sp^3 orbital has two lobes. The lobes differ in size, however, because the s orbital adds to one lobe of the p orbital and subtracts from the other lobe (Figure 1.5).



◀ Figure 1.5

The s orbital adds to one lobe of the p orbital and subtracts from the other. The result is a hybrid orbital with two lobes that differ in size.

The larger lobe of the sp^3 orbital is used to form covalent bonds. The stability of an sp^3 orbital reflects its composition; it is more stable than a p orbital, but not as stable as an s orbital (Figure 1.6). (To simplify the orbital depictions that follow, the phases of the orbitals will not be shown.)



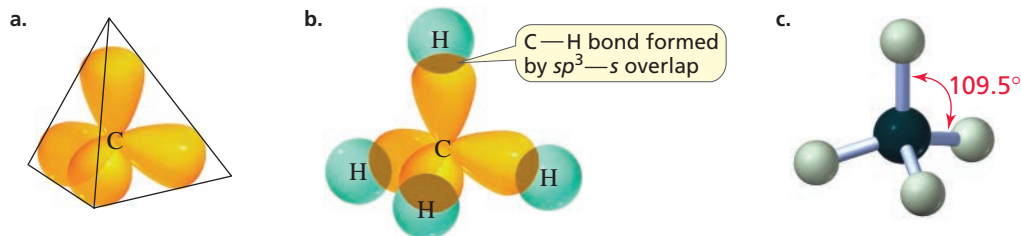
◀ Figure 1.6

An s orbital and three p orbitals hybridize to form four sp^3 orbitals. An sp^3 orbital is more stable (lower in energy) than a p orbital but less stable (higher in energy) than an s orbital.

Tetrahedral Carbon; Tetrahedral Bond Angle

The four sp^3 orbitals adopt a spatial arrangement that keeps them as far away from each other as possible. They do this because electrons repel each other, and moving as far from each other as possible minimizes the repulsion. (See the description of the VSEPR model on p. 60.)

When four sp^3 orbitals move as far from each other as possible, they point toward the corners of a regular tetrahedron—a pyramid with four faces, each an equilateral triangle (Figure 1.7a). Each of the four C—H bonds in methane is formed from the overlap of an sp^3 orbital of carbon with the s orbital of a hydrogen (Figure 1.7b). This explains why the four C—H bonds are identical.



Electron pairs stay as far from each other as possible.

◀ Figure 1.7

For clarity, the smaller lobes of the sp^3 orbitals are not shown.

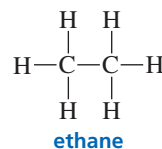
- (a) The four sp^3 orbitals are directed toward the corners of a tetrahedron, causing each bond angle to be 109.5°. This arrangement allows the four orbitals to be as far apart as possible.
- (b) An orbital picture of methane, showing the overlap of each sp^3 orbital of carbon with the s orbital of a hydrogen.
- (c) The tetrahedral bond angle is 109.5°.

The angle between any two lines that point from the center to the corners of a tetrahedron is 109.5° (Figure 1.7c). Therefore, the bond angles in methane are 109.5°. This is called a **tetrahedral bond angle**. A carbon, such as the one in methane, that forms covalent bonds using four equivalent sp^3 orbitals is called a **tetrahedral carbon**.

If you are thinking that hybrid orbital theory appears to have been contrived just to make things fit, then you are right. Nevertheless, it gives us a very good picture of the bonding in organic compounds.

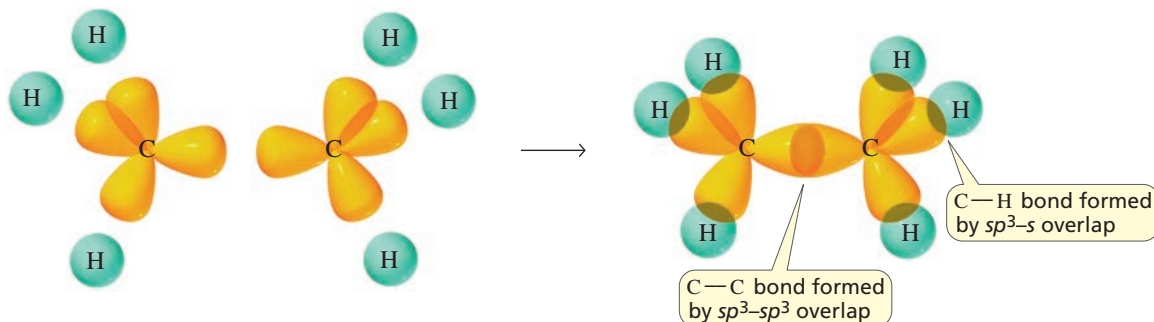
The Bonds in Ethane

Each carbon in ethane (CH_3CH_3) is bonded to four other atoms.



One bond connecting two atoms is called a **single bond**. All the bonds in ethane are single bonds.

To bond to four atoms, each carbon uses four sp^3 orbitals as they do in methane. (Figure 1.8). One sp^3 orbital of one carbon of ethane overlaps an sp^3 orbital of the other carbon to form the C—C bond.



▲ **Figure 1.8**

An orbital picture of ethane. The C—C bond is formed by sp^3 – sp^3 overlap, and each C—H bond is formed by sp^3 – s overlap. (The smaller lobes of the sp^3 orbitals are not shown.) As a result, both carbons are tetrahedral and all bond angles are $\sim 109.5^\circ$.

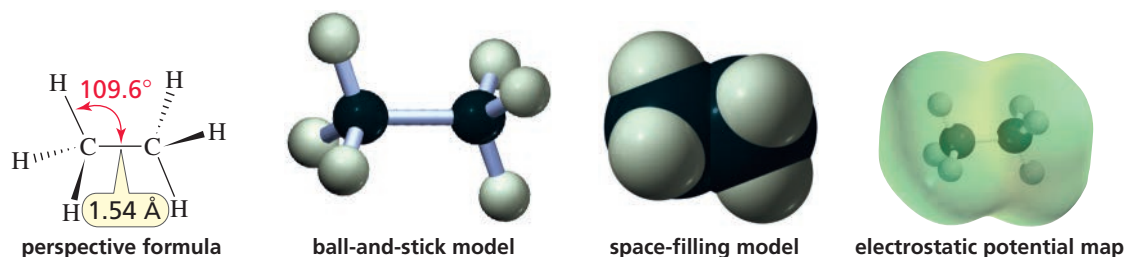
The three remaining sp^3 orbitals of each carbon overlap the s orbital of a hydrogen to form a C—H bond. Thus, the C—C bond is formed by sp^3 – sp^3 overlap, and each C—H bond is formed by sp^3 – s overlap.

Because both carbons are tetrahedral, each of the bond angles in ethane is nearly the tetrahedral bond angle of 109.5° . The length of the C—C bond is $1.54 \text{ \AA}$. The potential map shows that ethane, like methane, is a nonpolar molecule.

Representations of Ethane

NOTE TO THE STUDENT

- It is important to understand what molecules look like in three dimensions. Therefore, be sure to visit the MasteringChemistry Study Area and look at the three-dimensional representations of molecules that can be found in the molecule gallery prepared for each chapter.



The MO diagram illustrating the overlap of an sp^3 orbital of one carbon with an sp^3 orbital of another carbon shows that the two sp^3 orbitals overlap end-on (Figure 1.9). End-on overlap forms a cylindrically symmetrical bond—a sigma (σ) bond (Section 1.6). *All single bonds in organic compounds are sigma bonds.* Thus, all the bonds in methane and ethane are sigma (σ) bonds.

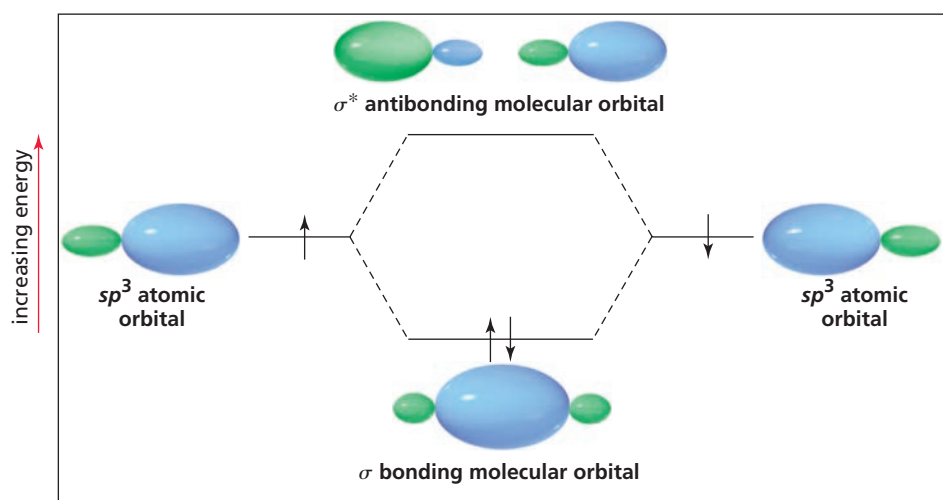
Notice in Figure 1.9 that the electron density of the σ bonding MO is concentrated between the nuclei. This causes the back lobes (the nonoverlapping green lobes) to be quite small.

PROBLEM 27 ♦

What orbitals are used to form the 10 sigma bonds in propane ($\text{CH}_3\text{CH}_2\text{CH}_3$)?

PROBLEM 28

Explain why a σ bond formed by overlap of an s orbital with an sp^3 orbital of carbon is stronger than a σ bond formed by overlap of an s orbital with a p orbital of carbon.



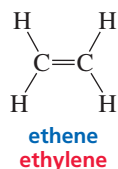
Sigma bonds are cylindrically symmetrical.

All single bonds in organic compounds are sigma bonds.

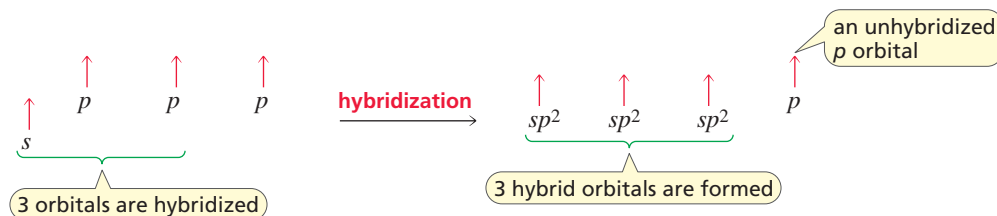
◀ **Figure 1.9**
End-on overlap of two sp^3 orbitals forms a σ bonding molecular orbital and a σ^* antibonding molecular orbital.

1.8 HOW A DOUBLE BOND IS FORMED: THE BONDS IN ETHENE

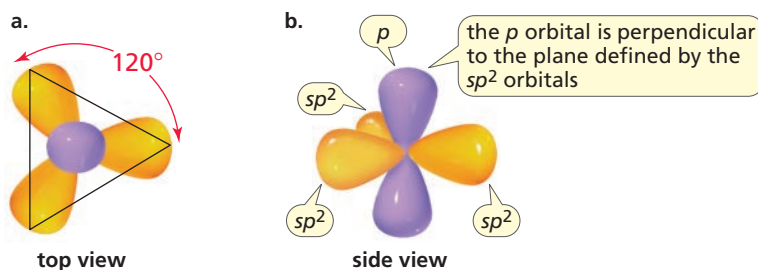
The carbons in ethene (also called ethylene) form two bonds with each other. Two bonds connecting two atoms is called a **double bond**. Each of the carbons forms four bonds, but each carbon is bonded to only three atoms.



To bond to three atoms, each carbon hybridizes three atomic orbitals: an s orbital and two of the p orbitals. Because three orbitals are hybridized, three hybrid orbitals are formed. These are called sp^2 orbitals. After hybridization, each carbon atom has three degenerate sp^2 orbitals and one unhybridized p orbital:



To minimize electron repulsion, the three sp^2 orbitals need to get as far from each other as possible. Therefore, the axes of the three orbitals lie in a plane, directed toward the corners of an equilateral triangle with the carbon nucleus at the center. As a result, the bond angles are all close to 120° (Figure 1.10a).



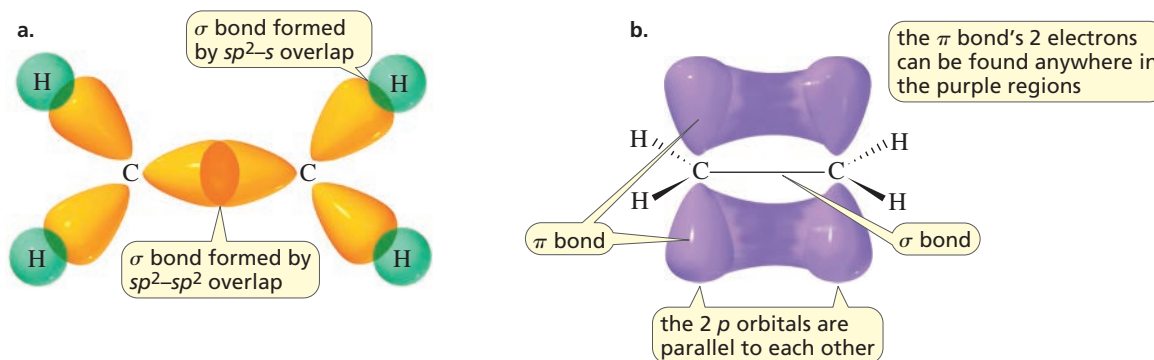
◀ **Figure 1.10**
(a) The three degenerate sp^2 orbitals lie in a plane, oriented 120° from each other. (The smaller lobes of the sp^2 orbitals are not shown.)
(b) The unhybridized p orbital is perpendicular to this plane.

A double bond consists of one σ bond and one π bond.

Because an sp^2 hybridized carbon is bonded to three atoms and three points define a plane, it is called a **trigonal planar carbon**. The unhybridized p orbital is perpendicular to the plane defined by the axes of the sp^2 orbitals (Figure 1.10b).

The two bonds in the double bond are not identical. One bond results from the overlap of an sp^2 orbital of one carbon with an sp^2 orbital of the other carbon; this is a sigma (σ) bond because it is cylindrically symmetrical (Figure 1.11a). Each carbon uses its other two sp^2 orbitals to overlap the s orbital of a hydrogen to form the C—H bonds.

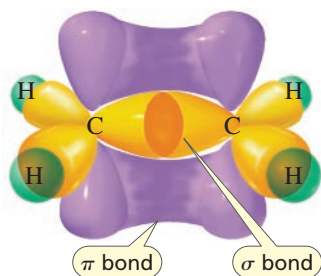
The second carbon–carbon bond results from side-to-side overlap of the two unhybridized p orbitals. Side-to-side overlap of p orbitals forms a pi (π) bond (Figure 1.11b). Thus, one of the bonds in a double bond is a σ bond, and the other is a π bond. All the C—H bonds are σ bonds. (Remember that all single bonds in organic compounds are σ bonds.)



▲ Figure 1.11

(a) One C—C bond in ethene is a σ bond formed by sp^2-sp^2 overlap, and the C—H bonds are σ bonds formed by sp^2-s overlap.

(b) The second C—C bond is a π bond formed by side-to-side overlap of a p orbital of one carbon with a p orbital of the other carbon. The two p orbitals are parallel to each other.



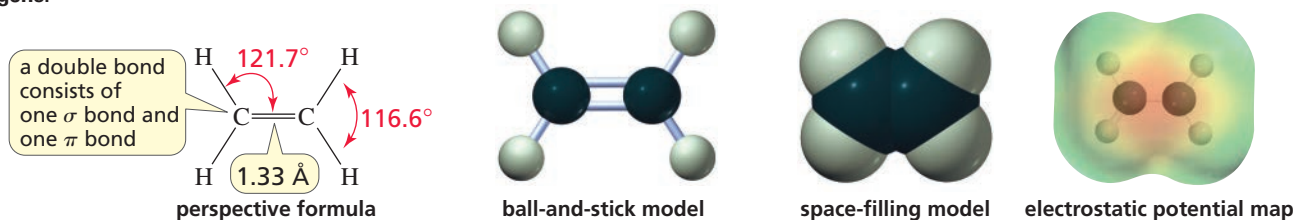
▲ Figure 1.12

The two carbons and four hydrogens lie in the same plane. Perpendicular to that plane are the two parallel p orbitals. This results in an accumulation of electron density above and below the plane containing the two carbons and four hydrogens.

To achieve maximum overlap, the two p orbitals that overlap to form the π bond must be parallel to each other (Figure 1.11b). This forces the triangle formed by one carbon and two hydrogens to lie in the same plane as the triangle formed by the other carbon and two hydrogens. As a result, all six atoms of ethene lie in the same plane, and the electrons in the p orbitals occupy a volume of space above and below the plane (Figure 1.12).

The potential map for ethene shows that it is a nonpolar molecule with a slight accumulation of negative charge (the pale orange area) above the two carbons. (If you could turn the potential map over, you would find a similar accumulation of negative charge on the other side.)

Representations of Ethene



Four electrons hold the carbons together in a carbon–carbon double bond, but only two electrons hold the carbons together in a carbon–carbon single bond. Therefore, a carbon–carbon double bond is stronger (174 kcal/mol) and shorter (1.33 Å) than a carbon–carbon single bond (90 kcal/mol and 1.54 Å).

Diamond, Graphite, Graphene, and Fullerenes: Substances That Contain Only Carbon Atoms

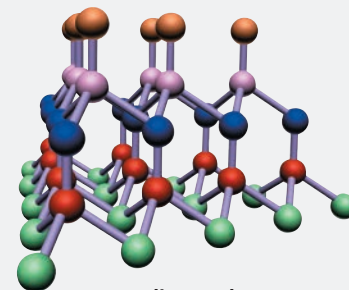
The difference that hybridization can make is illustrated by diamond and graphite. Diamond is the hardest of all substances, whereas graphite is a slippery, soft solid most familiar to us as the lead in pencils. Both materials, in spite of their very different physical properties, contain only carbon atoms. The two substances differ solely in the hybridization of the carbon atoms.

Diamond consists of a rigid three-dimensional network of carbon atoms, with each carbon bonded to four others via sp^3 orbitals.

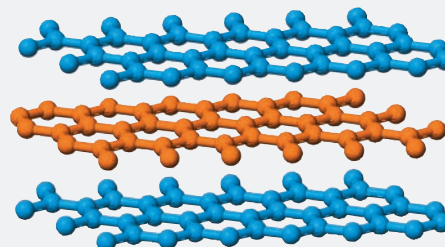
The carbon atoms in graphite, on the other hand, are sp^2 hybridized, so each bonds to only three other carbons. This trigonal planar arrangement causes the atoms in graphite to lie in flat, layered sheets. Because there are no covalent bonds between the sheets, they can shear off from neighboring sheets.

Diamond and graphite have been known since ancient times—but a third substance found in nature that contains only carbon atoms was discovered in 2004. Graphene is a one-atom-thick planar sheet of graphite. It is the thinnest and lightest material known. It is transparent and can be bent, stacked, or rolled. It is harder than diamond, and it conducts electricity better than copper. In 2010, the Nobel Prize in Physics was given to Andre Geim and Konstantin Novoselov of the University of Manchester for their ground-breaking experiments on graphene.

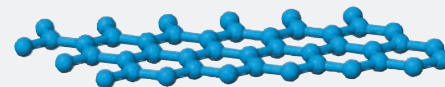
Fullerenes are also naturally occurring compounds that contain only carbon. Like graphite and graphene, fullerenes consist solely of sp^2 carbons, but instead of forming planar sheets, the carbons join to form spherical structures. (Fullerenes are discussed in Section 8.18.)



diamond



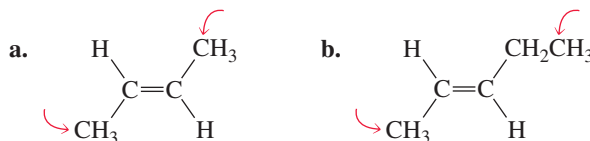
graphite



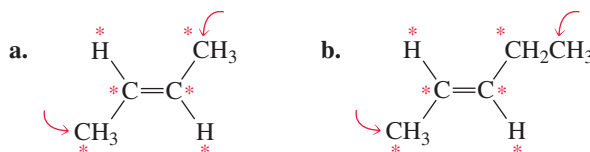
graphene

PROBLEM 29 SOLVED

Do the sp^2 carbons and the indicated sp^3 carbons have to lie in the same plane?

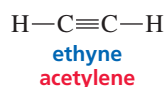


SOLUTION The two sp^2 carbons and the atoms that are bonded to each of the sp^2 carbons all lie in the same plane. The other atoms in the molecule will not necessarily lie in the same plane as these six atoms. By putting stars on the six atoms that do lie in the same plane, you will be able to see whether the indicated atoms lie in the same plane. They are in the same plane in part **a**, but they are not necessarily in the same plane in part **b**.



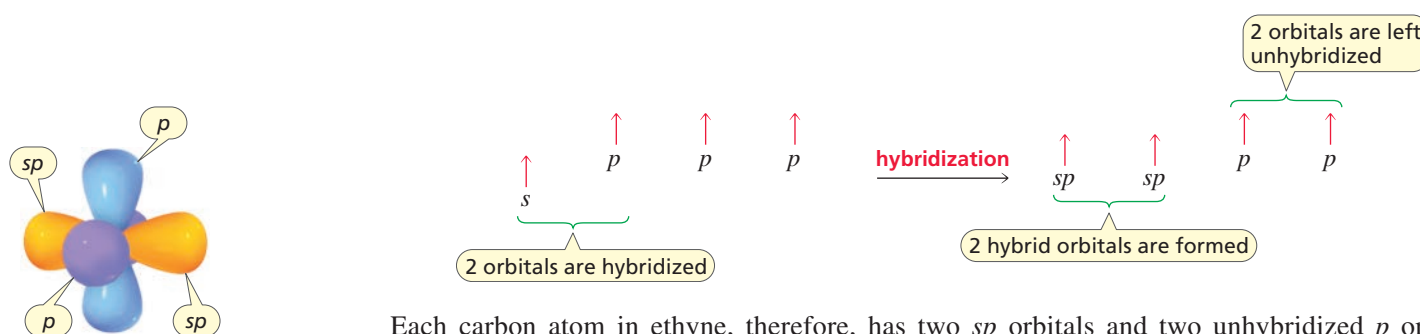
1.9 HOW A TRIPLE BOND IS FORMED: THE BONDS IN ETHYNE

The two carbons in ethyne (also called acetylene) are held together by three bonds. Three bonds connecting two atoms is called a **triple bond**. Each of the carbons forms four bonds, but each carbon is bonded to only two atoms—a hydrogen and another carbon:



Oxyacetylene torches are used to weld and cut metals. The torch uses acetylene and mixes it with oxygen to increase the temperature of the flame. An acetylene/oxygen flame burns at $\sim 3,500^\circ\text{C}$.

To bond to two atoms, each carbon hybridizes two atomic orbitals—an s and a p . Two degenerate sp orbitals result.

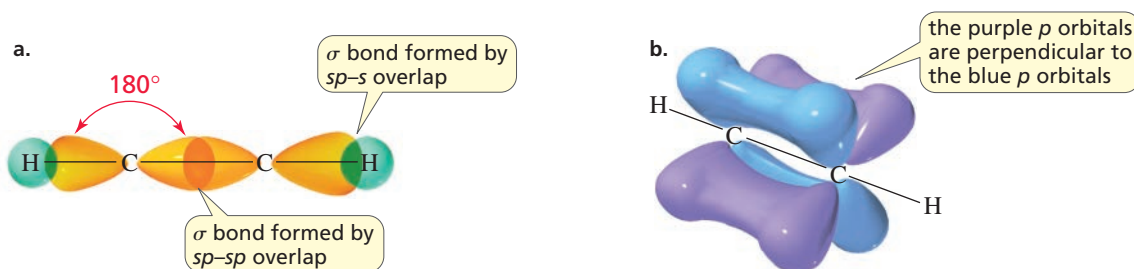


▲ **Figure 1.13**
The two orbitals point in opposite directions. The two unhybridized p orbitals are perpendicular to each other and to the sp orbitals. (The smaller lobes of the sp orbitals are not shown.)

Each carbon atom in ethyne, therefore, has two sp orbitals and two unhybridized p orbitals. To minimize electron repulsion, the two sp orbitals point in opposite directions. The two unhybridized p orbitals are perpendicular to each other and are perpendicular to the sp orbitals (Figure 1.13).

One of the sp orbitals of one carbon in ethyne overlaps an sp orbital of the other carbon to form a carbon–carbon σ bond. The other sp orbital of each carbon overlaps the s orbital of a hydrogen to form a C–H σ bond (Figure 1.14a). Because the two sp orbitals point in opposite directions, the bond angles are 180° .

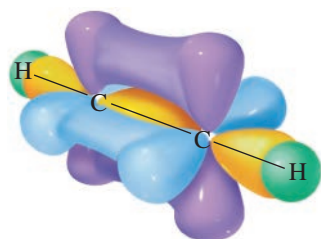
Each of the unhybridized p orbitals engages in side-to-side overlap with a parallel p orbital on the other carbon, resulting in the formation of two π bonds (Figure 1.14b).



▲ **Figure 1.14**
(a) The C—C σ bond in ethyne is formed by sp – sp overlap, and the C—H bonds are formed by sp – s overlap. The carbon atoms and the atoms bonded to them form a straight line.
(b) The two carbon–carbon π bonds are formed by side-to-side overlap of the two p orbitals of one carbon with the two p orbitals of the other carbon.

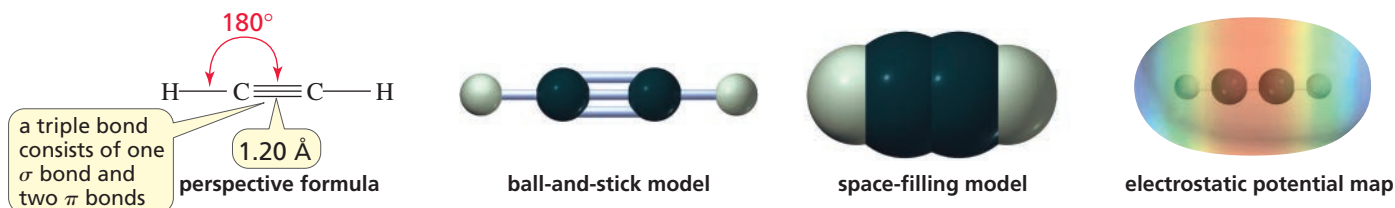
Thus, a triple bond consists of one σ bond and two π bonds. Because the two unhybridized p orbitals on each carbon are perpendicular to each other, they create regions of high electron density above and below and in front of and in back of the internuclear axis of the molecule (Figure 1.15).

The overall result can be seen in the potential map for ethyne—the negative charge accumulates in a cylinder that wraps around the egg-shaped molecule.



▲ **Figure 1.15**
The triple bond has an electron-dense region above and below and in front of and in back of the internuclear axis of the molecule.

Representations of Ethyne



A triple bond consists of one σ bond and two π bonds.

The two carbon atoms in a triple bond are held together by six electrons, so a triple bond is stronger (231 kcal/mol) and shorter (1.20 Å) than a double bond (174 kcal/mol and 1.33 Å).

PROBLEM 30

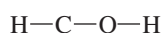
Put a number in each of the blanks:

- ___ s orbital and ___ p orbitals form ___ sp^3 orbitals.
- ___ s orbital and ___ p orbitals form ___ sp^2 orbitals.
- ___ s orbital and ___ p orbitals form ___ sp orbitals.

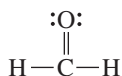
PROBLEM 31 SOLVED

- Draw the Lewis structure of H_2CO .
- Describe the orbitals used by the carbon atom in bonding and indicate the approximate bond angles.

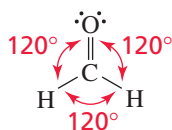
SOLUTION TO 31 a. Our first attempt at a Lewis structure (drawing the atoms with the hydrogens on the outside of the molecule) shows that carbon is the only atom that does not form the needed number of bonds.



If we place a double bond between carbon and oxygen and move the H from O to C (which still keeps it on the outside of the molecule), then all the atoms end up with the correct number of bonds. Lone-pair electrons are used to give oxygen a filled outer shell. When we check to see if any atom needs to be assigned a formal charge, we find that none of them does.



SOLUTION TO 31 b. Because carbon forms a double bond, we know that it uses sp^2 orbitals (as it does in ethene) to bond to the two hydrogens and the oxygen. It uses its “leftover” p orbital to form the second bond to oxygen. Because carbon is sp^2 hybridized, the bond angles are approximately 120° .



PROBLEM 32

For each of the given species:

- Draw its Lewis structure.
 - Describe the orbitals used by each carbon atom in bonding and indicate the approximate bond angles.
1. H_2CO_2 2. HCN 3. CCl_4 4. H_2CO_3

LEARN THE STRATEGY

USE THE STRATEGY

1.10 THE BONDS IN THE METHYL CATION, THE METHYL RADICAL, AND THE METHYL ANION

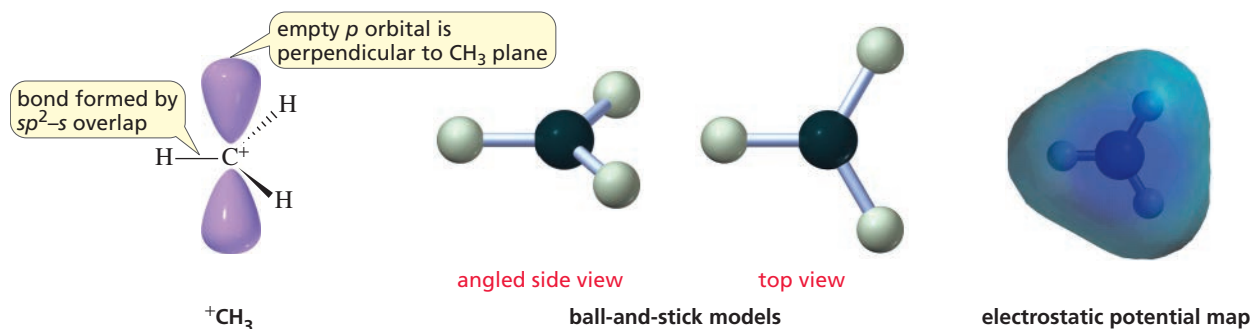
Not all carbon atoms form four bonds. A carbon with a positive charge, a negative charge, or an unpaired electron forms only three bonds. Now we will see the orbitals that carbon uses when it forms three bonds.

The Methyl Cation ($^+\text{CH}_3$)

The positively charged carbon in the methyl cation is bonded to three atoms, so it hybridizes three orbitals—an s orbital and two p orbitals. Therefore, it forms its three covalent bonds using sp^2 orbitals. Its unhybridized p orbital remains empty. The positively charged carbon (and the three atoms bonded to it) lie in a plane. The unhybridized p orbital stands perpendicular to the plane.

The carbon in $^+\text{CH}_3$ is sp^2 hybridized.

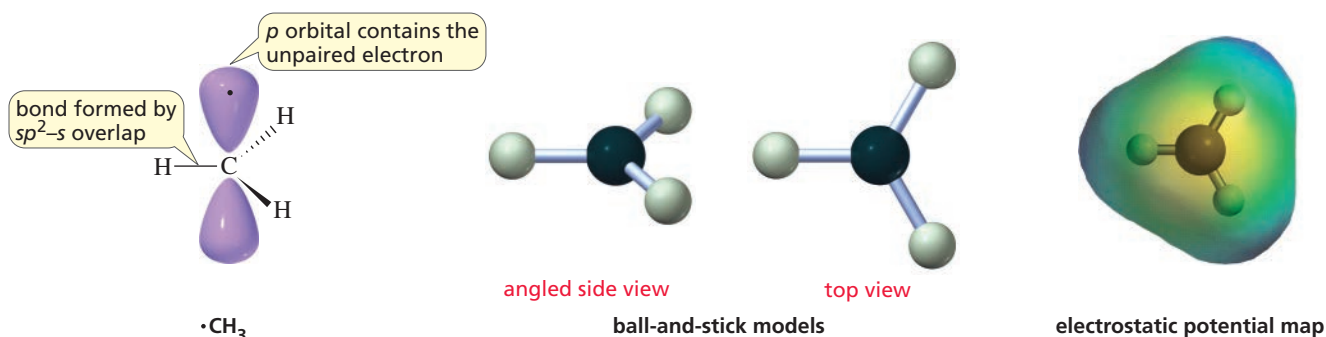
Representations of Methyl Cation

The Methyl Radical ($\cdot\text{CH}_3$)

The carbon in $\cdot\text{CH}_3$ is sp^2 hybridized.

The carbon atom in the methyl radical is also sp^2 hybridized. The methyl radical, though, has one more electron than the methyl cation. That electron is unpaired, and it resides in the p orbital, with half of the electron density in each lobe. Although the methyl cation and the methyl radical have similar ball-and-stick models, the potential maps are quite different because of the additional electron in the methyl radical.

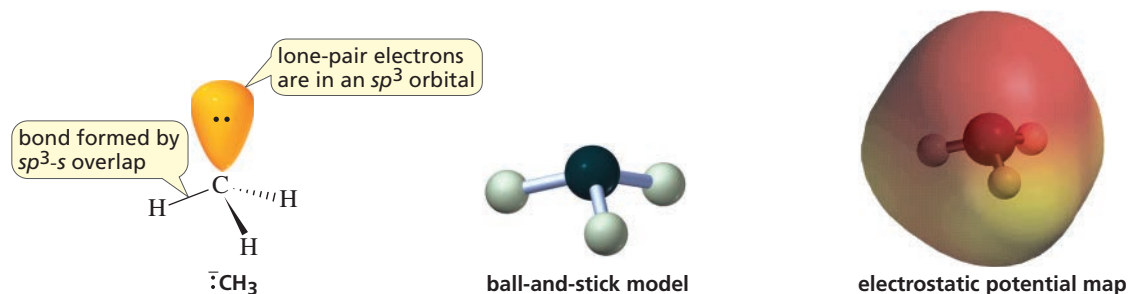
Representations of the Methyl Radical

The Methyl Anion ($^-\text{CH}_3$)

The carbon in $^-\text{CH}_3$ is sp^3 hybridized.

The negatively charged carbon in the methyl anion has three pairs of bonding electrons and one lone pair. Four pairs of electrons are farthest apart when the four orbitals containing the bonding and lone-pair electrons point toward the corners of a tetrahedron. Thus, the negatively charged carbon in the methyl anion is sp^3 hybridized. In the methyl anion, three of carbon's sp^3 orbitals each overlap the s orbital of a hydrogen, and the fourth sp^3 orbital holds the lone pair.

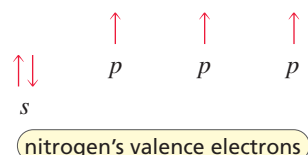
Representations of the Methyl Anion



Take a moment to compare the potential maps for the methyl cation, the methyl radical, and the methyl anion.

1.11 THE BONDS IN AMMONIA AND IN THE AMMONIUM ION

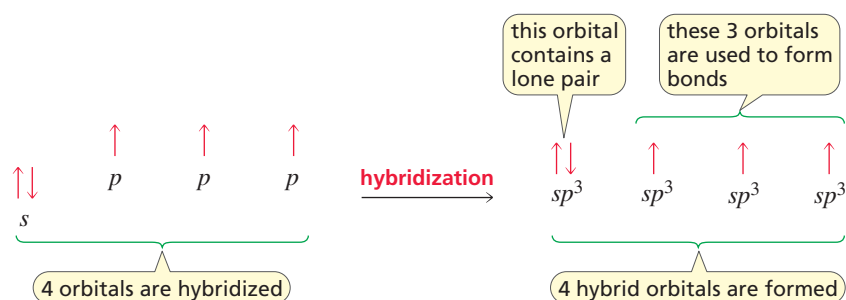
The nitrogen atom in ammonia (NH_3) forms three covalent bonds and has one lone pair. Nitrogen's electronic configuration shows that it has three unpaired valence electrons (Table 1.2), so it does not need to promote an electron to form the three covalent bonds required to achieve an outer shell of eight electrons—that is, to complete its octet.



However, this simple picture presents a problem. If nitrogen uses p orbitals to form the three $\text{N}-\text{H}$ bonds, as predicted by its electronic configuration, then we would expect bond angles of about 90° because the three p orbitals are at right angles to each other. But the experimentally observed bond angles in NH_3 are 107.3° .

The observed bond angles can be explained if we assume that nitrogen uses hybrid orbitals to form covalent bonds—just as carbon does. The s orbital and three p orbitals hybridize to form four degenerate sp^3 orbitals.

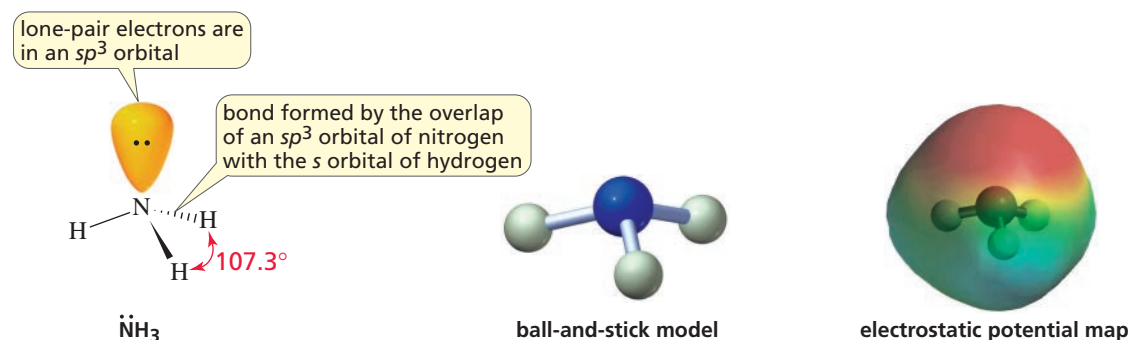
The bond angles in a molecule indicate which orbitals are used in bond formation.



Nitrogen hybridizes four orbitals because it forms three bonds and has one lone pair.

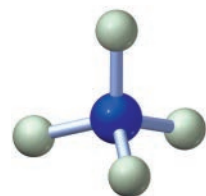
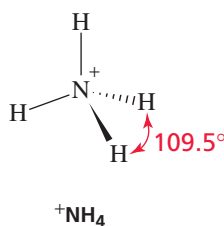
Each of the three $\text{N}-\text{H}$ bonds in NH_3 is formed from the overlap of an sp^3 orbital of nitrogen with the s orbital of a hydrogen. The lone pair occupies the fourth sp^3 orbital. The observed bond angle (107.3°) is a little smaller than the tetrahedral bond angle (109.5°) because of the lone pair. A lone pair occupies more space around the atom than does a bonding pair that is attracted by two nuclei and relatively confined between them. Consequently, a lone pair exerts more electron repulsion, which squeezes the $\text{N}-\text{H}$ bonds together and decreases the bond angle.

Representations of Ammonia

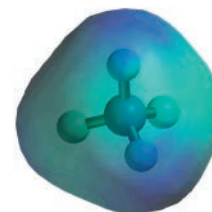


Because the ammonium ion ($^+\text{NH}_4$) has four identical N—H bonds and no lone pairs, all the bond angles are 109.5° , just like the bond angles in methane.

Representations of the Ammonium Ion



ball-and-stick model



electrostatic potential map

Take a moment to compare the potential maps for ammonia and the ammonium ion.

PROBLEM 33 ♦

Predict the approximate bond angles in

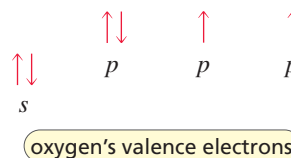
- a. the methyl cation. b. the methyl radical. c. the methyl anion.

PROBLEM 34 ♦

According to the potential map for the ammonium ion, which atom has the greatest electron density?

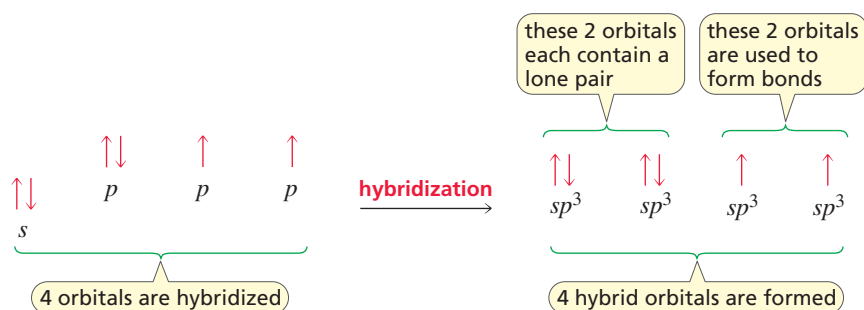
1.12 THE BONDS IN WATER

The oxygen atom in water ($\text{H}_2\ddot{\text{O}}:$) forms two covalent bonds and has two lone pairs. Because oxygen's electronic configuration shows that it has two unpaired valence electrons, oxygen does not need to promote an electron to form the two covalent bonds required to complete its octet.



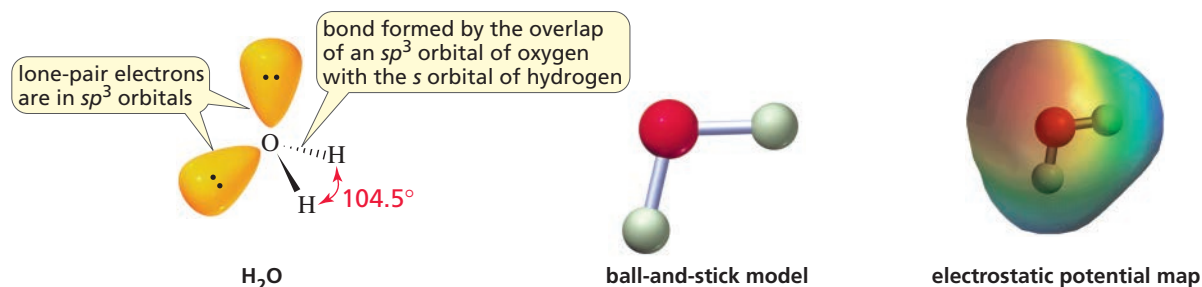
The experimentally observed bond angle in H_2O of 104.5° indicates that oxygen, like carbon and nitrogen, uses hybrid orbitals to form covalent bonds. Also like carbon and nitrogen, the one s and three p orbitals hybridize to form four degenerate sp^3 orbitals:

Oxygen hybridizes four orbitals because it forms two bonds and has two lone pairs.



Each of the two O—H bonds is formed by the overlap of an sp^3 orbital of oxygen with the s orbital of a hydrogen. A lone pair occupies each of the two remaining sp^3 orbitals.

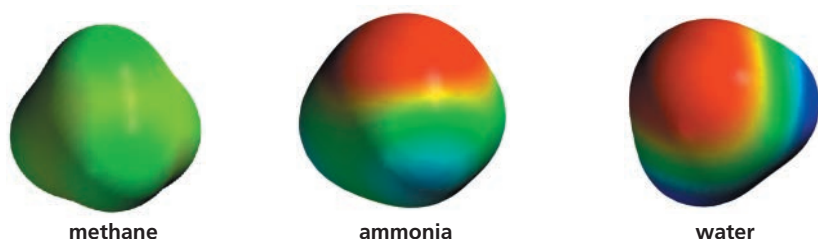
Representations of Water



The bond angle in water (104.5°) is even smaller than the bond angles in NH_3 (107.3°) because oxygen has two relatively diffuse lone pairs, whereas nitrogen has only one.

PROBLEM 35 ♦

Compare the electrostatic potential maps for methane, ammonia, and water. Which is the most polar molecule? Which is the least polar?



PROBLEM 36 SOLVED

The bond angles in H_3O^+ are less than _____ and greater than _____.

SOLUTION The carbon atom in CH_4 has no lone pairs; its bond angles are 109.5° . The oxygen atom in H_3O^+ has one lone pair. A lone pair is more diffuse than a bonding pair, so the O—H bonds squeeze together to minimize electron repulsion. However, they do not squeeze as closely together as they do in water (104.5°), where oxygen has two lone pairs. Therefore, the bond angles in H_3O^+ are less than 109.5° and greater than 104.5° .

Water—A Unique Compound

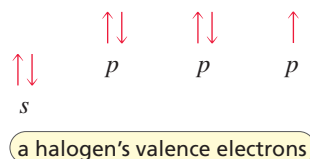
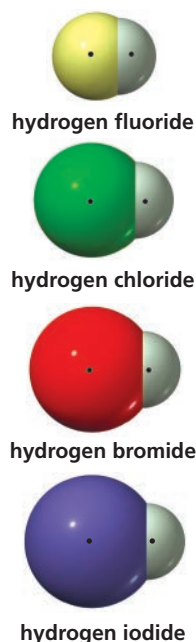
Water is the most abundant compound found in living organisms. Its unique properties have allowed life to originate and evolve. For example, its high heat of fusion (the heat required to convert a solid to a liquid) protects organisms from freezing at low temperatures because a great deal of heat must be removed from water to freeze it. Its high heat capacity (the heat required to raise the temperature of a substance by a given amount) minimizes temperature changes in organisms, and its high heat of vaporization (the heat required to convert a liquid to a gas) allows animals to cool themselves with a minimal loss of body fluid.

Because liquid water is denser than ice, ice formed on the surface of water floats and insulates the water below. That is why oceans and lakes freeze from the top down (not from the bottom up) and why plants and aquatic animals can survive when the ocean or lake in which they live freezes.

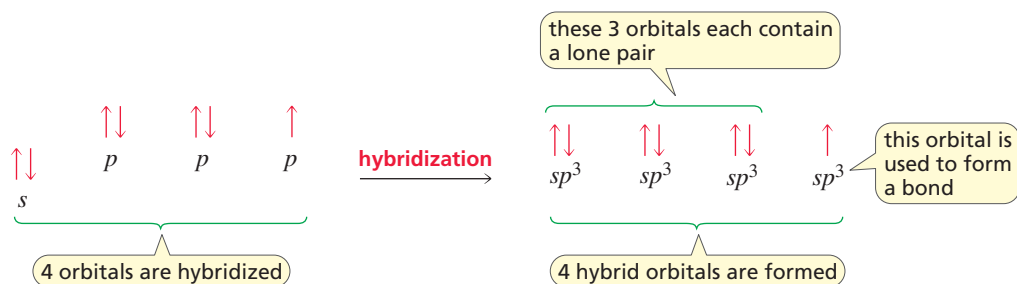


1.13 THE BOND IN A HYDROGEN HALIDE

HF, HCl, HBr, and HI are called hydrogen halides. A halogen has only one unpaired valence electron (Table 1.2), so it forms only one covalent bond.

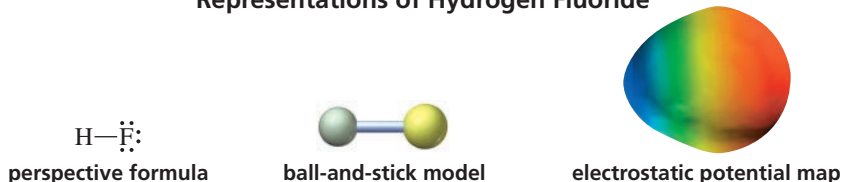


Bond angles will not help us determine the orbitals that form the hydrogen halide bond, as they did with other molecules, because hydrogen halides have only one bond and, therefore, no bond angles. We do know, however, that a halogen's three lone pairs are energetically identical and that lone-pair electrons position themselves to minimize electron repulsion. Both of these observations suggest that the halogen's three lone pairs are in hybrid orbitals.

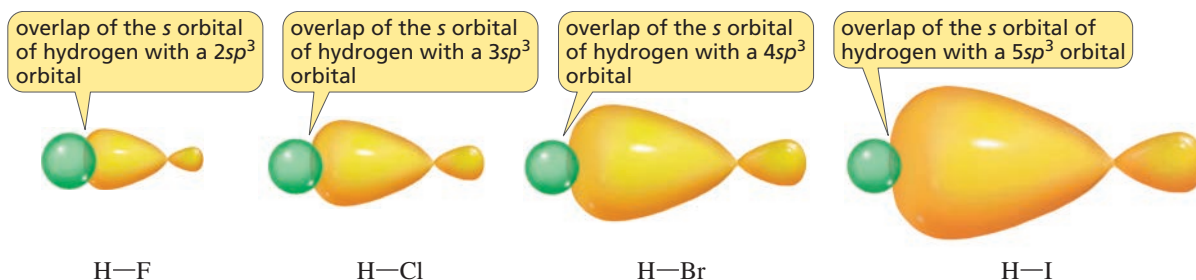


Therefore, we will assume that the hydrogen–halogen bond is formed by the overlap of an sp^3 orbital of the halogen with the s orbital of hydrogen.

Representations of Hydrogen Fluoride



In the case of fluorine, the sp^3 orbital used in bond formation belongs to the second shell of electrons. In chlorine, the sp^3 orbital belongs to the third shell. Because the average distance from the nucleus is greater for an electron in the third shell than it is for an electron in the second shell, the average electron density is less in a $3sp^3$ orbital than in a $2sp^3$ orbital. This means that the electron density in the region of orbital overlap *decreases* as the size of the halogen *increases* (Figure 1.16). Therefore, the hydrogen–halogen bond becomes longer and weaker as the size (atomic weight) of the halogen increases (Table 1.6).



► Figure 1.16

There is greater electron density in the region of overlap of the s orbital of hydrogen with a $2sp^3$ orbital than in the region of overlap of the s orbital of hydrogen with a $3sp^3$ orbital, which is greater than in the region of overlap of the s orbital of hydrogen with a $4sp^3$ orbital.

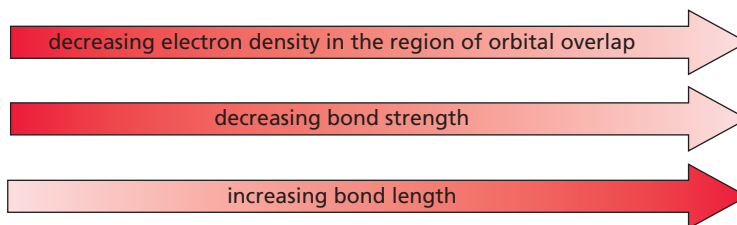


Table 1.6 Hydrogen–Halogen Bond Lengths and Bond Strengths

Hydrogen halide		Bond length (Å)	Bond strength (kcal/mol)
H—F		0.917	136
H—Cl		1.275	103
H—Br		1.415	87
H—I		1.609	71

The hydrogen–halogen bond becomes longer and weaker as the size of the halogen increases.

PROBLEM 37 ♦

- What are the relative lengths and strengths of the bonds in Cl_2 and Br_2 ?
- What are the relative lengths and strengths of the carbon–halogen bonds in CH_3F , CH_3Cl , and CH_3Br ?

PROBLEM 38

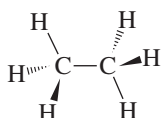
- Which bond would be longer?
 - Which bond would be stronger?
- C—Cl or C—I
 - C—C or C—Cl
 - H—Cl or H—F

1.14 HYBRIDIZATION AND MOLECULAR GEOMETRY

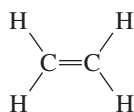
We have seen that the *hybridization* of an atom determines the *arrangement* of the bonds around the atom and that this arrangement determines the *bond angle*. Thus, *molecular geometry is determined by hybridization*.

For example:

- If carbon is bonded to four groups, it is sp^3 hybridized and, therefore, tetrahedral with bond angles of 109.5° .
- If carbon is bonded to three groups, it is sp^2 hybridized and, therefore, trigonal planar with bond angles of 120° .
- If carbon is bonded to two groups, it is sp hybridized and, therefore, linear with bond angles of 180° .



sp^3
 109.5°
tetrahedral



sp^2
 120°
trigonal planar



sp
 180°
linear

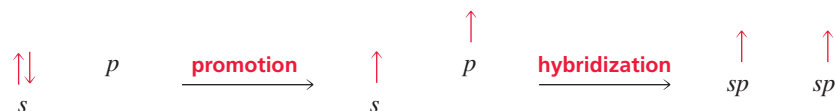
Molecular geometry is determined by hybridization.

PROBLEM-SOLVING STRATEGY**Predicting the Orbitals and Bond Angles Used in Bonding**

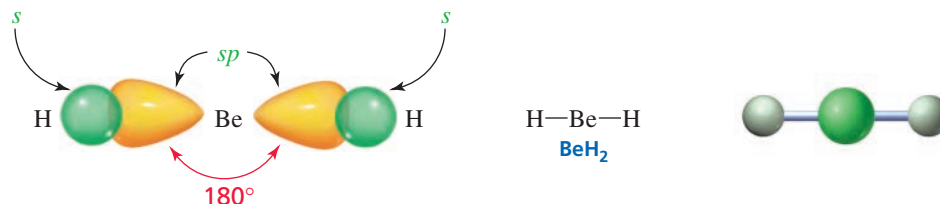
Describe the orbitals used in bonding and the bond angles in the following compounds:

- BeH_2
 - BH_3
- Beryllium (Be) does not have any unpaired valence electrons (Table 1.2). Therefore, it cannot form any bonds unless it promotes an electron. After promoting an electron from the s orbital to an empty p orbital and hybridizing the two orbitals that now each contain an unpaired electron, two sp orbitals result.

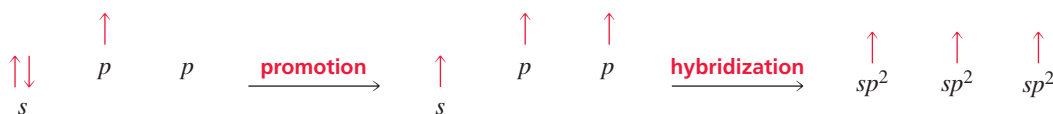
LEARN THE STRATEGY



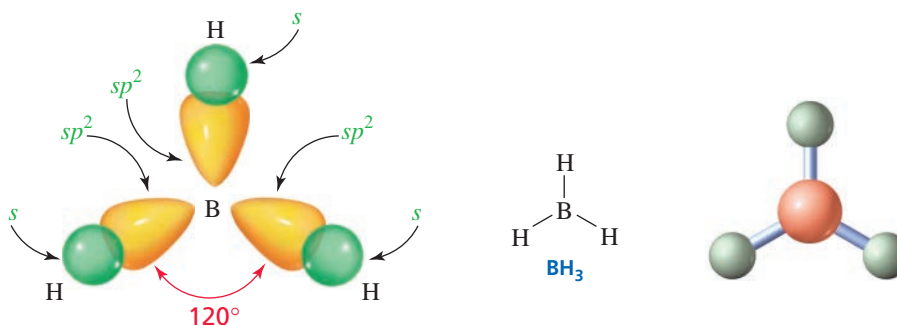
Each sp orbital of beryllium overlaps the s orbital of a hydrogen. To minimize electron repulsion, the two sp orbitals point in opposite directions, resulting in a bond angle of 180° .



- b. Without promotion, boron (B) could form only one bond because it has only one unpaired valence electron (Table 1.2). Promotion gives it three unpaired electrons. When the three orbitals that contain an unpaired electron (one s orbital and two p orbitals) are hybridized, three sp^2 orbitals result.



Each sp^2 orbital of boron overlaps the s orbital of a hydrogen. When the three sp^2 orbitals orient themselves to get as far away from each other as possible, the resulting bond angles are 120° .



USE THE STRATEGY

PROBLEM 39 ♦

Describe the orbitals used in bonding and the bond angles in the following compounds:

- a. CH_3O^- b. CO_2 c. H_2CO d. N_2 e. BF_3

1.15 SUMMARY: HYBRIDIZATION, BOND LENGTHS, BOND STRENGTHS, AND BOND ANGLES

You may wonder how an electron “knows” what orbital it should go into. In fact, electrons know nothing about orbitals. They simply occupy the space around atoms in the most stable arrangement possible. It is chemists who use the concept of orbitals to explain this arrangement. We will now review what we have learned about orbitals and the bonds they form.

Bond Order

We have seen that all *single bonds* are σ bonds, all double bonds are composed of one σ bond and one π bond, and all triple bonds are composed of one σ bond and two π bonds.

The shorter the bond,
the stronger it is.

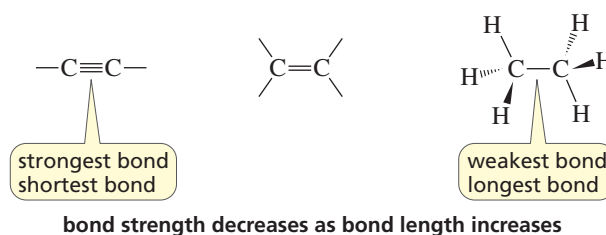
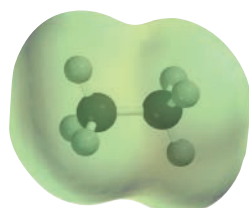
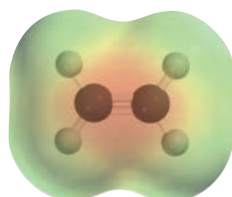


Table 1.7 Comparison of the Bond Angles and the Lengths and Strengths of the Carbon–Carbon and Carbon–Hydrogen Bonds in Ethane, Ethene, and Ethyne

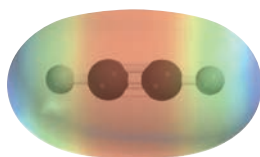
Molecule	Hybridization of carbon	Bond angles	Length of C—C bond (Å)	Strength of C—C bond (kcal/mol)	Length of C—H bond (Å)	Strength of C—H bond (kcal/mol)
 ethane	sp^3	109.5°	1.54	90.2	1.10	101.1
 ethene	sp^2	120°	1.33	174.5	1.08	110.7
 ethyne	sp	180°	1.20	230.4	1.06	133.3



Ethane

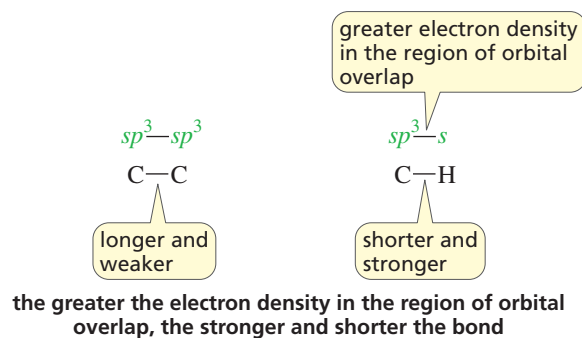


Ethene



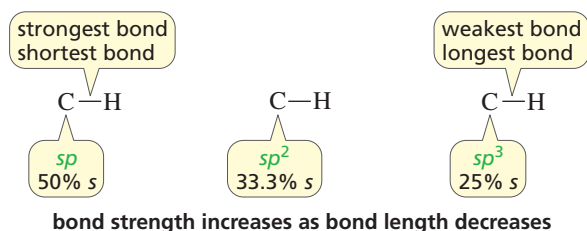
Ethyne

A C—H σ bond is shorter than a C—C σ bond (Table 1.7) because the s orbital of hydrogen is closer to the nucleus than is the sp^3 orbital of carbon. Consequently, the nuclei are closer together in a bond formed by sp^3 – s overlap than they are in a bond formed by sp^3 – sp^3 overlap. In addition to being shorter, a C—H σ bond is stronger than a C—C σ bond because there is greater electron density in the region of overlap of an sp^3 orbital with an s orbital than in the region of overlap of an sp^3 orbital with an sp^3 orbital.



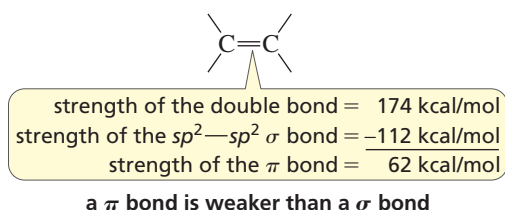
Hybridization Affects Bond Length and Bond Strength

The length and strength of a C—H bond depend on the hybridization of the carbon. The more s character in the orbital used by carbon to form the bond, the shorter and stronger the bond—again because an s orbital is closer to the nucleus than is a p orbital. Thus, a C—H bond formed by an sp carbon (50% s) is shorter and stronger than a C—H bond formed by an sp^2 carbon (33.3% s), which, in turn, is shorter and stronger than a C—H bond formed by an sp^3 carbon (25% s).



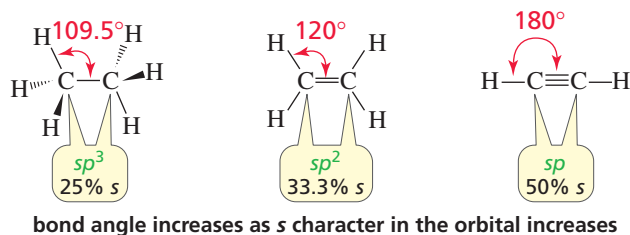
A double bond (a σ bond plus a π bond) is stronger (174 kcal/mol) than a single bond (a σ bond; 90 kcal/mol), but it is not twice as strong. Therefore, we can conclude that the π bond of a double bond is weaker than the σ bond. The π bond is weaker because the side-to-side overlap that forms a π bond is less effective for bonding than is the end-on overlap that forms a σ bond (Section 1.6).

The strength of a C—C σ bond given in Table 1.7 (90 kcal/mol) is for a bond formed by sp^3-sp^3 overlap. A C—C σ bond formed by sp^2-sp^2 overlap is expected to be stronger, however, because of the greater s character in the overlapping sp^2 orbitals; it has been estimated to be ~ 112 kcal/mol. We can conclude then that the strength of the π bond of ethene is about 62 kcal/mol ($174 - 112 = 62$).



Hybridization Affects Bond Angles

We saw that bond angles depend on the orbital used by carbon to form the bond. The greater the amount of s character in the orbital, the larger the bond angle. For example, sp^3 carbons have bond angles of 109.5° , sp^2 carbons have bond angles of 120° , and sp carbons have bond angles of 180° .



The more s character in the orbital, the shorter the bond.

The more s character in the orbital, the stronger the bond.

The more s character in the orbital, the larger the bond angle.

A π bond is weaker than a σ bond.

PROBLEM 41 ♦

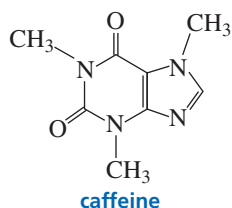
Which of the bonds in a carbon–oxygen double bond has more effective orbital–orbital overlap: the σ bond or the π bond?

PROBLEM 42 ♦

Would you expect a C—C σ bond formed by sp^2-sp^2 overlap to be stronger or weaker than a C—C σ bond formed by sp^3-sp^3 overlap?

PROBLEM 43

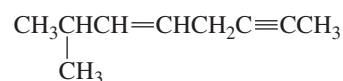
Caffeine is a natural insecticide found in the seeds and leaves of certain plants, where it kills insects that feed on the plant. Caffeine is extracted for human consumption from beans of the coffee plant, from Kola nuts, and from the leaves of tea plants. Because it stimulates the central nervous system, it temporarily prevents drowsiness. Add caffeine's missing lone pairs to its structure.



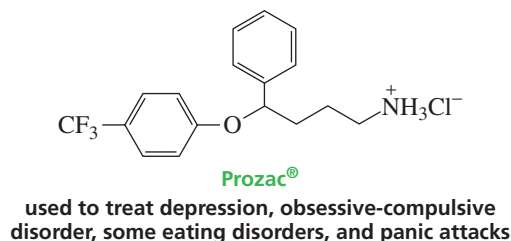
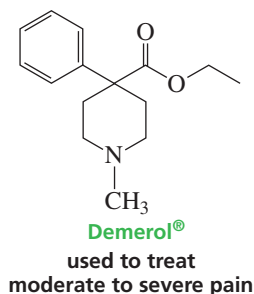
coffee beans

PROBLEM 44

- a. What is the hybridization of each of the carbon atoms in the following compound?



- b. What is the hybridization of each of the C, N, and O atoms in demerol and Prozac? (Generic names are not capitalized; trade names are capitalized.)



LEARN THE STRATEGY

PROBLEM-SOLVING STRATEGY

Predicting Bond Angles

Predict the approximate bond angle of the C—N—H bond in $(\text{CH}_3)_2\text{NH}$.

First, we need to determine the hybridization of the central atom (the N). Because the nitrogen atom forms only single bonds, we know that it is sp^3 hybridized. Next, we look to see if there are lone pairs that affect the bond angle. An uncharged nitrogen has one lone pair. Based on these observations, we can predict that the C—N—H bond angle is about 107.3° . This is the same as the H—N—H bond angle in NH_3 , which is another compound with an sp^3 nitrogen and one lone pair.

USE THE STRATEGY

PROBLEM 45 ♦

Predict the approximate bond angles for

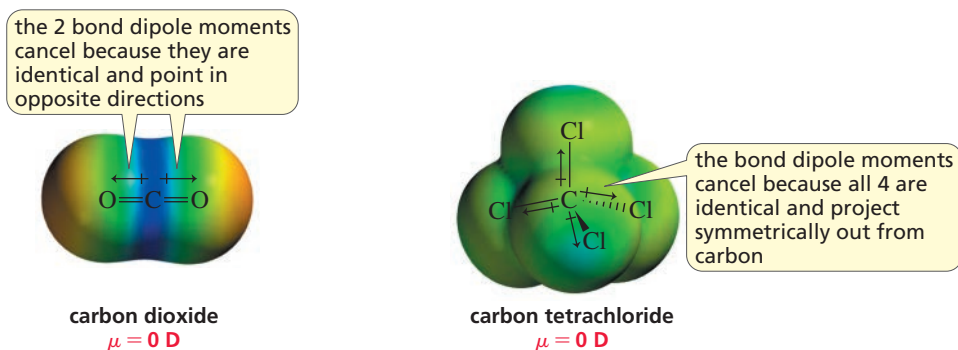
- | | |
|--|---|
| a. the C—N—C bond angle in $(\text{CH}_3)_2\text{NH}_2^+$. | c. the H—C—N bond angle in $(\text{CH}_3)_2\text{NH}$. |
| b. the C—N—H bond angle in $\text{CH}_3\text{CH}_2\text{NH}_2$. | d. the H—C—O bond angle in CH_3OCH_3 . |

1.16 DIPOLE MOMENTS OF MOLECULES

In Section 1.3, we saw that if a molecule has one covalent bond, then the dipole moment of the molecule is identical to the dipole moment of the bond. When molecules have more than one covalent bond, the geometry of the molecule must be taken into account because both the *magnitude* and the *direction* of the individual bond dipole moments (the vector sum) determine the overall dipole moment of the molecule.

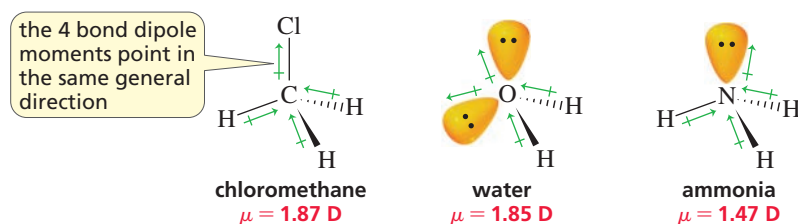
*The dipole moment depends on
the magnitude and direction of the individual bond dipoles.*

Because the direction of the bond dipoles must be taken into account, symmetrical molecules have no dipole moment. In carbon dioxide (CO_2), for example, the carbon is bonded to two oxygens; so it uses sp orbitals to form the two C—O σ bonds. The remaining two p orbitals on the carbon form the two C—O π bonds. The sp orbitals form a bond angle of 180° , which causes the individual carbon–oxygen bond dipole moments to cancel each other. Carbon dioxide, therefore, has a dipole moment (symbolized by the Greek letter μ) of 0 D.



Carbon tetrachloride (CCl_4) is another symmetrical molecule. The four atoms bonded to the sp^3 carbon atom are identical and project symmetrically out from the carbon atom. Thus, as with CO_2 , the symmetry of the molecule causes the bond dipole moments to cancel. Therefore, carbon tetrachloride also has no dipole moment.

The dipole moment of chloromethane (CH_3Cl) is greater (1.87 D) than the dipole moment of its $\text{C}-\text{Cl}$ bond (1.5 D) because the $\text{C}-\text{H}$ dipoles are oriented so that they reinforce the dipole of the $\text{C}-\text{Cl}$ bond. In other words, all the electrons are pulled in the same general direction.



The dipole moment of water (1.85 D) is greater than the dipole moment of a single $\text{O}-\text{H}$ bond (1.5 D) because the dipoles of the two $\text{O}-\text{H}$ bonds reinforce each other; the lone-pair electrons also contribute to the dipole moment. Similarly, the dipole moment of ammonia (1.47 D) is greater than the dipole moment of a single $\text{N}-\text{H}$ bond (1.3 D).

PROBLEM 46 ♦

Which of the following molecules would you expect to have a dipole moment of zero? To answer parts **g** and **h**, you may need to review the Problem Solving Strategy on p. 75.

- | | | | |
|---|------------------------------------|--|---------------------------|
| a. CH_3CH_3 | c. CH_2Cl_2 | e. $\text{H}_2\text{C}=\text{CH}_2$ | g. BeCl_2 |
| b. $\text{H}_2\text{C}=\text{O}$ | d. NH_3 | f. $\text{H}_2\text{C}=\text{CHBr}$ | h. BF_3 |

PROBLEM 47

Account for the difference in the shape and color of the potential maps for ammonia and the ammonium ion in Section 1.11.

PROBLEM 48 ♦

If the dipole moment of CH_3F is 1.847 D and the dipole moment of CD_3F is 1.858 D, which is more electronegative: hydrogen or deuterium?

ESSENTIAL CONCEPTS

Section 1.0

- **Organic compounds** are compounds that are based on carbon.

Section 1.1

- The **atomic number** of an atom is the number of protons in its nucleus.
- The **mass number** of an atom is the sum of its protons and neutrons.
- **Isotopes** have the same atomic number but different mass numbers.
- **Atomic mass** is the weighted average of the isotopes in the element.
- **Molecular weight** is the sum of the atomic masses of all the atoms in the molecule.

Section 1.2

- The closer the atomic orbital is to the nucleus, the lower its energy.
- **Degenerate** orbitals have the same energy.
- The **electronic configuration** of an atom describes the atomic orbitals occupied by the atom's electrons.
- Electrons are assigned to orbitals (atomic or molecular) following the **aufbau principle**, the **Pauli exclusion principle**, and **Hund's rule**.
- **Core electrons** are electrons in inner shells. **Valence electrons** are electrons in the outermost shell.

Section 1.3

- An atom is most stable if its outer shell is either filled or contains eight electrons and it has no electrons of higher energy.
- The **octet rule** states that an atom will give up, accept, or share electrons in order to fill its outer shell or attain an outer shell with eight electrons.
- **Electronegative** elements readily acquire electrons.
- **Electrostatic attractions** are attractive forces between opposite charges.
- A **covalent bond** is formed when two atoms share a pair of electrons.
- A **polar covalent bond** is a covalent bond between atoms with different **electronegativities**. A nonpolar covalent bond is a bond between atoms with similar electronegativities.
- The greater the difference in electronegativity between the atoms forming the bond, the closer the bond is to the ionic end of the continuum.
- A polar covalent bond has a **dipole** (a positive end and a negative end), measured by a **dipole moment**.
- The **dipole moment** of a bond is equal to the size of the charge times the distance between the charges.

Section 1.4

- **Lone-pair electrons** are valence electrons that are not used in bonding.
- A **proton** is a positively charged hydrogen ion; a **hydride ion** is a negatively charged hydrogen ion.

- **formal charge** = the number of valence electrons – the number of electrons the atom has to itself (all the lone-pair electrons and one-half of the bonding electrons)
- **Lewis structures** indicate which atoms are bonded together and show **lone pairs** and **formal charges**.
- When the atom is neutral, C forms 4 bonds, N forms 3 bonds, O forms 2 bonds, and H or a halogen forms 1 bond.
- When the atom is neutral, C has no lone pairs, N has 1 lone pair, O has 2 lone pairs, and a halogen has 3 lone pairs.
- A **carbocation** has a positively charged carbon, a **carbanion** has a negatively charged carbon, and a **radical** has an unpaired electron.

Section 1.5

- An **atomic orbital** tells us the volume of space around the nucleus where an electron is most likely to be found.
- There is zero probability of finding an electron at a **node**.

Section 1.6

- According to **molecular orbital (MO) theory**, covalent bonds result when atomic orbitals combine to form **molecular orbitals**.
- **Minimum energy** corresponds to **maximum stability**.
- Two atomic orbitals combine to give a **bonding MO** and a higher energy **antibonding MO**.
- Electrons in a bonding MO assist in bonding. Electrons in an antibonding MO detract from bonding.
- Cylindrically symmetrical bonds are called **sigma (σ) bonds**; side-to-side overlap of parallel *p* orbitals forms a **pi (π) bond**.
- Bond strength is measured by the **bond dissociation energy**.

Section 1.7

- To be able to form four bonds, carbon must promote an electron from an *s* orbital to an empty *p* orbital.
- Carbon forms bonds using **hybrid orbitals**.
- Bonding pairs and lone-pair electrons around an atom stay as far apart as possible.
- All **single bonds** in organic compounds are σ bonds.

Section 1.8

- A **double bond** consists of one σ bond and one π bond; the doubly bonded carbon is sp^2 hybridized.

Section 1.9

- A **triple bond** consists of one σ bond and two π bonds; the triply bonded carbon is sp hybridized.

Section 1.10

- Carbocations and carbon radicals form bonds using sp^2 orbitals; carbanions form bonds using sp^3 orbitals.

Sections 1.11–1.13

- Nitrogen, oxygen, and the halogens form bonds using **hybrid orbitals**.

- Lone pairs decrease the bond angle because they are more diffuse than bonding electrons.

Section 1.14

- **Molecular geometry is determined by hybridization:** sp^3 is tetrahedral, sp^2 is trigonal planar, and sp is linear.

Section 1.15

- The **hybridization** of C, N, or O depends on the number of π bonds the atom forms: no π bonds = sp^3 , one π bond = sp^2 , and two π bonds = sp . Exceptions are carbocations and carbon radicals, which are sp^2 .
- The greater the electron density in the region of orbital overlap, the shorter and stronger the bond.

- The more s character in the orbital used to form a bond, the shorter and stronger the bond and the larger the bond angle.
- The shorter the bond, the stronger it is.
- Triple bonds are shorter and stronger than double bonds, which are shorter and stronger than single bonds.
- A π bond is weaker than a σ bond.

Section 1.16

- The **dipole moment** of a molecule depends on the magnitude and direction of all the individual bond dipoles.

GLOSSARY

The definitions of all the key words used in this book can be found in the Glossary on p. 1307.

PROBLEMS

49. Draw a Lewis structure for each of the following:

- a. N_2H_4 b. CO_3^{2-} c. N_2H_2 d. CO_2 e. $HOCl$

50. a. Which of the following has a nonpolar covalent bond?

- b. Which of the following has a bond closest to the ionic end of the bond spectrum?



51. What is the hybridization of all the atoms (other than hydrogen) in each of the following?
What are the bond angles around each atom?

- a. NH_3 c. $^-CH_3$ e. $^+NH_4$ g. HCN i. H_3O^+
b. BH_3 d. $\cdot CH_3$ f. $^+CH_3$ h. $C(CH_3)_4$ j. $H_2C=O$

52. Draw the condensed structure of a compound that contains only carbon and hydrogen atoms and that has

- a. three sp^3 hybridized carbons.
b. one sp^3 hybridized carbon and two sp^2 hybridized carbons.
c. two sp^3 hybridized carbons and two sp hybridized carbons.

53. Predict the approximate bond angles:

- a. the $H-N-H$ bond angle in NH_3 c. the $N-C-C$ bond angle in H_2NCH_2COOH
b. the $C-O-C$ bond angle in CH_3OCH_3 d. the $C-O-H$ bond angle in CH_3COOH

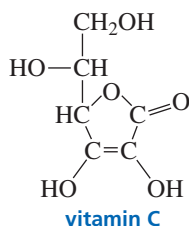
54. Draw the ground-state electronic configuration for each of the following:

- a. Na b. Na^+ c. Ne d. Ne^{2-}

55. Draw a Lewis structure for each of the following:

- a. CH_3NH_2 b. HNO_2 c. $NaNH_2$ d. NH_2O^-

56. What is the hybridization of each of the carbon and oxygen atoms in vitamin C?



57. Rank the bonds from most polar to least polar.

- a. C—C, C—Si, C—Ge b. Si—H, C—H, H—H c. H—F, H—I, H—Br d. C—H, C—Br, C—N

58. Draw a Lewis structure for each of the following:

- a. CH₃CHO b. CH₃OCH₃ c. CH₃COOH

59. Draw a skeletal structure for each of the compounds in Problem 58.

60. What is the hybridization of the indicated atom in each of the following molecules?

- a. $\text{CH}_3\text{CH}_2\overset{\text{red arrow}}{\text{C}}\text{CH}_3$ b. $\text{CH}_3\text{CH}_2\overset{\text{red arrow}}{\text{C}}\text{CH}_2\text{CH}_3$ c. $\text{NH}(\text{CH}_3)_2$ (red arrow on N)
 d. $\text{CH}_3\text{CH}_2\overset{\text{red arrow}}{\text{C}}\equiv\text{N}$ e. $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{red arrow}}{\text{C}}=\text{NCH}_3$ f. $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{red arrow}}{\text{N}}\text{H}_2$

61. Predict the approximate bond angles for the following:

- a. the C—N—H bond angle in NH(CH₃)₂ c. the C—C—H bond angle in CH₃CH₂NH₂
 b. the C—C—C bond angle in H₃C≡CH₃ d. the H—C—C bond angle in H₃C≡CH₃

62. Show the direction of the dipole moment in each of the following bonds (use the electronegativities given in Table 1.3):

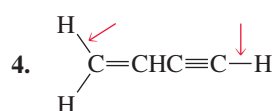
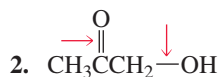
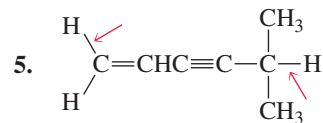
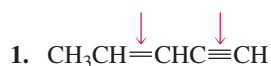
- a. H₃C—Br b. H₃C—Li c. HO—NH₂ d. I—Br e. H₃C—OH f. (CH₃)₂N—H

63. Draw the missing lone-pair electrons and assign the missing formal charges for the following:

- a. $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{O}-\text{H} \\ | \\ \text{H} \end{array}$ b. $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{O}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ c. $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{O} \\ | \\ \text{H} \end{array}$ d. $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{N}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$

64. a. Which of the indicated bonds in each molecule is shorter?

b. Indicate the hybridization of the C, O, and N atoms in each of the molecules.



65. For each of the following molecules, indicate the hybridization of each carbon and give the approximate values of all the bond angles:

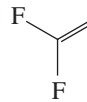
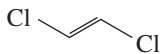
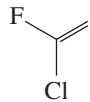
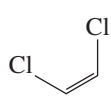
- a. CH₃C≡CH b. CH₃CH=CH₂ c. CH₃CH₂CH₃ d. CH₂=CH—CH=CH₂

66. Draw a Lewis structure for each of the following:

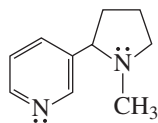
- a. (CH₃)₃COH b. CH₃CH(OH)CH₂CN c. (CH₃)₂CHCH(CH₃)CH₂C(CH₃)₃

67. Draw a skeletal structure for each of the compounds in Problem 66.

68. Rank the following compounds from highest dipole moment to lowest dipole moment:



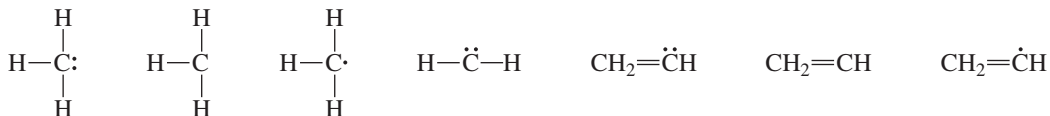
69. In which orbitals are the lone pairs in nicotine?



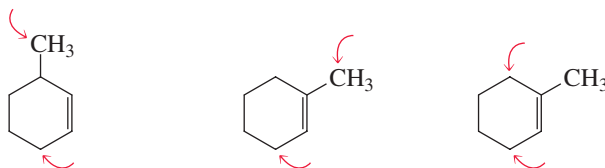
nicotine

nicotine increases the concentration of dopamine in the brain; the release of dopamine makes a person feel good—the reason nicotine is addictive

70. Indicate the formal charge on each carbon that has one. All lone pairs are shown.



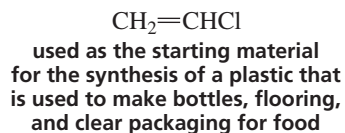
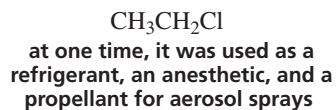
71. Do the sp^2 carbons and the indicated sp^3 carbons lie in the same plane?



72. a. Which of the species have bond angles of 109.5° ?
b. Which of the species have bond angles of 120° ?

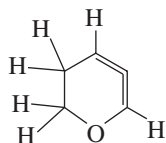


73. Which compound has a longer C—Cl bond?



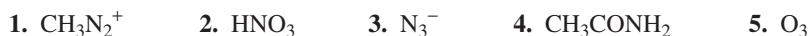
74. Which compound has a larger dipole moment: CH_3Cl or CH_2Cl_2 ?

75. Explain why the following compound is not stable:



76. Explain why CH_3Cl has a greater dipole moment than CH_3F even though F is more electronegative than Cl.

77. a. Draw a Lewis structure for each of the following:



- b. Draw a structure for each of the species that shows approximate bond angles.
c. Which species have no dipole moment?

78. There are three constitutional isomers with molecular formula $\text{C}_2\text{H}_2\text{Cl}_2$. Draw their structures. Which one does not have a dipole moment?

2

Acids and Bases: Central to Understanding Organic Chemistry

Decades of acid rain have devastated the Norway spruce trees near Hora Svatého Šebestiána in the Czech Republic.



The chemistry in this chapter explains such things as the cause of acid rain and why it destroys monuments and plants, why exercise increases the rate of breathing, how Fosamax prevents bones from being nibbled away, and why blood has to be buffered and how that buffering is accomplished. Acids and bases play an important role in organic chemistry. What you learn about them in this chapter will reappear in almost every other chapter in the book in one form or another. The importance of organic acids and bases will become particularly clear when you learn how and why organic compounds react.

It is hard to believe now, but at one time, chemists characterized compounds by tasting them. Early chemists called any compound that tasted sour an acid (from *acidus*, Latin for “sour”). Some familiar acids are citric acid (found in lemons and other citrus fruits), acetic acid (found in vinegar), and hydrochloric acid (found in stomach acid—the sour taste associated with vomiting).

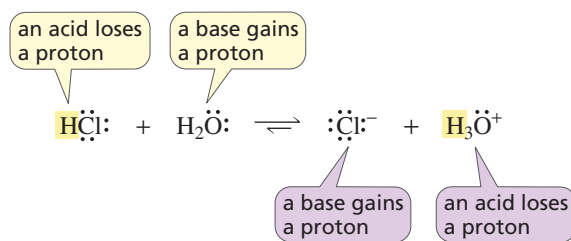
Compounds that neutralize acids, thereby destroying their acidic properties, were called bases, or alkaline compounds. Glass cleaners and solutions designed to unclog drains are familiar alkaline solutions.

2.1 AN INTRODUCTION TO ACIDS AND BASES

We will look at two definitions for the terms *acid* and *base*, the Brønsted–Lowry definitions and the Lewis definitions. We will begin with the Brønsted–Lowry definitions.

According to Brønsted and Lowry, an **acid** is a species that loses a proton, and a **base** is a species that gains a proton. (Remember that positively charged hydrogen ions are called protons.) For

example, in the reaction shown below, hydrogen chloride (HCl) is an acid because it loses a proton, and water is a base because it gains a proton. The reaction of an acid with a base is called an **acid–base reaction** or a **proton transfer reaction**. Notice that the reverse of an acid–base reaction is also an acid–base reaction. In the reverse reaction, H_3O^+ is an acid because it loses a proton, and Cl^- is a base because it gains a proton.

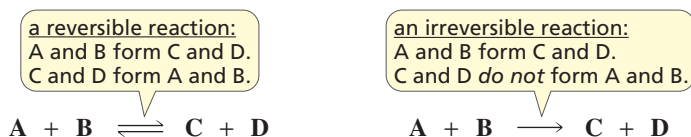


Water can accept a proton because it has two lone pairs, either of which can form a covalent bond with the proton, and Cl^- can accept a proton because any one of its four lone pairs can form a covalent bond with a proton. Thus, according to the Brønsted–Lowry definitions:

Any species that has a hydrogen can potentially act as an acid.

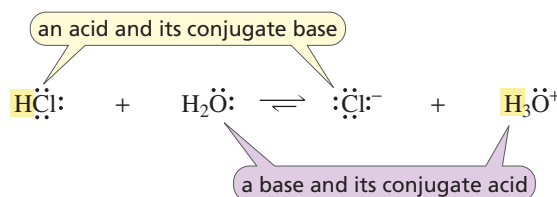
Any species that has a lone pair can potentially act as a base.

Both an acid and a base must be present in an acid–base reaction, because an acid cannot lose a proton unless a base is present to accept it. Most acid–base reactions are **reversible**. Two half-headed arrows are used to designate reversible reactions.



Most acid–base reactions are reversible.

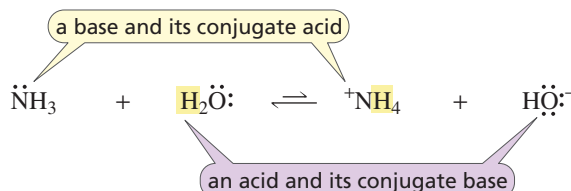
When an acid loses a proton, the resulting species without the proton is called the **conjugate base** of the acid. Thus, Cl^- is the conjugate base of HCl, and H_2O is the conjugate base of H_3O^+ . When a base gains a proton, the resulting species with the proton is called the **conjugate acid** of the base. Thus, HCl is the conjugate acid of Cl^- , and H_3O^+ is the conjugate acid of H_2O .



A conjugate base is formed by removing a proton from an acid.

A conjugate acid is formed by adding a proton to a base.

Another example of an acid–base reaction is the reaction between ammonia and water: ammonia (NH_3) is a base because it gains a proton, and water is an acid because it loses a proton. In the reverse reaction, ammonium ion ($^+\text{NH}_4$) is an acid because it loses a proton, and hydroxide ion (HO^-) is a base because it gains a proton. (In Section 2.5, you will learn why the arrows in these acid–base reactions are not the same length.)



- $^+\text{NH}_4$ is conjugate acid of NH_3 .
- HO^- is conjugate base of H_2O .
- H_2O is conjugate acid of HO^- .
- NH_3 is conjugate base of $^+\text{NH}_4$.

Notice in the first of these two reactions that water is a base and in the second that water is an acid. Water can behave as a base because it has a lone pair, and it can behave as an acid because it

A strong base has a high affinity for a proton.

A weak base has a low affinity for a proton.

has a proton that it can lose. In Section 2.4, we will see how we can predict that water is a base in the first reaction and is an acid in the second reaction.

Acidity is a measure of the tendency of a compound to lose a proton, whereas **basicity** is a measure of a compound's affinity for a proton. A strong acid has a strong tendency to lose a proton. This means that its conjugate base must be weak because it has little affinity for the proton. A weak acid has little tendency to lose its proton, indicating that its conjugate base is strong because it has a high affinity for the proton. Thus, the following important relationship exists between an acid and its conjugate base:

The stronger the acid, the weaker its conjugate base.

For example, HBr is a stronger acid than HCl, so Br^- is a weaker base than Cl^- .

PROBLEM 1 ♦

Which of the following are *not* acids?



PROBLEM 2 ♦

Consider the following reaction:



- What is the acid on the left side of the equation?
- What is the base on the left side of the equation?
- What is the conjugate base of the acid on the left?
- What is the conjugate acid of the base on the left?
- What is the acid on the right side of the equation?
- What is the base on the right side of the equation?
- What is the conjugate base of the acid on the right?
- What is the conjugate acid of the base on the right?

PROBLEM 3 ♦

Draw the products of the acid–base reaction when

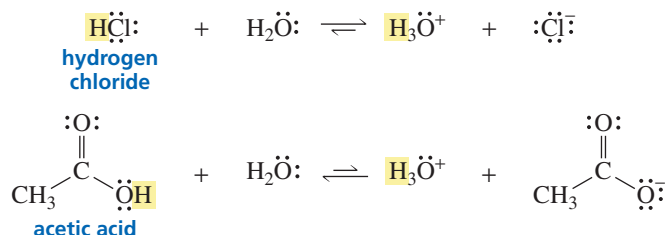
- HCl is the acid and NH_3 is the base.
- H_2O is the acid and NH_2^- is the base.

PROBLEM 4 ♦

- What is the conjugate acid of each of the following?
 - NH_3
 - Cl^-
 - HO^-
 - H_2O
- What is the conjugate base of each of the following?
 - NH_3
 - HBr
 - HNO_3
 - H_2O

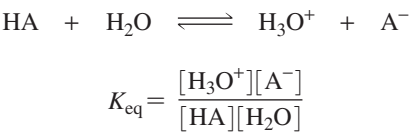
2.2 $\text{p}K_a$ AND pH

When a strong acid such as hydrogen chloride is dissolved in water, almost all the molecules dissociate (break into ions), which means that the *products* are favored at equilibrium—the equilibrium lies to the right. When a much weaker acid, such as acetic acid, is dissolved in water, very few molecules dissociate, so the *reactants* are favored at equilibrium—the equilibrium lies to the left. A longer arrow is drawn toward the species favored at equilibrium.



Defining K_{eq}

The degree to which an acid (HA) dissociates in an aqueous solution is indicated by the **equilibrium constant** of the reaction, K_{eq} . Brackets are used to indicate the concentrations of the reactants and products (in moles/liter).



Defining K_a

The degree to which an acid (HA) dissociates is normally determined in a dilute solution, so the concentration of water remains essentially constant. Combining the two constants (K_{eq} and H_2O) allows the equilibrium expression to be rewritten using a new equilibrium constant, K_a , called the **acid dissociation constant**.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = K_{eq} [H_2O]$$

Thus, the acid dissociation constant is the equilibrium constant multiplied by the molar concentration of water (55.5 M).

Defining pK_a

The larger the acid dissociation constant, the stronger the acid—that is, the greater its tendency to lose a proton. Hydrogen chloride, with an acid dissociation constant of 10^7 , is a stronger acid than acetic acid, with an acid dissociation constant of 1.74×10^{-5} . For convenience, the strength of an acid is generally indicated by its **pK_a** value rather than its K_a value, where

$$pK_a = -\log K_a$$

The pK_a of hydrogen chloride is -7 , and the pK_a of acetic acid, a much weaker acid, is 4.76 . Notice that the stronger the acid, the smaller its pK_a value.

The stronger the acid,
the more readily it loses
a proton.

The stronger the acid,
the smaller its pK_a value.

very strong acids	$pK_a < 1$
moderately strong acids	$pK_a = 1-3$
weak acids	$pK_a = 3-5$
very weak acids	$pK_a = 5-15$
extremely weak acids	$pK_a > 15$

Unless otherwise stated, the pK_a values given in this text indicate the strength of the acid *in water*. Later (in Section 9.14), you will see how the pK_a value of an acid is affected when the solvent is changed.

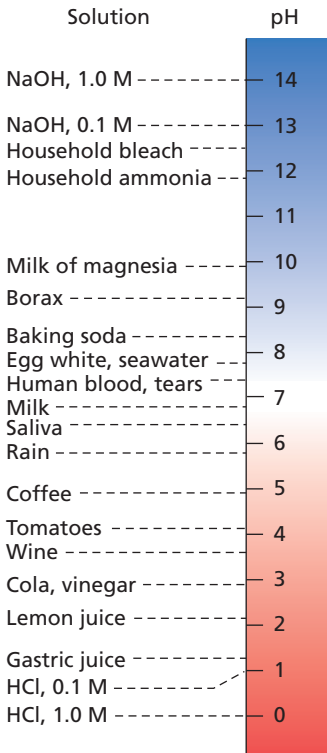
Defining pH

The concentration of protons in a solution is indicated by **pH**. This concentration is written as either $[H^+]$ or, because a proton in water is solvated, as $[H_3O^+]$.

$$pH = -\log [H^+]$$

The pH values of some commonly encountered solutions are shown in the margin. Because pH values decrease as the acidity of the solution increases, we see that lemon juice is more acidic than coffee and that rain is more acidic than milk. Solutions with pH values less than 7 are acidic, whereas those with pH values greater than 7 are basic. The pH of a solution can be changed simply by adding acid or base to the solution.

Do not confuse pH and pK_a . The pH scale is used to describe the acidity of a *solution*, whereas the pK_a indicates the tendency of a compound to lose its proton. Thus, the pK_a is characteristic of a particular compound, much like a melting point or a boiling point.



PROBLEM 5 ♦

- a. Which is a stronger acid: one with a pK_a of 5.2 or one with a pK_a of 5.8?
 b. Which is a stronger acid: one with an acid dissociation constant of 3.4×10^{-3} or one with an acid dissociation constant of 2.1×10^{-4} ?

PROBLEM 6 ♦

An acid has a K_a of 4.53×10^{-6} in water. What is its K_{eq} for reaction with water in a dilute solution? ($[H_2O] = 55.5 \text{ M}$)

LEARN THE STRATEGY

PROBLEM-SOLVING STRATEGY

Determining K_a from pK_a

Vitamin C has a pK_a value of 4.17. What is its K_a value?

You will need a calculator to answer this question. Remember that $pK_a = -\log K_a$. Press the key labeled 10^x ; then enter the negative value of the pK_a and press $=$. You should find that vitamin C has a K_a value of 6.8×10^{-5} .

USE THE STRATEGY

PROBLEM 7

Butyric acid, the compound responsible for the unpleasant odor and taste of sour milk, has a pK_a value of 4.82. What is its K_a value? Is it a stronger acid or a weaker acid than vitamin C?

PROBLEM 8

Antacids are compounds that neutralize stomach acid. Write the equations that show how Milk of Magnesia, Alka-Seltzer, and Tums remove excess acid.

- a. Milk of Magnesia: $Mg(OH)_2$ b. Alka-Seltzer: $KHCO_3$ and $NaHCO_3$ c. Tums: $CaCO_3$

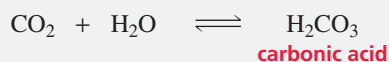
PROBLEM 9 ♦

Are the following body fluids acidic or basic?

- a. bile (pH = 8.4) b. urine (pH = 5.9) c. spinal fluid (pH = 7.4)

Acid Rain

Rain is mildly acidic (pH = 5.5) because water reacts with the CO_2 in the air to form carbonic acid (a weak acid with a pK_a value of 6.4).



In some parts of the world, rain has been found to be much more acidic (pH values as low as 4.3). This so-called acid rain is formed where sulfur dioxide and nitrogen oxides are produced, because water reacts with these gases to form strong acids—sulfuric acid ($pK_a = -5.0$) and nitric acid ($pK_a = -1.3$). Burning fossil fuels for the generation of electric power is the factor most responsible for forming these acid-producing gases.

Acid rain has many deleterious effects. It can destroy aquatic life in lakes and streams; it can make soil so acidic that crops cannot grow and forests are destroyed (see p. 86); and it can cause the deterioration of paint and building materials, including monuments and statues that are part of our cultural heritage. Marble—a form of calcium carbonate—decays because protons react with CO_3^{2-} in the marble to form carbonic acid, which decomposes to CO_2 and H_2O (the reverse of the reaction shown above on the left).

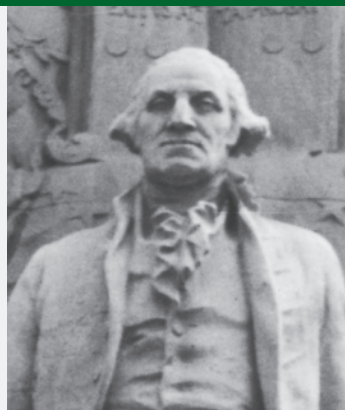
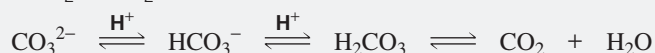


photo taken in 1935

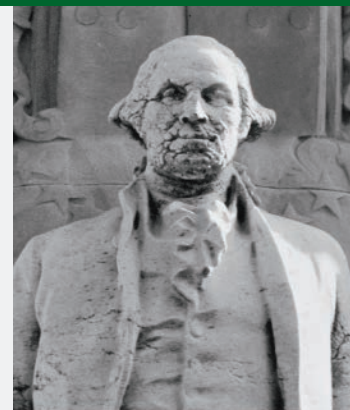


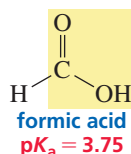
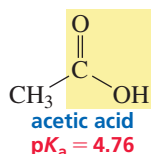
photo taken in 1994

Statue of George Washington in Washington Square Park
in Greenwich Village, New York.

2.3 ORGANIC ACIDS AND BASES

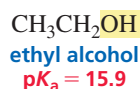
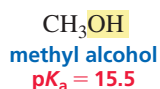
Carboxylic Acids

The most common organic acids are carboxylic acids—compounds that have a COOH group. Acetic acid and formic acid are examples of carboxylic acids. Carboxylic acids have pK_a values ranging from about 3 to 5, so they are weak acids. The pK_a values of a wide variety of organic compounds are listed in Appendix I.



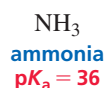
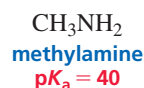
Alcohols

Alcohols—compounds that have an OH group—are much weaker acids than carboxylic acids, with pK_a values close to 16. Methyl alcohol and ethyl alcohol are examples of alcohols. We will see why carboxylic acids are stronger acids than alcohols in Section 2.8.



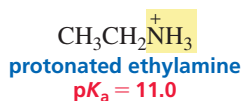
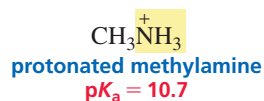
Amines

Amines are compounds that result from replacing one or more of the hydrogens bonded to ammonia with a carbon-containing substituent. Amines and ammonia have such high pK_a values that they rarely behave as acids—they are more likely to act as bases. In fact, they are the most common organic bases. We will see why alcohols are stronger acids than amines in Section 2.6.

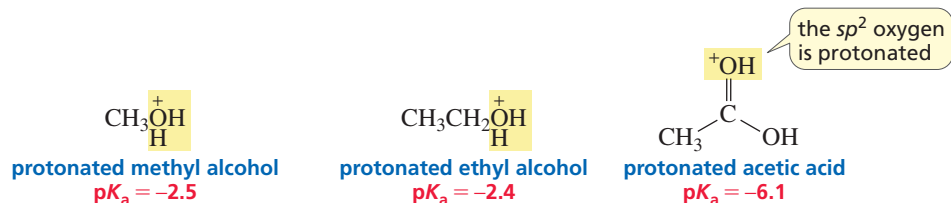


Protonated Compounds

We can assess the strength of a base by considering the strength of its conjugate acid—remembering that *the stronger the acid, the weaker its conjugate base*. For example, based on their pK_a values, protonated methylamine (10.7) is a stronger acid than protonated ethylamine (11.0), which means that methylamine is a weaker base than ethylamine. (A protonated compound is a compound that has gained an additional proton.) Notice that the pK_a values of protonated amines are about 11.



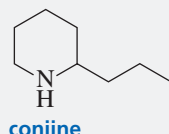
Protonated alcohols and protonated carboxylic acids are very strong acids, with pK_a values < 0 .



Notice that it is the doubly bonded oxygen of the carboxylic acid that is protonated (meaning that it acquires the proton). You will see why this is so when you read the Problem-Solving Strategy on p. 104.

Poisonous Amines

Exposure to poisonous plants is responsible for an average of 63,000 calls each year to poison control centers. Hemlock is an example of a plant known for its toxicity. It contains eight different poisonous amines—the most abundant is coniine, a neurotoxin that disrupts the central nervous system. Ingesting even a small amount can be fatal because it causes respiratory paralysis, which results in oxygen deprivation to the brain and heart. A poisoned person can recover if artificial respiration is applied until the drug is flushed from the system. A drink made of hemlock was used to put Socrates to death in 399 B.C.; he was condemned for failing to acknowledge the gods that the natives of the city of Athens worshipped.



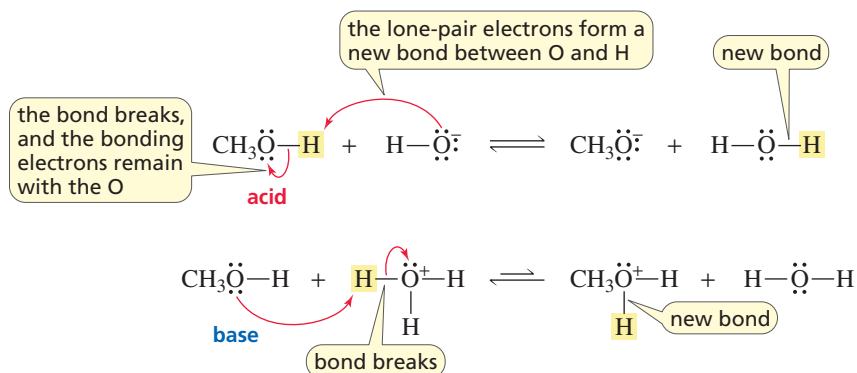
hemlock



Alcohols, Carboxylic Acids, and Amines are Acids and Bases

We saw in Section 2.1 that water can behave as both an acid and a base. An alcohol, too, can behave as an acid and lose a proton, or it can behave as a base and gain a proton.

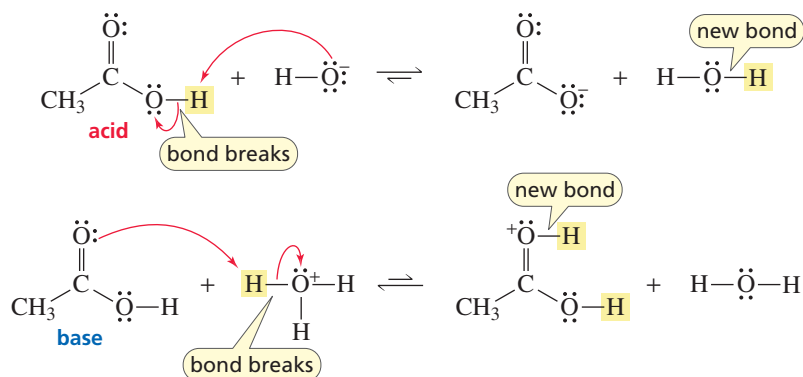
A curved arrow points from the electron donor to the electron acceptor.



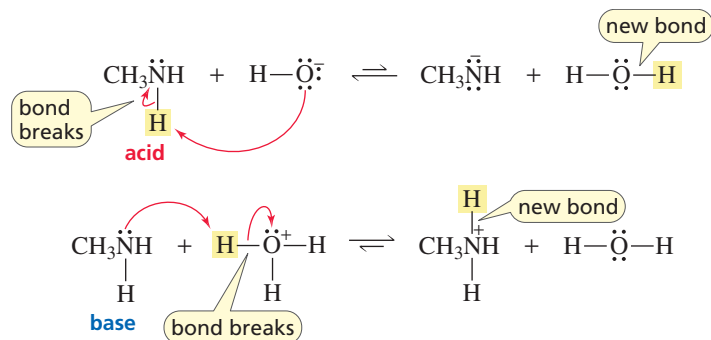
Chemists frequently use curved arrows to indicate the bonds that are broken and formed as reactants are converted into products. They are called *curved arrows* (and are always red in this book) to distinguish them from the *straight* arrows used to link reactants with products in the equation for a chemical reaction. Each curved arrow with a two-barbed arrowhead signifies the movement of two electrons. The arrow always points *from* the electron donor *to* the electron acceptor.

In an acid–base reaction, one of the arrows is drawn *from* a lone pair on the base *to* the proton of the acid. A second arrow is drawn *from* the electrons that the proton shared *to* the atom on which they are left behind. As a result, the curved arrows let you follow the electrons to see what bond is broken and what bond is formed in the reaction.

A carboxylic acid also can behave as an acid (lose a proton) or as a base (gain a proton).



Similarly, an amine can behave as an acid (lose a proton) or as a base (gain a proton).



It is important to know the approximate pK_a values of the various classes of compounds we have looked at. An easy way to remember them is in increments of five, as shown in Table 2.1. (R is used when the particular carboxylic acid, alcohol, or amine is not specified.)

- Protonated alcohols, protonated carboxylic acids, and protonated water have pK_a values less than 0.
- Carboxylic acids have pK_a values of ~ 5 .
- Protonated amines have pK_a values of ~ 10 .
- Alcohols and water have pK_a values of ~ 15 .

Table 2.1 Approximate pK_a Values

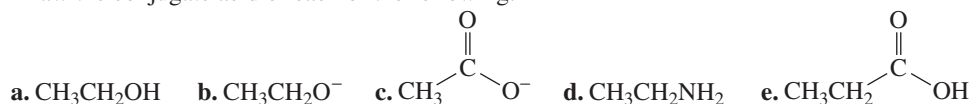
$pK_a < 0$	$pK_a \sim 5$	$pK_a \sim 10$	$pK_a \sim 15$
ROH_2^+ protonated alcohol $\text{R}-\text{C}(\text{OH})_2^+$ protonated carboxylic acid H_3O^+ protonated water	$\text{R}-\text{C}(=\text{O})\text{OH}$ carboxylic acid	RNH_3^+ protonated amine	ROH alcohol H_2O water

NOTE TO THE STUDENT

- You need to remember these approximate pK_a values because they will be very important when you learn about the reactions of organic compounds. These values are also listed on p. 1337 of this book for easy reference.

PROBLEM 10 ♦

Draw the conjugate acid of each of the following:



PROBLEM 11

- Write an equation showing CH_3OH reacting as an acid with NH_3 and an equation showing it reacting as a base with HCl .
- Write an equation showing NH_3 reacting as an acid with CH_3O^- and an equation showing it reacting as a base with HBr .

PROBLEM 12 ♦

Estimate the pK_a values of the following compounds:



LEARN THE STRATEGY

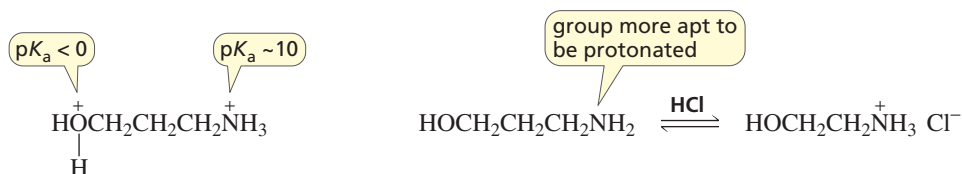
PROBLEM-SOLVING STRATEGY

Determining the Most Basic Atom in a Compound

Which atom of the following compound is more apt to be protonated when an acid is added to a solution of the compound?



An easy way to solve this problem is to look at the $\text{p}K_{\text{a}}$ values of the conjugate acids of the groups, remembering that the weaker acid has the stronger conjugate base. The stronger base is the one more apt to be protonated.



The conjugate acids have $\text{p}K_{\text{a}}$ values of ~ 0 and ~ 10 . Because the $^+\text{NH}_3$ group is the weaker acid, the NH_2 group is the stronger base, so it is the group more apt to be protonated.

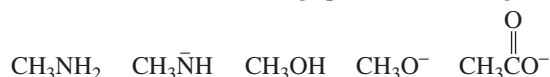
USE THE STRATEGY

PROBLEM 13 ♦

- Which is a stronger base: CH_3COO^- or HCOO^- ? (The $\text{p}K_{\text{a}}$ of CH_3COOH is 4.8; the $\text{p}K_{\text{a}}$ of HCOOH is 3.8.)
- Which is a stronger base: HO^- or $^-\text{NH}_2$? (The $\text{p}K_{\text{a}}$ of H_2O is 15.7; the $\text{p}K_{\text{a}}$ of NH_3 is 36.)
- Which is a stronger base: H_2O or CH_3OH ? (The $\text{p}K_{\text{a}}$ of H_3O^+ is -1.7 ; the $\text{p}K_{\text{a}}$ of CH_3OH_2^+ is -2.5 .)

PROBLEM 14 ♦

Using the $\text{p}K_{\text{a}}$ values in Section 2.3, rank the following species from strongest base to weakest base:



2.4 HOW TO PREDICT THE OUTCOME OF AN ACID-BASE REACTION

Now let's see how to predict that water behaves as a base when it reacts with HCl (the first reaction in Section 2.1) and as an acid when it reacts with NH_3 (the second reaction in Section 2.1). To determine which of two reactants is the acid, we need to compare their $\text{p}K_{\text{a}}$ values.

Reaction of H_2O with HCl

The reactants are water ($\text{p}K_{\text{a}} = 15.7$) and HCl ($\text{p}K_{\text{a}} = -7$). Because HCl is the stronger acid (it has the lower $\text{p}K_{\text{a}}$ value), it is the reactant that loses a proton. Therefore, HCl is the acid and water is the base in this reaction.



Reaction of H_2O with NH_3

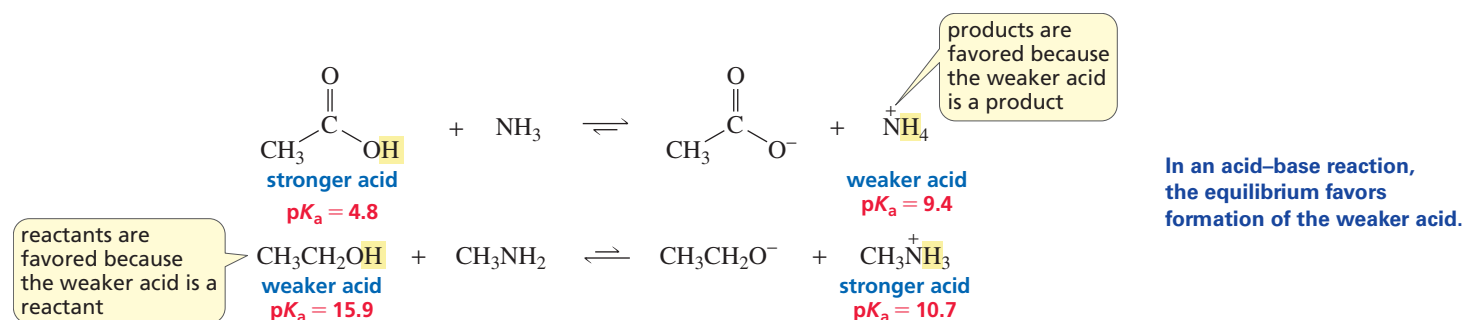
The reactants are water ($\text{p}K_{\text{a}} = 15.7$) and NH_3 ($\text{p}K_{\text{a}} = 36$). Because water is the stronger acid (it has the lower $\text{p}K_{\text{a}}$ value), it is the reactant that loses a proton. Therefore, water is the acid and ammonia is the base in this reaction.

PROBLEM 15 ♦

Does methanol behave as an acid or a base when it reacts with methylamine? (*Hint*: See page 91 for the structures of methanol and methylamine.)

2.5 HOW TO DETERMINE THE POSITION OF EQUILIBRIUM

To determine the position of equilibrium for an acid–base reaction (that is, to determine whether reactants or products are favored), we need to compare the pK_a value of the acid on the left of the equilibrium arrows with the pK_a value of the acid on the right of the arrows. The equilibrium favors *formation* of the weaker acid (the one with the higher pK_a value). In other words, the equilibrium lies toward the weaker acid.



Because the equilibrium favors formation of the weaker acid, we can say that

*an acid–base reaction will favor products
if the conjugate acid of the base that gains the proton
is a weaker acid than the acid that loses a proton in the first place.*

The precise value of the equilibrium constant can be calculated from the following equation:

$$pK_{eq} = pK_a (\text{reactant acid}) - pK_a (\text{product acid})$$

Thus, the equilibrium constant for the reaction of acetic acid with ammonia is 4.0×10^4 .

$$pK_{eq} = 4.8 - 9.4 = -4.6$$

$$K_{eq} = 10^{4.6} = 4.0 \times 10^4$$

And the equilibrium constant for the reaction of ethyl alcohol with methylamine is 6.3×10^{-6} .

$$pK_{eq} = 15.9 - 10.7 = 5.2$$

$$K_{eq} = 10^{-5.2} = 6.3 \times 10^{-6}$$

PROBLEM 16

- For each of the acid–base reactions in Section 2.3, compare the pK_a values of the acids on either side of the equilibrium arrows to prove that the equilibrium lies in the direction indicated. (The pK_a values you need are found in Section 2.3 or in Problem 13.)
- Do the same for the acid–base reactions in Section 2.1.

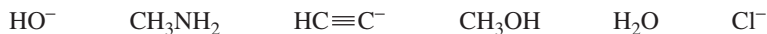
PROBLEM 17

Ethyne ($\text{HC}\equiv\text{CH}$) has a pK_a value of 25, water has a pK_a value of 15.7, and ammonia (NH_3) has a pK_a value of 36. Draw the equation, showing equilibrium arrows that indicate whether reactants or products are favored, for the acid–base reaction of ethyne with

- HO^- .
- NH_2^- .
- Which would be a better base to use if you wanted to remove a proton from ethyne, HO^- or NH_2^- ?

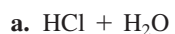
PROBLEM 18 ♦

Which of the following bases can remove a proton from acetic acid in a reaction that favors products?



PROBLEM 19 ♦

Calculate the equilibrium constant for the acid–base reaction between the reactants in each of the following pairs:



2.6 HOW THE STRUCTURE OF AN ACID AFFECTS ITS $\text{p}K_{\text{a}}$ VALUE

Stable bases are weak bases.

The more stable the base,
the stronger its conjugate acid.

The weaker the base,
the stronger its conjugate acid.

The strength of an acid is determined by the stability of the conjugate base that forms when the acid loses its proton: the more stable the conjugate base, the stronger the acid. (The reason for this is explained in Section 5.7.)

A stable base readily bears the electrons it formerly shared with a proton. In other words, stable bases are weak bases—they do not share their electrons well. Thus, we can say:

The weaker the base, the stronger its conjugate acid.

OR

The more stable the base, the stronger its conjugate acid.

Now let's look at two factors that affect the stability of a base—its electronegativity and its size.

Electronegativity

The atoms in the second row of the periodic table are all *similar in size*, but they have very *different electronegativities*, which increase across the row from left to right. Of the atoms shown, carbon is the least electronegative and fluorine is the most electronegative.

relative electronegativities



most
electronegative

If we look at the acids formed by attaching hydrogens to these elements, we see that the most acidic compound is the one that has its hydrogen attached to the most electronegative atom. Thus, HF is the strongest acid and methane is the weakest acid.

*When atoms are similar in size,
the strongest acid has its hydrogen attached to the most electronegative atom.*

relative acidities



strongest
acid

If we look at the stabilities of the conjugate bases of these acids, we find that they, too, increase from left to right, because the more electronegative the atom, the better it bears its negative charge. Thus, *the strongest acid has the most stable (weakest) conjugate base*.

relative stabilities

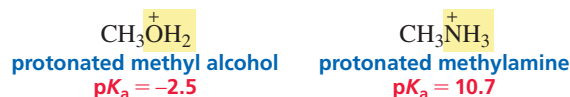


most
stable

The effect that the electronegativity of the atom bonded to a hydrogen has on the compound's acidity can be appreciated when the $\text{p}K_{\text{a}}$ values of alcohols and amines are compared. Because oxygen is more electronegative than nitrogen, an alcohol is more acidic than an amine.



Again, because oxygen is more electronegative than nitrogen, a protonated alcohol is more acidic than a protonated amine.



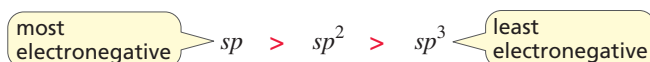
PROBLEM 20 ♦

Rank the ions ($^-\text{CH}_3$, $^-\text{NH}_2$, HO^- , and F^-) from most basic to least basic.

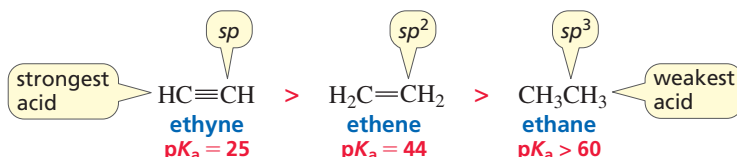
Hybridization

Because hybridization affects electronegativity and electronegativity affects acidity, the hybridization of an atom affects the acidity of the hydrogen bonded to it. An sp hybridized atom is more electronegative than the same atom that is sp^2 hybridized, which is more electronegative than the same atom that is sp^3 hybridized.

relative electronegativities



Therefore, ethyne is a stronger acid than ethene and ethene is a stronger acid than ethane, because the most acidic compound is the one with its hydrogen attached to the most electronegative atom.



Why does the hybridization of the atom affect its electronegativity? Electronegativity is a measure of the ability of an atom to pull the bonding electrons toward itself. Thus, the most electronegative atom is the one with its bonding electrons closest to the nucleus. The average distance of a $2s$ electron from the nucleus is less than the average distance of a $2p$ electron from the nucleus. Therefore, an sp hybridized atom with 50% s character is the most electronegative, an sp^2 hybridized atom (33.3% s character) is next, and an sp^3 hybridized atom (25% s character) is the least electronegative.

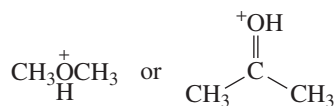
Pulling the electrons closer to the nucleus stabilizes the carbanion. Once again we see that the stronger the acid, the more stable (the weaker) its conjugate base. Notice that the electrostatic potential maps show that the strongest base (the least stable) is the most electron-rich (the most red).

PROBLEM 21 ♦

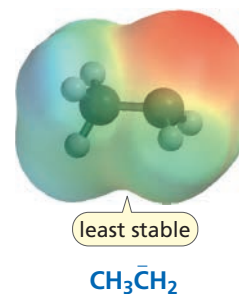
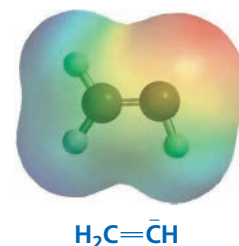
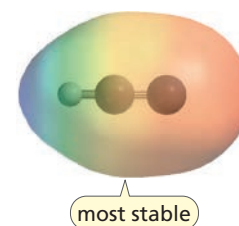
Rank the carbanions shown in the margin from most basic to least basic.

PROBLEM 22 ♦

Which is a stronger acid?

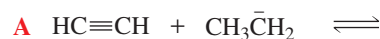


An sp carbon is more electronegative than an sp^2 carbon, which is more electronegative than an sp^3 carbon.



PROBLEM 23

a. Draw the products of the following reactions:



b. Which of the reactions favor formation of the products?

PROBLEM 24

Which reaction in Problem 23 has the smallest equilibrium constant?

Size

Size overrides electronegativity
when determining relative acidities.

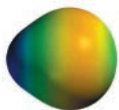
When comparing atoms that are very different in size, the *size* of the atom is more important than its *electronegativity* in determining how well it bears its negative charge. For example, as we proceed down a column in the periodic table, the atoms get larger and the *stability* of the anions *increases* even though the electronegativity of the atoms *decreases*. Because the stability of the bases increases going down the column, the strength of their conjugate acids *increases*. Thus, HI is the strongest acid of the hydrogen halides (that is, I^- is the weakest, most stable base), even though iodine is the least electronegative of the halogens (Table 2.2).

When atoms are very different in size,
the strongest acid has its hydrogen attached to the largest atom.

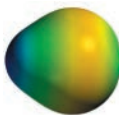
When atoms are very different
in size, the strongest acid
has its hydrogen attached to
the largest atom.



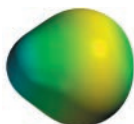
HF



HCl



HBr

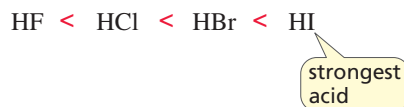


HI

relative size



relative acidities



Why does the size of an atom have such a significant effect on stability that it more than overcomes any difference in electronegativity?

The valence electrons of F^- are in a $2sp^3$ orbital, the valence electrons of Cl^- are in a $3sp^3$ orbital, those of Br^- are in a $4sp^3$ orbital, and those of I^- are in a $5sp^3$ orbital. The volume of space occupied by a $3sp^3$ orbital is significantly larger than the volume of space occupied by a $2sp^3$ orbital because a $3sp^3$ orbital extends out farther from the nucleus. Because its negative charge is spread over a larger volume of space, Cl^- is more stable than F^- .

Thus, as a halide ion increases in size (going down the column of the periodic table), its stability increases because its negative charge is spread over a larger volume of space. As a result, HI is the strongest acid of the hydrogen halides because I^- is the most stable halide ion. The potential maps shown in the margin illustrate the large difference in size of the hydrogen halides.

Table 2.2 The pK_a Values of Some Simple Acids

CH_4 $pK_a = 60$	NH_3 $pK_a = 36$	H_2O $pK_a = 15.7$	HF $pK_a = 3.2$
		H_2S $pK_a = 7.0$	HCl $pK_a = -7$
			HBr $pK_a = -9$
			HI $pK_a = -10$

In summary:

- atomic size does not change much as we move from left to right across a row of the periodic table, so the atoms' orbitals have approximately the same volume. Thus, electronegativity determines the stability of the base and, therefore, the acidity of its conjugate acid.
- atomic size increases as we move down a column of the periodic table, so the volume of the orbitals increases. The volume of an orbital is more important than electronegativity in determining the stability of a base and, therefore, the acidity of its conjugate acid.

LEARN THE STRATEGY

PROBLEM 25 ♦

Rank the halide ions (F^- , Cl^- , Br^- , and I^-) from strongest base to weakest base.

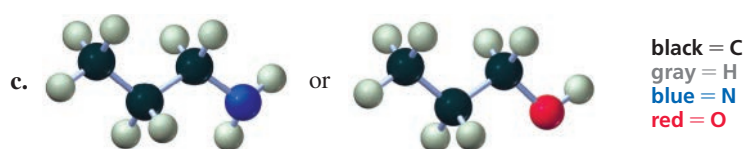
PROBLEM 26 ♦

- Which is more electronegative, oxygen or sulfur?
- Which is a stronger acid, H_2O or H_2S ?
- Which is a stronger acid, CH_3OH or CH_3SH ?

PROBLEM 27 ♦

Which is a stronger acid?

- HCl or HBr
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}_2^+$



- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$

PROBLEM 28 ♦

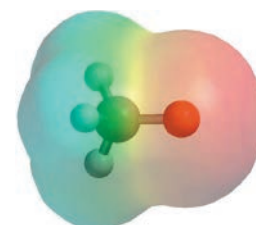
- Which of the halide ions (F^- , Cl^- , Br^- , and I^-) is the most stable base?
- Which is the least stable base?

PROBLEM 29 ♦

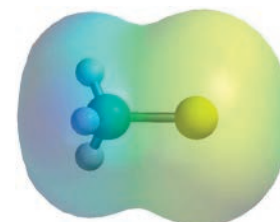
Which is a stronger base? (The potential maps in the margin can help you answer part a.)

- CH_3O^- or CH_3S^-
- H_2O or HO^-
- H_2O or NH_3
- CH_3COO^- or CH_3O^-

USE THE STRATEGY



CH_3O^-

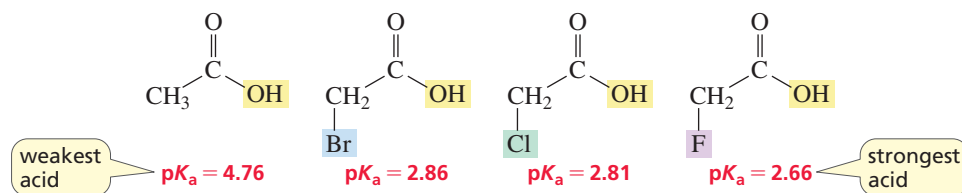


CH_3S^-

2.7 HOW SUBSTITUENTS AFFECT THE STRENGTH OF AN ACID

Although the acidic proton of each of the following carboxylic acids is attached to the same atom (an oxygen), the four compounds have different pK_a values:

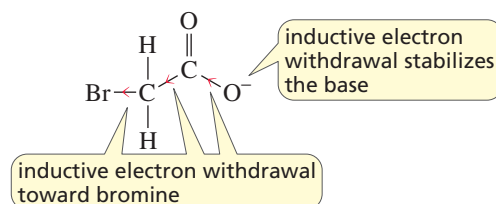
Inductive electron withdrawal increases the strength of an acid.



The different pK_a values indicate that there must be another factor that affects acidity other than the atom to which the hydrogen is bonded.

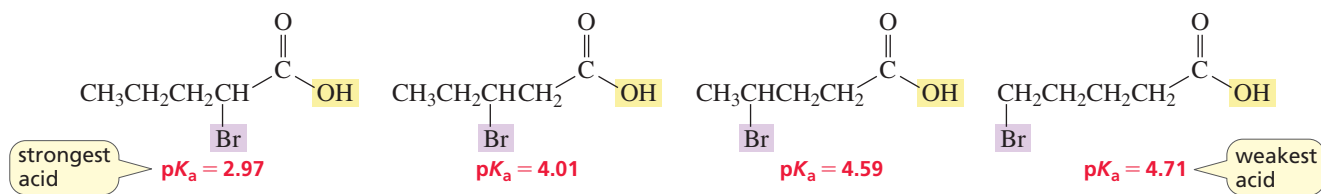
From the pK_a values of the four carboxylic acids, we see that replacing one of the hydrogens of the CH_3 group with a halogen increases the acidity of the compound. (The term for replacing an atom in a compound is *substitution*, and the new atom is called a *substituent*.) The halogen is more electronegative than the hydrogen it has replaced, so the halogen pulls the bonding electrons toward itself more than a hydrogen would. Pulling electrons through sigma (σ) bonds is called **inductive electron withdrawal**.

If we look at the conjugate base of a carboxylic acid, we see that inductive electron withdrawal *decreases the electron density* about the oxygen that bears the negative charge, thereby stabilizing it. And we know that stabilizing a base increases the acidity of its conjugate acid.



The pK_a values of the four carboxylic acids shown above decrease (become more acidic) as the electron-withdrawing ability (electronegativity) of the halogen increases. Thus, the fluoro-substituted compound is the strongest acid because its conjugate base is the most stabilized by inductive electron withdrawal.

As shown below, the effect a substituent has on the acidity of a compound decreases as the distance between the substituent and the acidic proton increases.

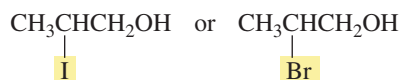


LEARN THE STRATEGY

PROBLEM-SOLVING STRATEGY

Determining Relative Acid Strength

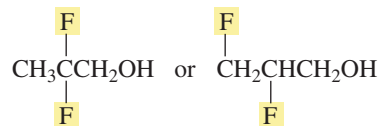
a. Which is a stronger acid?



When you are asked to compare two items, pay attention to where they differ and ignore where they are the same. These two compounds differ only in the halogen that is attached to the middle carbon. Because

bromine is more electronegative than iodine, there is greater inductive electron withdrawal from oxygen in the brominated compound. The brominated compound, therefore, has the more stable conjugate base, so it is the stronger acid.

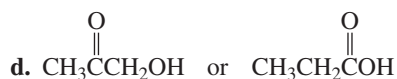
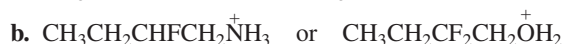
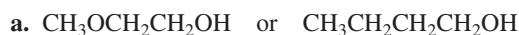
b. Which is a stronger acid?



These two compounds differ in the location of one of the fluorines. Because the second fluorine in the compound on the left is closer to the O—H bond than is the second fluorine in the compound on the right, the compound on the left is more effective at withdrawing electrons from the oxygen. Thus, the compound on the left has the more stable conjugate base, so it is the stronger acid.

PROBLEM 30 ♦

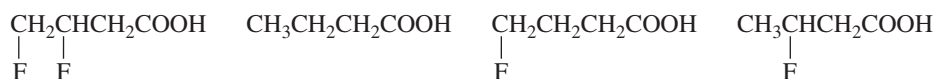
Which is a stronger acid?



USE THE STRATEGY

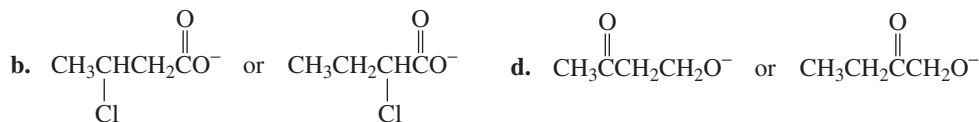
PROBLEM 31 ♦

Rank the following compounds from strongest acid to weakest acid:



PROBLEM 32 ♦

Which is a stronger base?



PROBLEM 33 SOLVED

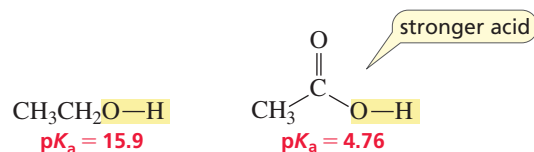
If HCl is a weaker acid than HBr, why is ClCH_2COOH a stronger acid than BrCH_2COOH ?

SOLUTION To compare the acidities of HCl and HBr, we need to compare the stabilities of their conjugate bases, Cl^- and Br^- . (Notice that an H—Cl bond breaks in one compound and an H—Br bond breaks in the other.) Because we know that the size of the atom to which the hydrogen is attached is the most important factor in determining its stability, we know that Br^- is more stable than Cl^- . Therefore, HBr is a stronger acid than HCl.

In comparing the acidities of the two carboxylic acids, we again need to compare the stabilities of their conjugate bases, $\text{ClCH}_2\text{COO}^-$ and $\text{BrCH}_2\text{COO}^-$. (Notice that an O—H bond breaks in both compounds.) The only way the conjugate bases differ is in the electronegativity of the atom that is drawing electrons away from the negatively charged oxygen. Because Cl is more electronegative than Br, Cl exerts greater inductive electron withdrawal. Thus, it has a greater stabilizing effect on the base that is formed when the proton leaves, so the chloro-substituted compound is the stronger acid.

2.8 AN INTRODUCTION TO DELOCALIZED ELECTRONS

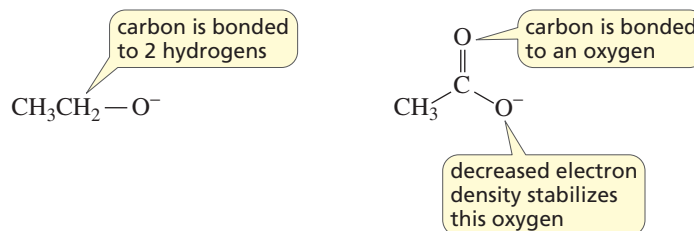
We have seen that a carboxylic acid has a pK_a value of about 5, whereas the pK_a value of an alcohol is about 15. Because a carboxylic acid is a much stronger acid than an alcohol, we know that the conjugate base of a carboxylic acid is considerably more stable than the conjugate base of an alcohol.



Two factors cause the conjugate base of a carboxylic acid to be more stable than the conjugate base of an alcohol.

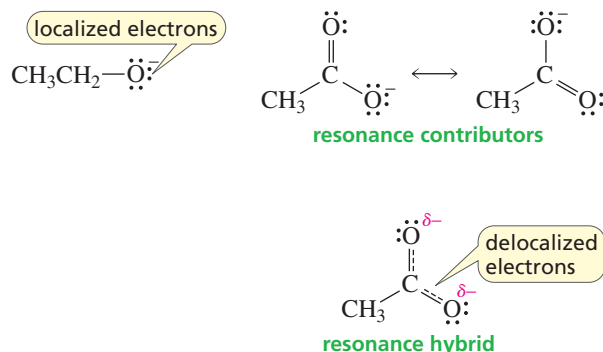
Inductive Electron Withdrawal

The conjugate base of a carboxylic acid has a doubly bonded oxygen where the conjugate base of an alcohol has two hydrogens. Inductive electron withdrawal by this electronegative oxygen decreases the electron density of the negatively charged oxygen, thereby stabilizing it and increasing the acidity of the conjugate acid.



Delocalized Electrons

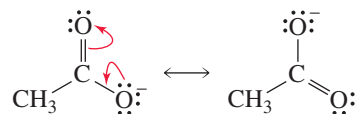
When an alcohol loses a proton, the electrons left behind reside on its single oxygen atom. These electrons are said to be *localized* because they belong to only *one* atom. The negative charge, therefore, resides only on the oxygen atom.



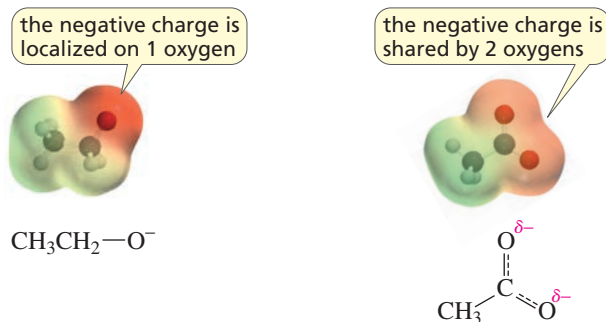
In contrast, when a carboxylic acid loses a proton, the electrons left behind are shared by three atoms—two oxygens and a carbon. These electrons are *delocalized* because they belong to more than two atoms. The negative charge, therefore, is shared by both oxygens. As a result, the conjugate base is stabilized because, as we have seen, decreasing the electron density of an atom stabilizes it.

The two structures shown for the conjugate base of the carboxylic acid are called **resonance contributors**. Neither resonance contributor alone represents the actual structure of the conjugate base—they only approximate the actual structure. Instead, the actual structure—called a **resonance hybrid**—is a composite of the two resonance contributors. The double-headed arrow between the two resonance contributors is used to indicate that the actual structure is a hybrid.

Notice that the second resonance contributor is obtained by moving a lone pair on an atom of the first resonance contributor toward an sp^2 carbon and breaking the π bond. Thus, the two resonance contributors differ only in the location of their π electrons and lone-pair electrons—all the atoms stay in the same place.



The negative charge is shared equally by the two oxygens, and both carbon–oxygen bonds are the same length—they are not as long as a single bond, but they are longer than a double bond. The resonance hybrid is drawn using dotted lines to show the delocalized electrons. We see that in the resonance hybrid, an electron pair is spread over *two oxygens and a carbon*.



Delocalized electrons are shared by more than two atoms.

Thus, the combination of inductive electron withdrawal and the ability of two atoms to share the negative charge makes the conjugate base of the carboxylic acid more stable than the conjugate base of the alcohol.

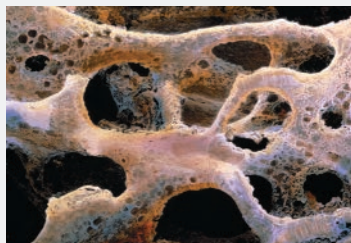
Delocalized electrons are very important in organic chemistry—so important that all of Chapter 8 is devoted to them. By that time, you will be thoroughly comfortable with compounds that have only localized electrons, and we can then further explore how to recognize when a compound has delocalized electrons and how delocalized electrons affect the stability, reactivity, and pK_a values of organic compounds.

Fosamax Prevents Bones from Being Nibbled Away

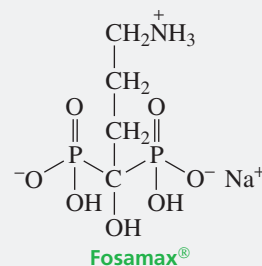
Fosamax is used to treat osteoporosis, a condition characterized by decreased bone density. Under normal conditions, the rate of bone formation and the rate of bone resorption (breakdown) are carefully matched. In osteoporosis, resorption is faster than formation, so bone is nibbled away, causing bones to become fragile (they actually start to resemble honeycombs). Fosamax goes specifically to the sites of bone resorption and inhibits the activity of cells responsible for resorption. Studies have shown that normal bone is then formed on top of Fosamax, and the rate of bone formation becomes faster than the rate of its breakdown. (Trade name labels in this book are green.)



normal bone



bone with osteoporosis



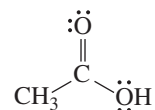
Fosamax®

LEARN THE STRATEGY

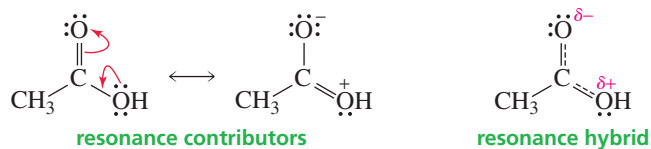
PROBLEM-SOLVING STRATEGY

Determining the Site of Protonation in a Compound with Delocalized Electrons

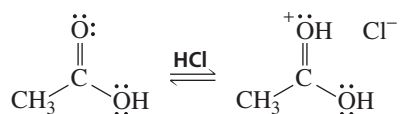
Which atom in the following compound is more apt to be protonated when an acid is added to a solution of the compound?



In the Problem-Solving Strategy on p. 94, you learned that when a compound has two basic atoms, the one that is the stronger base is the one more apt to be protonated in an acidic solution. When a compound has delocalized electrons, you need to draw its resonance contributors to determine which atom is the stronger base.



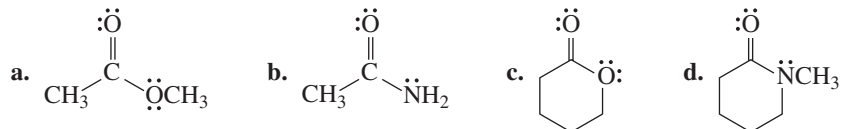
One of the resonance contributors has a negative charge on one of the oxygens and a positive charge on the other. Therefore, those oxygens in the resonance hybrid have a partial negative charge and a partial positive charge, respectively. The oxygen with the partial negative charge is the stronger base, so it is the oxygen that is more apt to be protonated in an acidic solution.



USE THE STRATEGY

PROBLEM 34

For each of the following compounds, indicate the atom that is protonated when an acid is added to a solution of the compound.



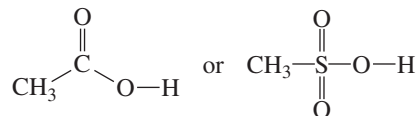
PROBLEM 35 ♦

Draw resonance contributors for each of the following:



PROBLEM 36 ♦

Which is a stronger acid? Why?



PROBLEM 37

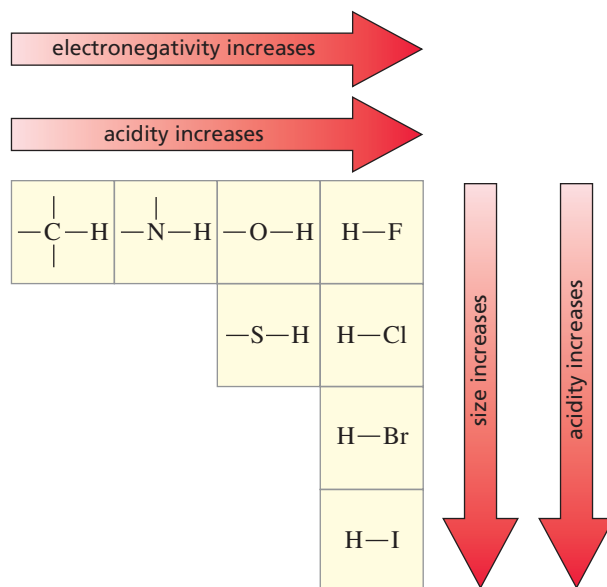
Fosamax (shown on the previous page) has six acidic groups. The active form of the drug, which has lost two of its acidic protons, is shown in the box. (Notice that the phosphorus atom in Fosamax and the sulfur atom in Problem 36 can be surrounded by more than eight electrons because P and S are below the second row of the periodic table.)

- Why are the OH groups bonded to phosphorus the strongest acids of the six groups?
- Which of the remaining four groups is the weakest acid?

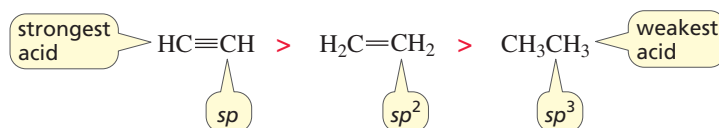
2.9 A SUMMARY OF THE FACTORS THAT DETERMINE ACID STRENGTH

We have seen that the strength of an acid depends on five factors: the *size* of the atom to which the hydrogen is attached, the *electronegativity* of the atom to which the hydrogen is attached, the *hybridization* of the atom to which the hydrogen is attached, *inductive electron withdrawal*, and *electron delocalization*. All five factors affect acidity by affecting the stability of the conjugate base.

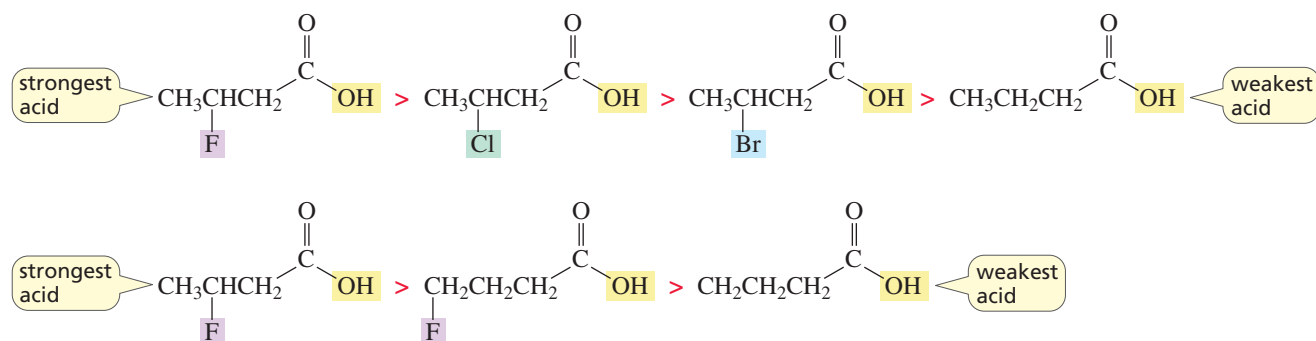
- 1. Size:** As the atom attached to the hydrogen increases in size (going down a column of the periodic table), the strength of the acid increases.
- 2. Electronegativity:** As the atom attached to the hydrogen increases in electronegativity (going from left to right across a row of the periodic table), the strength of the acid increases.



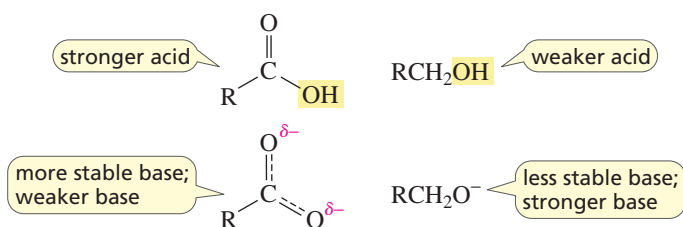
- 3. Hybridization:** The electronegativity of an atom changes with hybridization as follows: $sp > sp^2 > sp^3$. Because an sp carbon is the most electronegative, a hydrogen attached to an sp carbon is the most acidic, and a hydrogen attached to an sp^3 carbon is the least acidic.



- 4. Inductive electron withdrawal:** An electron-withdrawing group increases the strength of an acid. As the electronegativity of the electron-withdrawing group increases or as it moves closer to the acidic hydrogen, the strength of the acid increases.



- 5. Electron delocalization:** An acid whose conjugate base has delocalized electrons is more acidic than a similar acid whose conjugate base has only localized electrons.

**PROBLEM 38** ♦

Using the table of $\text{p}K_{\text{a}}$ values given in Appendix I, answer the following:

- Which is the most acidic organic compound in the table?
- Which is the least acidic organic compound in the table?
- Which is the most acidic carboxylic acid in the table?
- Which is more electronegative: an sp^3 oxygen or an sp^2 oxygen? (*Hint:* Pick a compound in Appendix I with a hydrogen attached to an sp^2 oxygen and one with a hydrogen attached to an sp^3 oxygen and compare their $\text{p}K_{\text{a}}$ values.)
- Which compounds demonstrate that the relative electronegativities of a hybridized nitrogen atom are $sp > sp^2 > sp^3$?

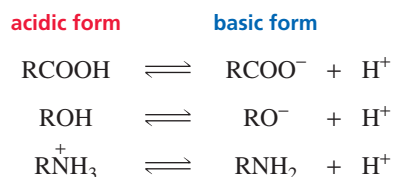
2.10 HOW pH AFFECTS THE STRUCTURE OF AN ORGANIC COMPOUND

Whether a given acid loses a proton in an aqueous solution depends on both the $\text{p}K_{\text{a}}$ of the acid and the pH of the solution. The relationship between the two is given by the **Henderson–Hasselbalch equation**. (Its derivation is on pp. 108–109.)

the Henderson–Hasselbalch equation

$$\text{p}K_{\text{a}} = \text{pH} + \log \frac{[\text{HA}]}{[\text{A}^-]}$$

This is an extremely useful equation because it tells us whether a compound exists in its acidic form (with its proton retained) or in its basic form (with its proton removed) at a particular pH. Knowing this will be important when we are assessing the reactivity of organic compounds.



The Henderson–Hasselbalch equation tells us

- when the pH of a solution equals the $\text{p}K_{\text{a}}$ of the compound that undergoes dissociation, the concentration of the compound in its acidic form (HA) equals the concentration of the compound in its basic form (A^-) (because $\log 1 = 0$).
- when the pH of the solution is less than the $\text{p}K_{\text{a}}$ of the compound, the compound exists primarily in its acidic form.
- when the pH of the solution is greater than the $\text{p}K_{\text{a}}$ of the compound, the compound exists primarily in its basic form.

In other words,

compounds exist primarily in their acidic forms in solutions that are more acidic than their $\text{p}K_{\text{a}}$ values and primarily in their basic forms in solutions that are more basic than their $\text{p}K_{\text{a}}$ values.

A compound exists primarily in its acidic form (HA) when the pH of the solution is less than the compound's $\text{p}K_{\text{a}}$ value.

A compound exists primarily in its basic form (A^-) when the pH of the solution is greater than the compound's $\text{p}K_{\text{a}}$ value.

PROBLEM-SOLVING STRATEGY

Determining the Structure at a Particular pH

Write the form of the compound that predominates in a solution with a pH = 5.5.

- a. $\text{CH}_3\text{CH}_2\text{OH}$ ($\text{p}K_a = 15.9$) b. $\text{CH}_3\text{CH}_2\text{OH}_2^+$ ($\text{p}K_a = -2.5$) c. CH_3NH_3^+ ($\text{p}K_a = 11.0$)

To answer this question, we need to compare the pH of the solution with the $\text{p}K_a$ value of the compound's dissociable proton.

- a. The pH of the solution is more acidic (5.5) than the $\text{p}K_a$ value of the compound (15.9). Therefore, the compound exists primarily as $\text{CH}_3\text{CH}_2\text{OH}$ (with its proton).
 b. The pH of the solution is more basic (5.5) than the $\text{p}K_a$ value of the compound (-2.5). Therefore, the compound exists primarily as $\text{CH}_3\text{CH}_2\text{OH}$ (without its proton).
 c. The pH of the solution is more acidic (5.5) than the $\text{p}K_a$ value of the compound (11.0). Therefore, the compound exists primarily as CH_3NH_3^+ (with its proton).

LEARN THE STRATEGY

PROBLEM 39 ♦

For each of the following compounds (here shown in their acidic forms), write the form that predominates in a solution with a pH = 5.5:

- a. CH_3COOH ($\text{p}K_a = 4.76$) d. HBr ($\text{p}K_a = -9$) g. HNO_2 ($\text{p}K_a = 3.4$)
 b. $\text{CH}_3\text{CH}_2\text{NH}_3^+$ ($\text{p}K_a = 11.0$) e. $^+\text{NH}_4$ ($\text{p}K_a = 9.4$) h. HNO_3 ($\text{p}K_a = -1.3$)
 c. H_3O^+ ($\text{p}K_a = -1.7$) f. $\text{HC}\equiv\text{N}$ ($\text{p}K_a = 9.1$) i. HONH_3^+ ($\text{p}K_a = 6.0$)

USE THE STRATEGY

PROBLEM 40 ♦

As long as the pH is not less than _____, at least 50% of a protonated amine with a $\text{p}K_a$ value of 10.4 will be in its neutral, nonprotonated form.

PROBLEM 41 SOLVED

Indicate whether a carboxylic acid (RCOOH) with a $\text{p}K_a$ value of 4.5 has more charged molecules or more neutral molecules in a solution with the following pH:

1. pH = 1 2. pH = 3 3. pH = 5 4. pH = 7 5. pH = 10 6. pH = 13

SOLUTION First determine whether the compound is charged or neutral in its acidic form and charged or neutral in its basic form: a carboxylic acid is neutral in its acidic form (RCOOH) and charged in its basic form (RCOO^-). Then compare the pH and $\text{p}K_a$ values and remember that when the pH of the solution is less than the $\text{p}K_a$ value of the compound, then more molecules are in the acidic form, but when the pH is greater than the $\text{p}K_a$ value of the compound, then more molecules are in the basic form. Therefore, at pH = 1 and 3, there are more neutral molecules in the solution, and at pH = 5, 7, 10, and 13, there are more charged molecules in the solution.

LEARN THE STRATEGY

You are what you're in:
 a compound is mostly in the acidic form in an acidic solution ($\text{pH} < \text{p}K_a$) and mostly in the basic form in a basic solution ($\text{pH} > \text{p}K_a$).

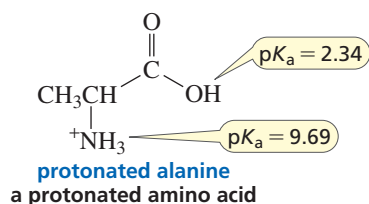
PROBLEM 42 ♦

- a. Indicate whether a protonated amine (RNH_3^+) with a $\text{p}K_a$ value of 9 has more charged or more neutral molecules in a solution with the pH values given in Problem 41.
 b. Indicate whether an alcohol (ROH) with a $\text{p}K_a$ value of 15 has more charged or more neutral molecules in a solution with the pH values given in Problem 41.

USE THE STRATEGY

PROBLEM 43

A naturally occurring amino acid such as alanine has a group that is a carboxylic acid and a group that is a protonated amine. The $\text{p}K_a$ values of the two groups are shown.



- a. If the $\text{p}K_a$ value of a carboxylic acid such as acetic acid is about 5 (see Table 2.1), then why is the $\text{p}K_a$ value of the carboxylic acid group of alanine so much lower?
 b. Draw the structure of alanine in a solution at pH = 0.
 c. Draw the structure of alanine in a solution at physiological pH (pH 7.4).

- d. Draw the structure of alanine in a solution at $\text{pH} = 12$.
- e. Is there a pH at which alanine is uncharged (that is, neither group has a charge)?
- f. At what pH does alanine have no net charge (that is, the amount of negative charge is the same as the amount of positive charge)?

If we know the pH of the solution and the $\text{p}K_{\text{a}}$ of the compound, the Henderson–Hasselbalch equation makes it possible to calculate precisely how much of the compound is in its acidic form and how much is in its basic form.

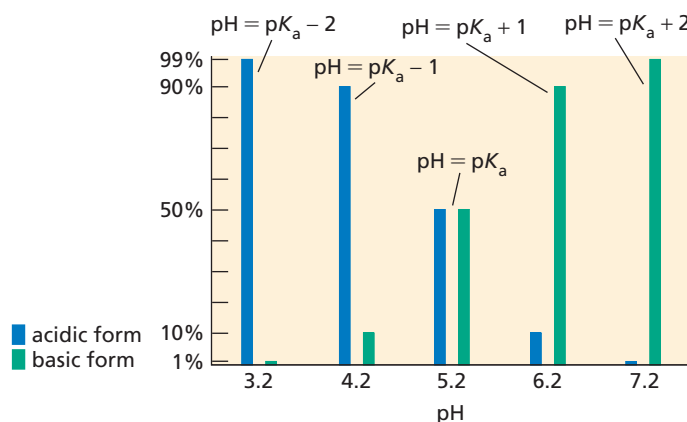
For example, when a compound with a $\text{p}K_{\text{a}}$ of 5.2 is in a solution of pH 5.2, half the compound is in the acidic form and the other half is in the basic form (Figure 2.1). When the pH is one unit less than the $\text{p}K_{\text{a}}$ of the compound ($\text{pH} = 4.2$), there is 10 times more compound present in the acidic form than in the basic form (because $\log 10 = 1$).

$$5.2 = 4.2 + \log \frac{[\text{HA}]}{[\text{A}^-]}$$

$$1.0 = \log \frac{[\text{HA}]}{[\text{A}^-]} = \log \frac{10}{1}$$

When the pH is two units less than the $\text{p}K_{\text{a}}$ of the compound ($\text{pH} = 3.2$), there is 100 times more compound present in the acidic form than in the basic form (because $\log 100 = 2$).

Now consider pH values that are greater than the $\text{p}K_{\text{a}}$ value: when the pH is 6.2, there is 10 times more compound in the basic form than in the acidic form, and at $\text{pH} = 7.2$, there is 100 times more compound present in the basic form than in the acidic form.



► **Figure 2.1**

The relative amounts of a compound with a $\text{p}K_{\text{a}}$ of 5.2 in the acidic and basic forms at different pH values.

Derivation of the Henderson–Hasselbalch Equation

The Henderson–Hasselbalch equation can be derived from the expression that defines the acid dissociation constant:

$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Take the logarithms of both sides of the equation remembering that when expressions are multiplied, their logs are added. Thus, we obtain

$$\log K_{\text{a}} = \log [\text{H}_3\text{O}^+] + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Multiplying both sides of the equation by -1 gives us

$$-\log K_{\text{a}} = -\log [\text{H}_3\text{O}^+] - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Substituting pK_a for $-\log K_a$, substituting pH for $-\log [H_3O^+]$, and inverting the fraction (which means the sign of its log changes), we get

$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

PROBLEM 44 SOLVED

- a. At what pH is the concentration of a compound, with a $pK_a = 8.4$, 100 times greater in its basic form than in its acidic form?
- b. At what pH is the concentration of a compound, with a $pK_a = 3.7$, 10 times greater in its acidic form than in its basic form?

SOLUTION 44 a. If the concentration in the basic form is 100 times greater than the concentration in the acidic form, then the Henderson–Hasselbalch equation becomes

$$\begin{aligned} pK_a &= pH + \log 1/100 \\ 8.4 &= pH + \log 0.01 \\ 8.4 &= pH - 2.0 \\ pH &= 10.4 \end{aligned}$$

There is a faster way to get the answer: if 100 times more compound is present in the basic form than in the acidic form, then the pH will be two units more basic than the pK_a value. Thus, $pH = 8.4 + 2.0 = 10.4$.

SOLUTION 44 b. If 10 times more compound is present in the acidic form than in the basic form, then the pH will be one unit more acidic than the pK_a value. Thus, $pH = 3.7 - 1.0 = 2.7$.

PROBLEM 45 ♦

- a. At what pH is the concentration of a compound, with a $pK_a = 8.4$, 100 times greater in its acidic form than in its basic form?
- b. At what pH is 50% of a compound, with a $pK_a = 7.3$, in its basic form?
- c. At what pH is the concentration of a compound, with a $pK_a = 4.6$, 10 times greater in its basic form than in its acidic form?

PROBLEM 46 ♦

For each of the following compounds, indicate the pH at which

- a. 50% of the compound is in a form that possesses a charge.
- b. more than 99% of the compound is in a form that possesses a charge.
1. CH_3CH_2COOH ($pK_a = 4.9$) 2. $CH_3NH_3^+$ ($pK_a = 10.7$)

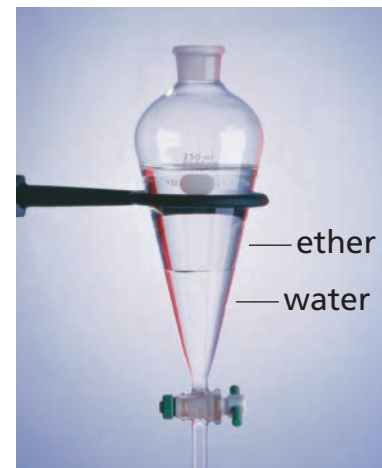
LEARN THE STRATEGY**USE THE STRATEGY**

The Henderson–Hasselbalch equation is very useful in the laboratory for separating compounds in a mixture. Water and diethyl ether are barely soluble in each other, so they form two layers when combined. Diethyl ether is less dense than water, so the ether layer lies above the water layer.

- Charged compounds are more soluble in water than in diethyl ether.
- Uncharged compounds are more soluble in diethyl ether than in water (Section 3.10).

Two compounds, such as a carboxylic acid ($RCOOH$) with a $pK_a = 5.0$ and a protonated amine (RNH_3^+) with a $pK_a = 10.0$, dissolved in a mixture of water and diethyl ether, can be separated by adjusting the pH of the water layer. For example, if the pH of the water layer is 2, then the carboxylic acid and the protonated amine are both in their acidic forms because the pH of the water is less than the pK_a values of both compounds. The acidic form of a carboxylic acid is not charged, whereas the acidic form of an amine is charged. Therefore, the uncharged carboxylic acid dissolves in the ether layer, and the positively charged protonated amine dissolves in the water layer.

For the most effective separation, the pH of the water layer should be at least two units away from the pK_a values of the compounds being separated. Then the relative amounts of the compounds in their acidic and basic forms will be at least 100:1 (Figure 2.1).



LEARN THE STRATEGY

PROBLEM 47 ♦ SOLVED

Given that $\text{C}_6\text{H}_{11}\text{COOH}$ has a $\text{p}K_{\text{a}} = 4.8$ and $\text{C}_6\text{H}_{11}\text{NH}_3^+$ has a $\text{p}K_{\text{a}} = 10.7$, what pH would you make the water layer to cause both compounds to dissolve in it?

SOLUTION The compounds must be charged to dissolve in the water layer. The carboxylic acid is charged in its basic form—it is a carboxylate ion. For $> 99\%$ of the carboxylic acid to be in its basic form, the pH must be two units *greater* than the $\text{p}K_{\text{a}}$ of the compound. Thus, the water should have a $\text{pH} > 6.8$. The amine is charged in its acidic form—it will be an ammonium ion. For $> 99\%$ of the amine to be in its acidic form, the pH must be two units *less* than the $\text{p}K_{\text{a}}$ value of the ammonium ion. Thus, the water should have a $\text{pH} < 8.7$. Both compounds will dissolve in the water layer if its pH is 6.8–8.7. A pH in the middle of the range (for example, $\text{pH} = 7.7$) is a good choice.

USE THE STRATEGY

PROBLEM 48 ♦

Given the data in Problem 47:

- What pH would you make the water layer to cause the carboxylic acid to dissolve in the water layer and the amine to dissolve in the ether layer?
- What pH would you make the water layer to cause the carboxylic acid to dissolve in the ether layer and the amine to dissolve in the water layer?

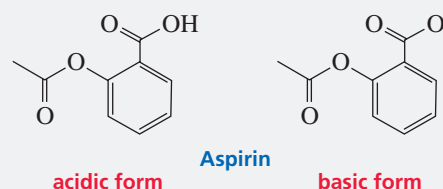
Aspirin Must Be in Its Basic Form to Be Physiologically Active

Aspirin has been used to treat fever, mild pain, and inflammation since it first became commercially available in 1899. It was the first drug to be tested clinically before it was marketed (Section 7.0). Currently one of the most widely used drugs in the world, aspirin is one of a group of over-the-counter drugs known as NSAIDs (nonsteroidal anti-inflammatory drugs).

Aspirin is a carboxylic acid. When we look at the reaction responsible for its fever-reducing, pain-reducing, and anti-inflammatory properties in Section 15.9, we will see that the carboxylic acid group must be in its basic form to be physiologically active.

The carboxylic acid group has a $\text{p}K_{\text{a}}$ value of ~ 5 . Therefore, it is in its acidic form while it is in the stomach ($\text{pH} = 1\text{--}2.5$). The uncharged acidic form can pass through membranes easily, whereas the negatively charged basic form cannot. Once the drug is in the cell ($\text{pH} 7.4$), it is in its active basic form and, therefore, is able to carry out the reaction that reduces fever, pain, and inflammation.

The undesirable side effects of aspirin (ulcers, stomach bleeding) led to the development of other NSAIDs (p. 150). Aspirin also has been linked to the development of Reye's syndrome, a rare but serious disease that affects children who are recovering from a viral infection such as a cold, the flu, or chicken pox. Therefore, it is now recommended that aspirin not be given to anyone under the age of 16 who has a fever-producing illness.



2.11 BUFFER SOLUTIONS

A solution of a weak acid (HA) and its conjugate base (A^-) is called a **buffer solution**. The components of three different buffer solutions are shown here.

acetic acid/sodium acetate	formic acid/sodium formate	methylammonium chloride/methylamine
CH_3COOH	HCOOH	$\text{CH}_3\text{NH}_3^+ \text{Cl}^-$
$\text{CH}_3\text{COO}^- \text{Na}^+$	$\text{HCOO}^- \text{Na}^+$	CH_3NH_2

A buffer solution maintains nearly constant pH when small amounts of acid or base are added to it, because the weak acid can give a proton to any HO^- added to the solution and its conjugate base can accept any H^+ that is added to the solution.

can give a proton to HO^-



can accept a proton from H_3O^+

PROBLEM 49 ♦

Write the equation that shows how a buffer made by dissolving CH_3COOH and $\text{CH}_3\text{COO}^-\text{Na}^+$ in water prevents the pH of a solution from changing appreciably when

- a small amount of H^+ is added to the solution.
- a small amount of HO^- is added to the solution.

PROBLEM 50 SOLVED

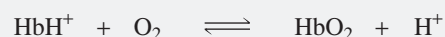
You are planning to carry out a reaction that produces hydroxide ion. For the reaction to take place at a constant pH, it will be buffered at $\text{pH} = 4.2$. Would it be better to use a formic acid/formate buffer or an acetic acid/acetate buffer? (Note: The $\text{p}K_a$ of formic acid = 3.75 and the $\text{p}K_a$ of acetic acid = 4.76.)

SOLUTION Constant pH is maintained because the hydroxide ion produced in the reaction removes a proton from the acidic form of the buffer. Thus, the better choice of buffer is the one that has the highest concentration of buffer in the acidic form at $\text{pH} = 4.2$. Because formic acid's $\text{p}K_a$ is 3.75, the majority of the buffer is in the basic form at $\text{pH} = 4.2$. Acetic acid, with $\text{p}K_a = 4.76$, has more buffer in the acidic form than in the basic form. Therefore, it is better to use acetic acid/acetate buffer for your reaction.

Blood: A Buffered Solution

Blood is the fluid that transports oxygen to all the cells of the human body. The normal pH of human blood is ~ 7.4 . Death results if this pH decreases to less than ~ 6.8 or increases to greater than ~ 8.0 for even a few seconds.

Oxygen is carried to cells by a protein in the blood called hemoglobin (HbH^+). When hemoglobin binds O_2 , hemoglobin loses a proton, which would make the blood more acidic if it did not contain a buffer to maintain its pH.

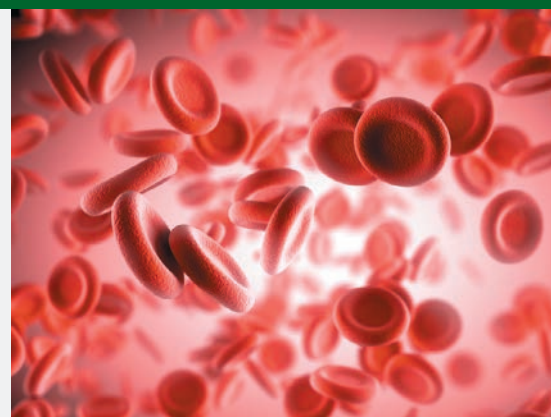


A carbonic acid/bicarbonate ($\text{H}_2\text{CO}_3/\text{HCO}_3^-$) buffer controls the pH of blood. An important feature of this buffer is that carbonic acid decomposes to CO_2 and H_2O , as shown below:



During exercise, our metabolism speeds up, producing large amounts of CO_2 . The increased concentration of CO_2 shifts the equilibrium between carbonic acid and bicarbonate to the left, which increases the concentration of H^+ . Significant amounts of lactic acid are also produced during exercise, which further increases the concentration of H^+ . Receptors in the brain respond to the increased concentration of H^+ by triggering a reflex that increases the rate of breathing. Hemoglobin then releases more oxygen to the cells, and more CO_2 is eliminated by exhalation. Both processes decrease the concentration of H^+ in the blood by shifting the equilibrium of the top reaction to the left and the equilibrium of the bottom reaction to the right.

Thus, any disorder that decreases the rate and depth of ventilation, such as emphysema, decreases the pH of the blood—a condition called acidosis. In contrast, any excessive increase in the rate and depth of ventilation, as with hyperventilation due to anxiety, increases the pH of blood—a condition called alkalosis.



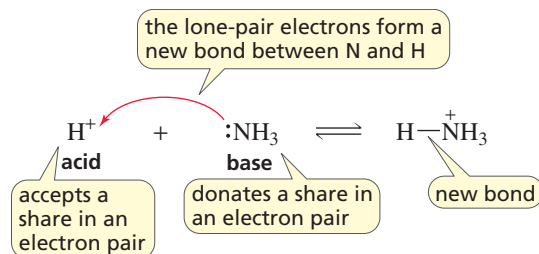
2.12 LEWIS ACIDS AND BASES

In 1923, G. N. Lewis offered new definitions for the terms acid and base. He defined

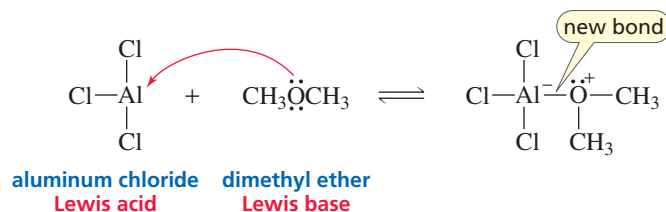
*an acid as a species that accepts a share in an electron pair and
a base as a species that donates a share in an electron pair.*

All Brønsted-Lowry (proton-donating) acids fit the Lewis definition because all proton-donating acids lose a proton and the proton accepts a share in an electron pair.

Remember that curved arrows show where the electrons start from and where they end up.

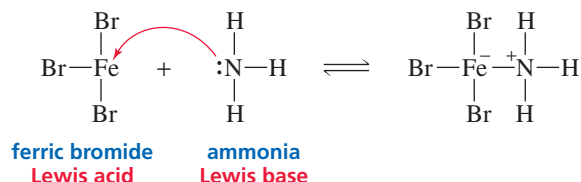


Lewis acids, however, are not limited to compounds that lose protons. Compounds such as aluminum chloride (AlCl_3), ferric bromide (FeBr_3), and borane (BH_3) are acids according to the Lewis definition because they have unfilled valence orbitals that can accept a share in an electron pair. These compounds react with a compound that has a lone pair, just as a proton reacts with a compound that has a lone pair.



Lewis acid: Need two from you.

Lewis base: Have pair, will share.

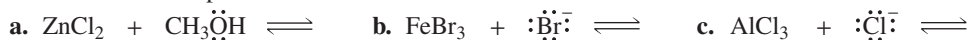


Thus, the Lewis definition of an acid includes all proton-donating compounds and some additional compounds that do not have protons. Throughout this text, the term *acid* is used to mean a proton-donating acid, and the term **Lewis acid** is used to refer to non-proton-donating acids such as AlCl_3 and BF_3 .

All bases are **Lewis bases** because they all have a pair of electrons that they can share, either with a proton or with an atom such as aluminum, boron, or iron.

PROBLEM 51

Draw the products of the following reactions. Use curved arrows to show where the pair of electrons starts and where it ends up.



PROBLEM 52

What products are formed when each of the following reacts with HO^- ?



ESSENTIAL CONCEPTS

Section 2.1

- An **acid** is a species that loses a proton; a **base** is a species that gains a proton.
- **Acidity** is a measure of the tendency of a compound to lose a proton.
- **Basicity** is a measure of a compound's affinity for a proton.
- A strong base has a high affinity for a proton; a weak base has a low affinity for a proton.
- The stronger the acid, the weaker its conjugate base.

Section 2.2

- The strength of an acid is given by the **acid dissociation constant** (K_a) or by its pK_a value.
- The stronger the acid, the smaller its pK_a value.
- The **pH** of a solution indicates the concentration of protons in the solution; the smaller the pH, the more acidic the solution.

Section 2.3

- Approximate pK_a values are as follows: protonated alcohols, protonated carboxylic acids, and protonated water < 0 ; carboxylic acids ~ 5 ; protonated amines ~ 10 ; alcohols and water ~ 15 .
- Curved arrows indicate the bonds that are broken and formed as reactants are converted into products.

Section 2.4

- The more acidic of two reactants is the one that loses a proton in an **acid–base reaction**.

Section 2.5

- In an acid–base reaction, the equilibrium favors formation of the weaker acid.

Section 2.6

- The strength of an acid is determined by the stability of its conjugate base: the more stable (weaker) the base, the stronger its conjugate acid.

- When atoms are similar in size, the strongest acid has its hydrogen attached to the most electronegative atom.
- Hybridization affects acidity because an sp hybridized atom is more electronegative than an sp^2 hybridized atom, which is more electronegative than an sp^3 hybridized atom.
- When atoms are very different in size, the strongest acid has its hydrogen attached to the largest atom.

Section 2.7

- **Inductive electron withdrawal** increases acidity: the more electronegative the electron-withdrawing group and the closer it is to the acidic hydrogen, the stronger the acid.

Section 2.8

- **Delocalized electrons** (electrons that are shared by more than two atoms) stabilize a compound.
- A **resonance hybrid** is a composite of the **resonance contributors**—structures that differ only in the location of their π electrons and lone-pair electrons.

Section 2.10

- The **Henderson–Hasselbalch equation** gives the relationship between pK_a and pH: a compound exists primarily in its acidic form (with its proton) in solutions more acidic than its pK_a value and primarily in its basic form (without its proton) in solutions more basic than its pK_a value.

Section 2.11

- A **buffer solution** contains both a weak acid and its conjugate base.

Section 2.12

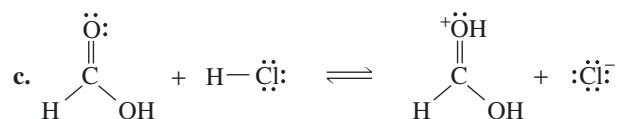
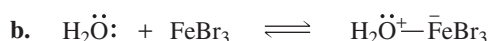
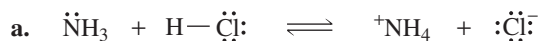
- A **Lewis acid** is a species that accepts a share in an electron pair; a **Lewis base** is a species that donates a share in an electron pair.
- In this text, the term *acid* is used to mean a proton-donating acid; the term **Lewis acid** is used to refer to non-proton-donating acids such as $AlCl_3$ or BF_3 .

PROBLEMS

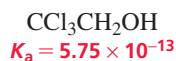
53. Which is a stronger base?

- | | | |
|--|-------------------------------------|------------------------------|
| a. $CH_3CH_2NH_2$ or $\underline{C}H_3CH_2NHCH_3$ | c. I^- or Cl^- | e. CF_3NH_2 or CBr_3NH_2 |
| b. $(CH_3)_3CNH_2$ or $\underline{C}H_3CH_2NHCH_2CH_3$ | d. $CH_3CH_2COO^-$ or $CHCl_2COO^-$ | f. CH_3^- or CH_2CH^- |

54. Draw curved arrows to show where the electrons start and where they end in the following reactions:

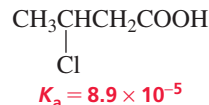
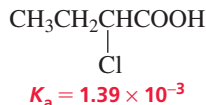
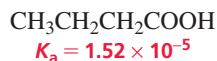


55. a. Rank the following alcohols from strongest to weakest acid:



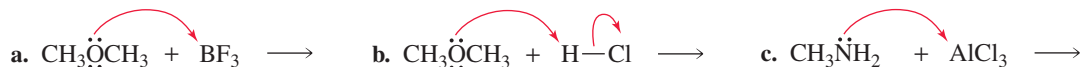
- b. Explain the relative acidities.

56. a. Rank the following carboxylic acids from strongest to weakest acid:



- b. How does the presence of an electronegative substituent such as Cl affect the acidity of a carboxylic acid?
c. How does the location of the substituent affect the acidity of the carboxylic acid?

57. Draw the products of the following reactions:



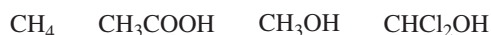
58. For the following compound,

- a. draw its conjugate acid.

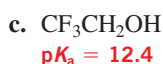
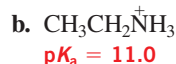
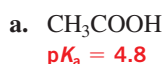
- b. draw its conjugate base.



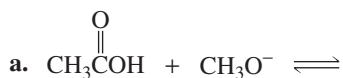
59. Rank the following compounds from strongest to weakest acid:



60. For each of the following compounds, draw the form that predominates at pH = 3, pH = 6, pH = 10, and pH = 14:



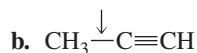
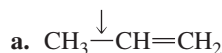
61. Give the products of the following acid–base reactions and indicate whether reactants or products are favored at equilibrium. (Use the $\text{p}K_a$ values that are given in Section 2.3.)



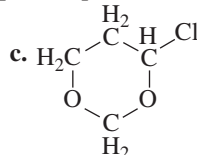
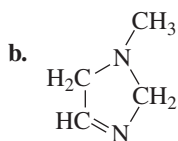
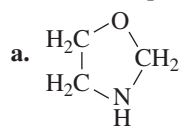
62. a. Rank the following alcohols from strongest to weakest acid.
b. Explain the relative acidities.



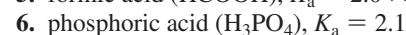
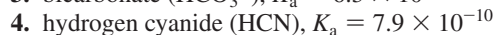
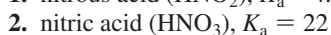
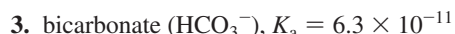
63. A single bond between two carbons with different hybridizations has a small dipole. What is the direction of the dipole in the indicated bonds?



64. For each compound, indicate the atom that is most apt to be protonated.

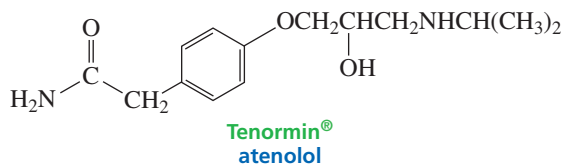


65. a. Given the K_a values, estimate the $\text{p}K_a$ value of each of the following acids without using a calculator (that is, is it between 3 and 4, between 9 and 10, and so on?):



- b. Determine the exact $\text{p}K_a$ values, using a calculator.
c. Which is the strongest acid?

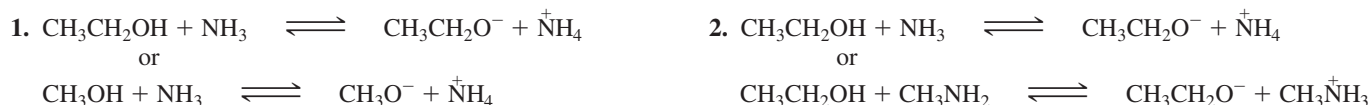
66. Tenormin, a member of the group of drugs known as beta-blockers, is used to treat high blood pressure and improve survival after a heart attack. It works by slowing down the heart to reduce its workload. Which atom in Tenormin is the most basic?



67. From which of the following compounds can HO^- remove a proton in a reaction that favors product formation?



68. a. For each of the following pairs of reactions, indicate which one has the more favorable equilibrium constant (that is, which one most favors products):



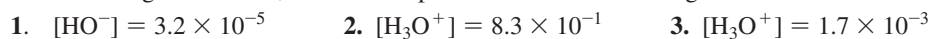
b. Which of the four reactions has the most favorable equilibrium constant?

69. You are planning to carry out a reaction that produces protons. The reaction will be buffered at pH = 10.5. Would it be better to use a protonated methylamine/methylamine buffer or a protonated ethylamine/ethylamine buffer? (pK_a of protonated methylamine = 10.7; pK_a of protonated ethylamine = 11.0)

70. Which is a stronger acid?



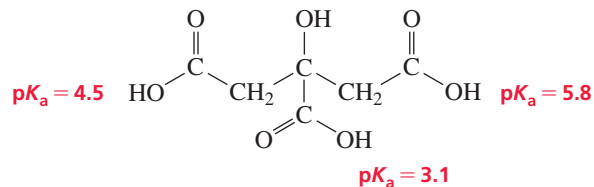
71. a. Without using a calculator, estimate the pH of each of the following solutions:



b. Determine the exact pH, using a calculator.

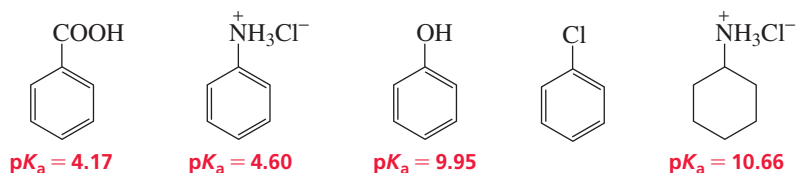
72. Citrus fruits are rich in citric acid, a compound with three COOH groups. Explain the following:

- The first $\text{p}K_{\text{a}}$ (for the COOH group in the center of the molecule) is lower than the $\text{p}K_{\text{a}}$ of acetic acid.
- The third $\text{p}K_{\text{a}}$ is greater than the $\text{p}K_{\text{a}}$ of acetic acid.



73. Given that $\text{pH} + \text{pOH} = 14$ and that the concentration of water in a solution of water is 55.5 M, show that the pK_a of water is 15.7. (Hint: $\text{pOH} = -\log [\text{HO}^-]$)

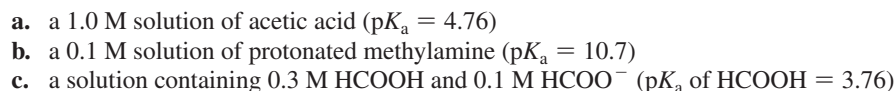
74. How could you separate a mixture of the following compounds? The reagents available to you are water, ether, 1.0 M HCl, and 1.0 M NaOH. (Hint: See Problem 47.)



75. Carbonic acid has a pK_a of 6.1 at physiological temperature. Is the carbonic acid/bicarbonate buffer system that maintains the pH of the blood at 7.4 better at neutralizing excess acid or excess base?

76. a. If an acid with a pK_a of 5.3 is in an aqueous solution of pH 5.7, what percentage of the acid is present in its acidic form?
b. At what pH does 80% of the acid exist in its acidic form?

77. Calculate the pH values of the following solutions:



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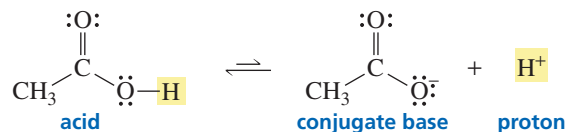
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TUTORIAL ACIDS AND BASES

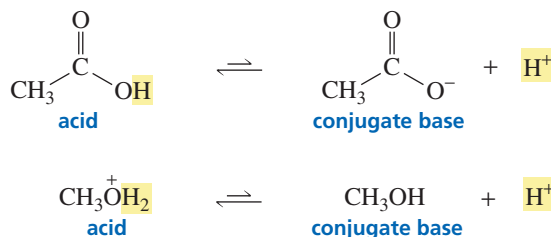
This tutorial is designed to give you practice working problems based on some of the concepts you learned in Chapter 2. Most of the concepts are given here without explanation because full explanations can be found in Chapter 2.

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 (H^+), it forms its conjugate base. When the proton comes off the acid, the conjugate base retains the electron pair that had attached the proton to the acid.



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



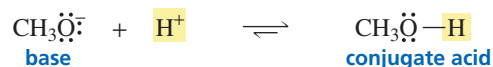
Notice that a neutral acid forms a negatively charged conjugate base, whereas a positively charged acid forms a neutral conjugate base. (The difference in charge *decreases* by one because the acid *loses* H^+ .)

PROBLEM 1 Draw the conjugate base of each of the following acids:

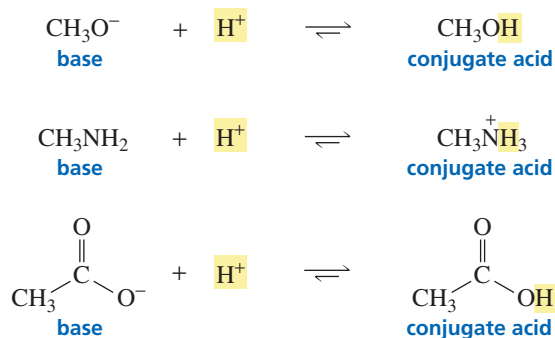
- a. CH_3OH b. CH_3NH_3^+ c. CH_3NH_2 d. H_3O^+ e. H_2O

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 (H^+), it forms its conjugate acid. To gain a proton, a base must have a lone pair that it can use to form a new bond with the proton.



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



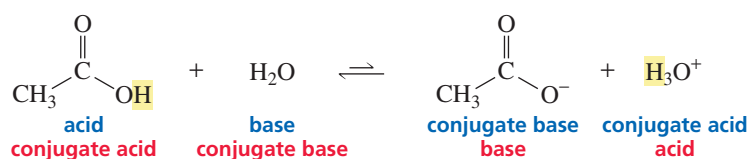
Notice that a negatively charged base forms a neutral conjugate acid, whereas a neutral base forms a positively charged conjugate acid. (The difference in charge *increases* by one because the compound *gains* H^+ .)

PROBLEM 2 Draw the conjugate acid of each of the following bases:

- a. H_2O b. HO^- c. CH_3OH d. NH_3 e. Cl^-

Acid–Base Reactions

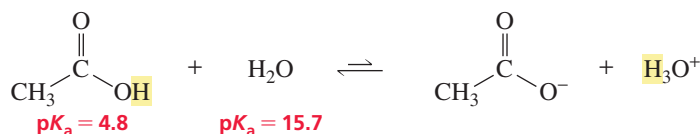
An acid cannot lose a proton unless a base is present to accept the proton. Therefore, an acid always reacts with a base. The reaction of an acid with a base is called an acid–base reaction or a proton transfer reaction. Most acid–base reactions are reversible reactions.



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 CH_3COOH and H_2O 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 loses a proton and which gains a proton? We can determine this by comparing the $\text{p}K_{\text{a}}$ values of the two reactants; these values are 4.8 for CH_3COOH and 15.7 for H_2O . The stronger acid (the one with the lower $\text{p}K_{\text{a}}$ value) is the one that acts as an acid (it loses a proton). The other reactant acts as a base (it gains a proton).

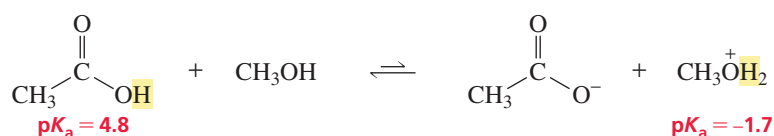


PROBLEM 3 Draw the products of the following acid–base reactions:

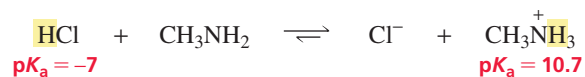
- a. $\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O}$ c. $\text{CH}_3\text{NH}_3^+ + \text{HO}^-$
 b. $\text{HBr} + \text{CH}_3\text{OH}$ d. $\text{CH}_3\text{NH}_2 + \text{CH}_3\text{OH}$

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 $\text{p}K_{\text{a}}$ value of the acid that loses a proton in the forward direction with the $\text{p}K_{\text{a}}$ value of the acid that loses a proton in the reverse direction. The equilibrium favors the reaction of the stronger acid to form the weaker acid. The following reaction favors formation of the reactants, because CH_3OH_2^+ is a stronger acid than CH_3COOH .



The next reaction favors formation of the products, because HCl is a stronger acid than CH_3NH_3^+ .



PROBLEM 4 Which of the reactions in Problem 3 favor formation of the reactants, and which favor formation of the products? (The pK_a values can be found in Sections 2.3 and 2.6.)

Relative Acid Strengths When the Proton Is Attached to Atoms Similar in Size

The atoms in the second row of the periodic table are similar in size, but they have different electronegativities.

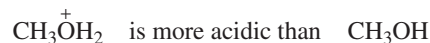
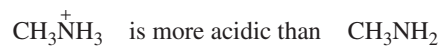
relative electronegativities



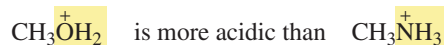
When acids have protons attached to atoms similar in size, the strongest acid is the one with the proton attached to the more electronegative atom. The relative acid strengths are as follows:



A positively charged atom is more electronegative than the same atom when it is neutral. Therefore,



When the relative strengths of two acids are determined by comparing the electronegativities of the atoms to which the protons are attached, both acids must possess the same charge. Therefore,

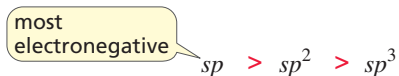


PROBLEM 5 Which is the stronger acid?

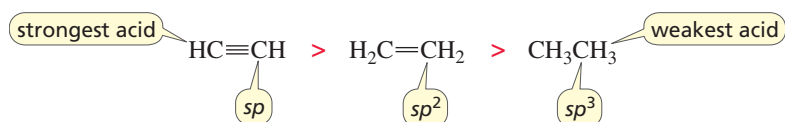
- | | |
|---|---|
| a. CH_3OH or CH_3CH_3 | c. CH_3NH_2 or HF |
| b. CH_3OH or HF | d. CH_3NH_2 or CH_3OH |

The Effect of Hybridization on Acidity

The electronegativity of an atom depends on its hybridization.



Once again, the strongest acid has its proton attached to the most electronegative atom. Thus, the relative acid strengths are as follows:



PROBLEM 6 Which is the stronger acid?

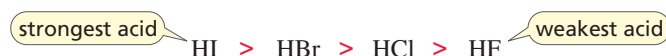
- a. CH_3CH_3 or $\text{HC}\equiv\text{CH}$ b. $\text{H}_2\text{C}=\text{CH}_2$ or $\text{HC}\equiv\text{CH}$ c. $\text{H}_2\text{C}=\text{CH}_2$ or CH_3CH_3

Relative Acid Strengths When the Proton Is Attached to Atoms Very Different in Size

The atoms in a column of the periodic table become considerably larger as you go down the column.



When comparing two acids with protons attached to atoms that are very different in size, the stronger acid is the one attached to the larger atom. Thus, the relative acid strengths are as follows:

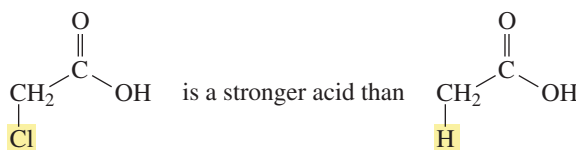


PROBLEM 7 ♦ Which is the stronger acid? (*Hint:* You can use the periodic table at the back of this book.)

- a. HCl or HBr b. CH_3OH or CH_3SH c. HF or HCl d. H_2S or H_2O

The Effect of Inductive Electron Withdrawal on Acidity

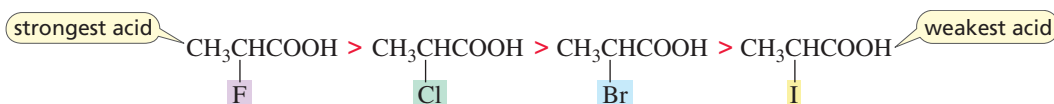
Replacing a hydrogen with an electronegative substituent—one that pulls bonding electrons toward itself—increases the strength of the acid.



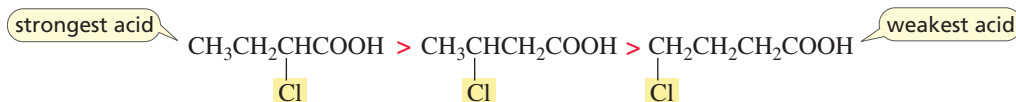
The halogens have the following relative electronegativities:



The more electronegative the substituent that replaces a hydrogen, the stronger the acid. Thus, the relative acid strengths are as follows:



The closer the electronegative substituent is to the group that loses a proton, the stronger the acid is. Thus, the relative acid strengths are as follows:



PROBLEM 8 Which is the stronger acid?

- a. $\text{ClCH}_2\text{CH}_2\text{OH}$ or $\text{FCH}_2\text{CH}_2\text{OH}$ c. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{OH}$ or $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$

- b. $\text{CH}_2\text{CH}(\text{Br})\text{CH}_2\text{OH}$ or $\text{CH}_3\text{C}(\text{Br})_2\text{CH}_2\text{OH}$ d. $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{OH}$

Relative Base Strengths

Strong bases readily share their electrons with a proton. In other words, the conjugate acid of a *strong* base is a *weak* acid because it does not readily lose a proton. This allows us to say, *the stronger the base, the weaker its conjugate acid* (or *the stronger the acid, the weaker its conjugate base*).

For example, which is the stronger base?

- a. CH_3O^- or CH_3NH^- b. $\text{HC}\equiv\text{C}^-$ or CH_3CH_2^-

To answer the question, first compare their conjugate acids:

- a. CH_3OH is a stronger acid than CH_3NH_2 (because O is more electronegative than N). Because the stronger acid has the weaker conjugate base, CH_3NH^- is a stronger base than CH_3O^- .
b. $\text{HC}\equiv\text{CH}$ is a stronger acid than CH_3CH_3 (an sp hybridized carbon is more electronegative than an sp^3 hybridized carbon). Therefore, CH_3CH_2^- is a stronger base.

PROBLEM 9 Which is the stronger base?

- a. Br^- or I^- d. $\text{H}_2\text{C}=\text{CH}^-$ or $\text{HC}\equiv\text{C}^-$
b. CH_3O^- or CH_3S^- e. $\text{FCH}_2\text{CH}_2\text{COO}^-$ or $\text{BrCH}_2\text{CH}_2\text{COO}^-$
c. $\text{CH}_3\text{CH}_2\text{O}^-$ or CH_3COO^- f. $\text{ClCH}_2\text{CH}_2\text{O}^-$ or $\text{Cl}_2\text{CHCH}_2\text{O}^-$

Weak Bases Are Stable Bases

Weak bases are stable bases because they readily bear the electrons they formerly shared with a proton. Therefore, we can say, *the weaker the base, the more stable it is*. We can also say, *the stronger the acid, the more stable (the weaker) its conjugate base*.

For example, which is a more stable base: Cl^- or Br^- ?

To determine this, first compare their conjugate acids:

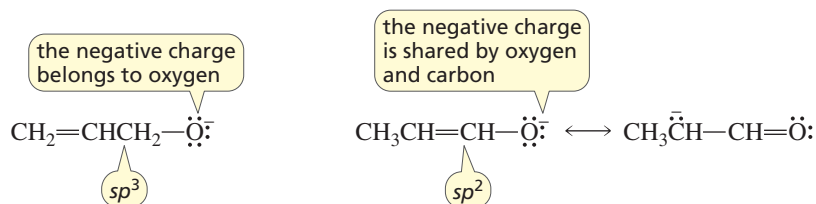
HBr is a stronger acid than HCl (because Br is larger than Cl). Therefore, Br^- is a more stable (weaker) base.

PROBLEM 10 Which is the more stable base?

- a. Br^- or I^- d. $\text{H}_2\text{C}=\text{CH}^-$ or $\text{HC}\equiv\text{C}^-$
b. CH_3O^- or CH_3S^- e. $\text{FCH}_2\text{CH}_2\text{COO}^-$ or $\text{BrCH}_2\text{CH}_2\text{COO}^-$
c. $\text{CH}_3\text{CH}_2\text{O}^-$ or CH_3COO^- f. $\text{ClCH}_2\text{CH}_2\text{O}^-$ or $\text{Cl}_2\text{CHCH}_2\text{O}^-$

Electron Delocalization Stabilizes a Base

If a base has localized electrons, then the negative charge that results when the base's conjugate acid loses a proton belongs to one atom. On the other hand, if a base has delocalized electrons, then the negative charge that results when the base's conjugate acid loses a proton is shared by two (or more) atoms. A base with delocalized electrons is more stable than a similar base with localized electrons.



To determine if a base has delocalized electrons, we simply need to check the electrons left behind when the base's conjugate acid loses a proton.

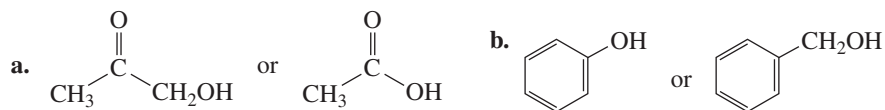
- If these electrons are on an atom bonded to an sp^3 carbon, then the electrons belong to only one atom—that is, the electrons are localized.
- If these electrons are on an atom bonded to an sp^2 carbon, then the electrons are delocalized.

PROBLEM 11 Which is a more stable base?



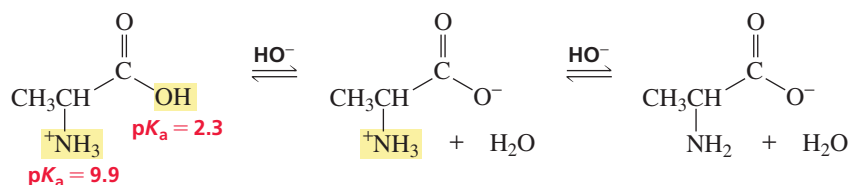
Remembering that the more stable (weaker) base has the stronger conjugate acid, solve Problem 12.

PROBLEM 12 Which is the stronger acid?

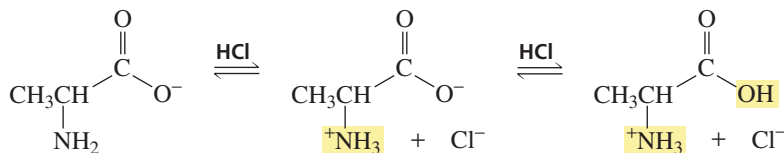


Compounds With More Than One Acidic Group

If a compound has two acidic groups, then a base will remove a proton from the more acidic of the two groups first. If a second equivalent of base is added, then the base will remove a proton from the less acidic group.

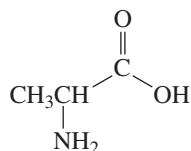


Similarly, if a compound has two basic groups, then an acid will protonate the more basic of the two groups first. If a second equivalent of acid is added, then the acid will protonate the less basic group.



PROBLEM 13

- What species is formed when one equivalent of HCl is added to $\text{HOCH}_2\text{CH}_2\text{NH}_2$?
- Does the following compound exist?



The Effect of pH on Structure

Whether an acid is in its acidic form (with its proton) or its basic form (without its proton) depends on the pK_a value of the acid and the pH of the solution:

- When $\text{pH} < pK_a$, the compound exists primarily in its acidic form.
- When $\text{pH} > pK_a$, the compound exists primarily in its basic form.

In other words, when the solution is more acidic than the pK_a value of the acid, the compound is in its acidic form. But when the solution is more basic than the pK_a value of the acid, the compound is in its basic form.

PROBLEM 14

- Draw the structure of CH_3COOH ($pK_a = 4.7$) at $\text{pH} = 2$, $\text{pH} = 7$, and $\text{pH} = 10$.
- Draw the structure of CH_3OH ($pK_a = 15.5$) at $\text{pH} = 2$, $\text{pH} = 7$, and $\text{pH} = 10$.
- Draw the structure of CH_3NH_3^+ ($pK_a = 10.7$) at $\text{pH} = 2$, $\text{pH} = 7$, and $\text{pH} = 14$.

ANSWERS TO PROBLEMS ON ACIDS AND BASES

PROBLEM 1 SOLVED

- CH_3O^-
- CH_3NH_2
- CH_3NH^-
- H_2O
- HO^-

PROBLEM 2 SOLVED

- H_3O^+
- H_2O
- CH_3OH_2^+
- NH_4^+
- HCl

PROBLEM 3 SOLVED

- $\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$
- $\text{HBr} + \text{CH}_3\text{OH} \rightleftharpoons \text{Br}^- + \text{CH}_3\text{OH}_2^+$
- $\text{CH}_3\text{NH}_3^+ + \text{HO}^- \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$
- $\text{CH}_3\text{NH}_2 + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{CH}_3\text{O}^-$

PROBLEM 4 SOLVED

- reactants
- products
- products
- reactants

PROBLEM 5 SOLVED

- CH_3OH
- HF
- HF
- CH_3OH

PROBLEM 6 SOLVED

- $\text{HC}\equiv\text{CH}$
- $\text{HC}\equiv\text{CH}$
- $\text{H}_2\text{C}=\text{CH}_2$

PROBLEM 7 SOLVED

- HBr
- CH_3SH
- HCl
- H_2S

PROBLEM 8 SOLVED

- $\text{FCH}_2\text{CH}_2\text{OH}$
- $$\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3\text{CCH}_2\text{OH} \\ | \\ \text{Br} \end{array}$$
- $\text{CH}_3\text{CH}_2\text{OCH}_2\text{OH}$
- $$\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2\text{CCH}_2\text{OH} \end{array}$$

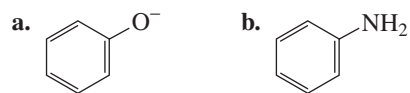
PROBLEM 9 SOLVED

- Br^-
- CH_3O^-
- $\text{CH}_3\text{CH}_2\text{O}^-$
- $\text{H}_2\text{C}=\text{CH}^-$
- $\text{BrCH}_2\text{CH}_2\text{COO}^-$
- $\text{ClCH}_2\text{CH}_2\text{O}^-$

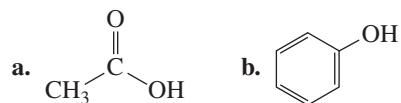
PROBLEM 10 SOLVED

- I^-
- CH_3S^-
- CH_3COO^-
- $\text{HC}\equiv\text{C}^-$
- $\text{FCH}_2\text{CH}_2\text{COO}^-$
- $\text{Cl}_2\text{CHCH}_2\text{O}^-$

PROBLEM 11 SOLVED



PROBLEM 12 SOLVED



PROBLEM 13 SOLVED

- a. $\text{HOCH}_2\text{CH}_2\text{NH}_3^+$
 b. The compound does not exist. For it to be formed, a base would have to be able to remove a proton from a group with a $\text{p}K_{\text{a}} = 9.9$ more readily than it would remove a proton from a group with a $\text{p}K_{\text{a}} = 2.3$. This is not possible, because the lower the $\text{p}K_{\text{a}}$, the stronger the acid—that is, the more readily the group loses a proton. In other words, a weak acid cannot lose a proton more readily than a strong acid can.

PROBLEM 14 SOLVED

- a. CH_3COOH at $\text{pH} = 2$, because $\text{pH} < \text{p}K_{\text{a}}$
 CH_3COO^- at $\text{pH} = 7$ and 10 , because $\text{pH} > \text{p}K_{\text{a}}$
 b. CH_3OH at $\text{pH} = 2, 7$, and 10 , because $\text{pH} < \text{p}K_{\text{a}}$
 c. CH_3NH_3^+ at $\text{pH} = 2$ and 7 , because $\text{pH} < \text{p}K_{\text{a}}$
 CH_3NH_2 at $\text{pH} = 14$, because $\text{pH} > \text{p}K_{\text{a}}$

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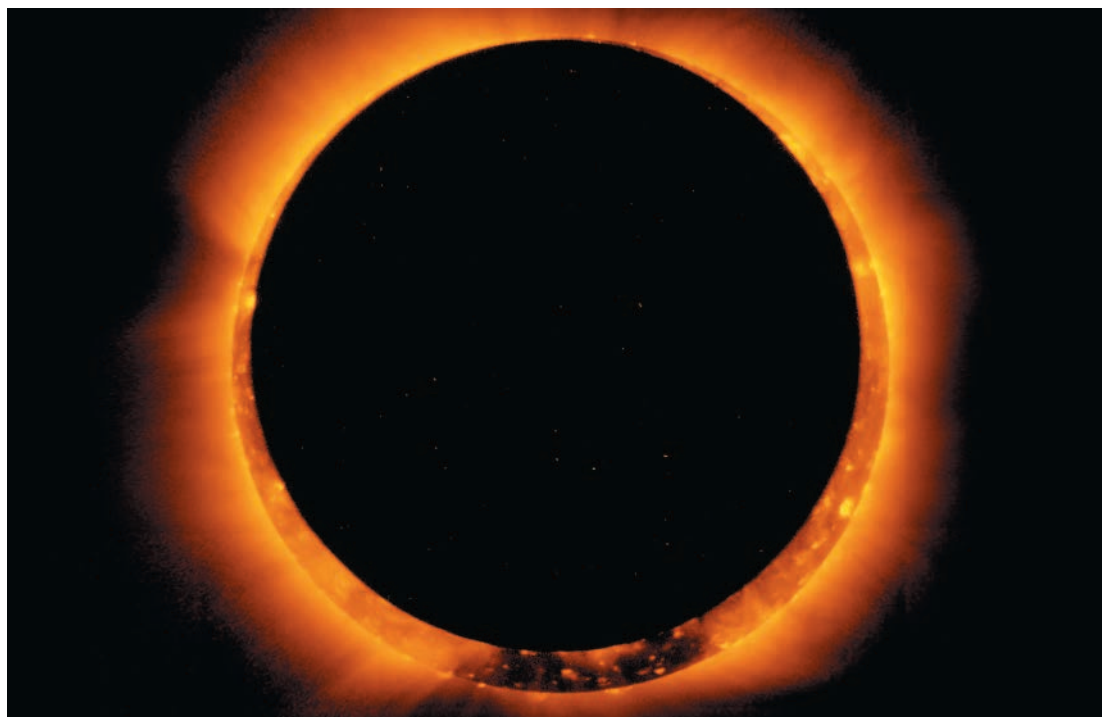
- Acids and Bases: Definitions
- Acids and Bases: Factors That Influence Acid Strength
- Acids and Bases: Base Strength and the Effect of pH on Structure
- Acids and Bases: Predicting the Position of Equilibrium

3

An Introduction to Organic Compounds

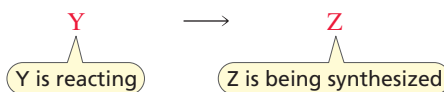
Nomenclature, Physical Properties, and Structure

A solar eclipse occurs when the Moon aligns with and obscures the Sun. Eclipsed conformers align the same way.



The material in this chapter explains why drugs with similar physiological effects often have similar structures, how high cholesterol is treated clinically, why fish is served with lemon, how the octane number of gasoline is determined, and why starch (a component of many of the foods we eat) and cellulose (the structural material of plants) have such different physical properties even though both are composed only of glucose.

The presentation of organic chemistry in this book is organized according to how organic compounds react. When a compound undergoes a reaction, a new compound is synthesized. In other words, while you are learning how organic compounds react, you are simultaneously learning how to synthesize organic compounds.



The compounds that are synthesized by the reactions we will study in Chapters 5–12 are primarily alkanes, alkyl halides, ethers, alcohols, and amines. Later in this chapter, we will look at the structures and physical properties of compounds in these five families. As we learn about these compounds, we must be able to refer to them by name. Therefore, we will begin our study of organic chemistry by learning how to name these five families of compounds.

Alkanes

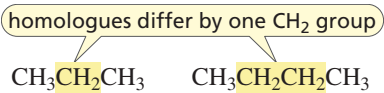
Alkanes are composed of only carbon atoms and hydrogen atoms and contain only *single bonds*. Compounds that contain only carbon and hydrogen are called **hydrocarbons**. Thus, an alkane is a hydrocarbon that has only single bonds.

Alkanes in which the carbons form a continuous chain with no branches are called **straight-chain alkanes**. The names of the four smallest straight-chain alkanes have historical roots, but the others are based on Greek numbers. It is important that you learn the names of at least the first 10 straight-chain alkanes in Table 3.1.

Number of carbons	Molecular formula	Name	Condensed structure	Boiling point (°C)	Melting point (°C)	Density ^a (g/mL)
1	CH ₄	methane	CH ₄	−167.7	−182.5	
2	C ₂ H ₆	ethane	CH ₃ CH ₃	−88.6	−183.3	
3	C ₃ H ₈	propane	CH ₃ CH ₂ CH ₃	−42.1	−187.7	
4	C ₄ H ₁₀	butane	CH ₃ CH ₂ CH ₂ CH ₃	−0.5	−138.3	
5	C ₅ H ₁₂	pentane	CH ₃ (CH ₂) ₃ CH ₃	36.1	−129.8	0.5572
6	C ₆ H ₁₄	hexane	CH ₃ (CH ₂) ₄ CH ₃	68.7	−95.3	0.6603
7	C ₇ H ₁₆	heptane	CH ₃ (CH ₂) ₅ CH ₃	98.4	−90.6	0.6837
8	C ₈ H ₁₈	octane	CH ₃ (CH ₂) ₆ CH ₃	125.7	−56.8	0.7026
9	C ₉ H ₂₀	nonane	CH ₃ (CH ₂) ₇ CH ₃	150.8	−53.5	0.7177
10	C ₁₀ H ₂₂	decane	CH ₃ (CH ₂) ₈ CH ₃	174.0	−29.7	0.7299
11	C ₁₁ H ₂₄	undecane	CH ₃ (CH ₂) ₉ CH ₃	195.8	−25.6	0.7402
12	C ₁₂ H ₂₆	dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	216.3	−9.6	0.7487
13	C ₁₃ H ₂₈	tridecane	CH ₃ (CH ₂) ₁₁ CH ₃	235.4	−5.5	0.7546
⋮	⋮	⋮	⋮	⋮	⋮	⋮
20	C ₂₀ H ₄₂	eicosane	CH ₃ (CH ₂) ₁₈ CH ₃	343.0	36.8	0.7886
21	C ₂₁ H ₄₄	heneicosane	CH ₃ (CH ₂) ₁₉ CH ₃	356.5	40.5	0.7917
⋮	⋮	⋮	⋮	⋮	⋮	⋮
30	C ₃₀ H ₆₂	triacontane	CH ₃ (CH ₂) ₂₈ CH ₃	449.7	65.8	0.8097

^aDensity is temperature-dependent. The densities given are those determined at 20 °C (*d*^{20°}).

The family of alkanes shown in the table is an example of a homologous series. A **homologous series** (*homos* is Greek for “the same as”) is a family of compounds in which each member differs from the one before it in the series by one **methylene (CH₂) group**. The members of a homologous series are called **homologues**.



The relative numbers of carbons and hydrogens in the alkanes in Table 3.1 show that the general molecular formula for an alkane is C_{*n*}H_{2*n*+2}, where *n* is any positive integer. So if an alkane has one carbon, it must have four hydrogens; if it has two carbons, it must have six hydrogens; and so on.

Methane, Ethane, and Propane

We saw that carbon forms four covalent bonds and hydrogen forms only one covalent bond (Section 1.4). This means that there is only one possible structure for an alkane with molecular formula CH₄ (methane) and only one possible structure for an alkane with molecular formula C₂H₆ (ethane). We examined the structures of these compounds in Section 1.7. There is also only one possible structure for an alkane with molecular formula C₃H₈ (propane).

name	molecular formula	Kekulé structure	condensed structure	ball-and-stick model
methane	CH ₄	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	CH ₄	
ethane	C ₂ H ₆	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	CH ₃ CH ₃	
propane	C ₃ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	CH ₃ CH ₂ CH ₃	
butane	C ₄ H ₁₀	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	CH ₃ CH ₂ CH ₂ CH ₃	

Butane

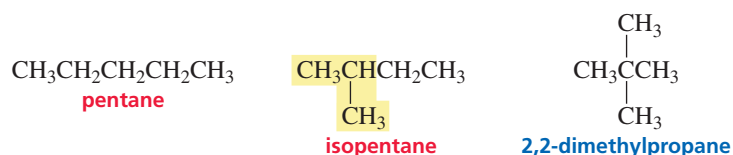
There are, however, two possible structures for an alkane with molecular formula C₄H₁₀—a straight-chain alkane called butane and a branched alkane called isobutane. Both of these structures fulfill the requirement that each carbon forms four bonds and each hydrogen forms one bond.



Compounds such as butane and isobutane that have the same molecular formula but differ in the way the atoms are connected are called **constitutional isomers**—their molecules have different constitutions. In fact, isobutane got its name because it is an *isomer* of butane. The structural unit consisting of a carbon bonded to a hydrogen and two CH₃ groups, which occurs in isobutane, has come to be called "iso." Thus, the name *isobutane* tells you that the compound is a four-carbon alkane with an iso structural unit.

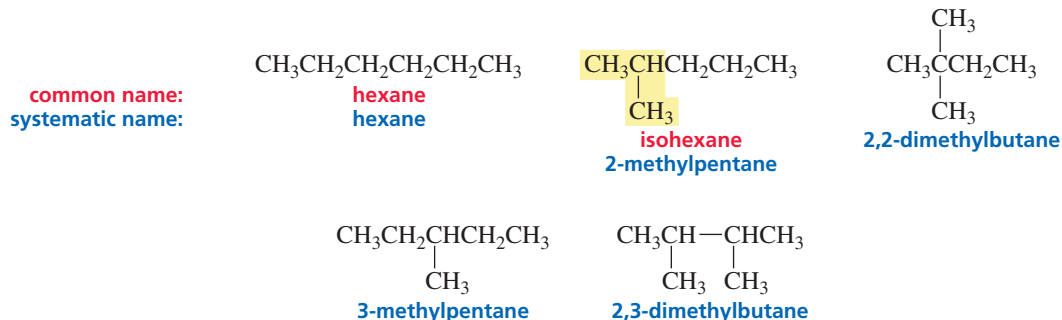
Pentane

There are three alkanes with molecular formula C₅H₁₂. You have already learned how to name two of them. Pentane is the straight-chain alkane. Isopentane, as its name indicates, has an iso structural unit and five carbons. We cannot name the other branched-chain alkane without defining a name for a new structural unit. (For now, ignore the names written in blue.)



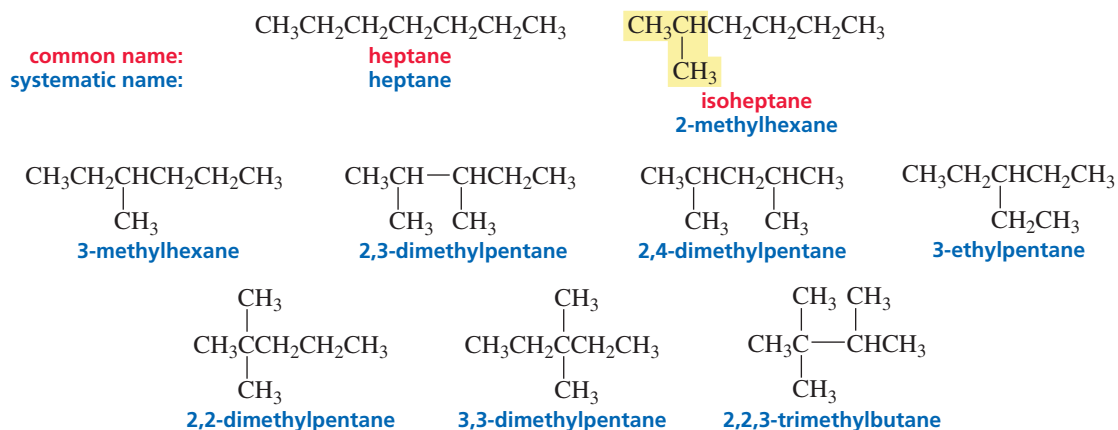
Hexane

There are five constitutional isomers with molecular formula C_6H_{14} . Again, we are able to name only two of them, unless we define new structural units.



Heptane

There are nine alkanes with molecular formula C_7H_{16} . We can name only two of them (heptane and isoheptane).



Systematic/IUPAC Nomenclature

The number of constitutional isomers increases rapidly as the number of carbons in an alkane increases. For example, there are 75 alkanes with molecular formula $C_{10}H_{22}$ and 4347 alkanes with molecular formula $C_{15}H_{32}$. To avoid having to memorize the names of thousands of structural units, chemists have devised rules for creating systematic names that describe the compound's structure. That way, only the rules must be learned. Because the name describes the structure, these rules make it possible to deduce the structure of a compound from its name.

This method of nomenclature is called **systematic nomenclature**. It is also called **IUPAC nomenclature** because it was designed by a commission of the International Union of Pure and Applied Chemistry (abbreviated IUPAC and pronounced “eye-you-pack”) in 1892.

The IUPAC rules have been continually revised by the commission since then. A name such as *isobutane*—a nonsystematic name—is called a **common name**. When both names are shown in this book, common names are shown in red and systematic (IUPAC) names in blue. Before we can understand how a systematic name for an alkane is constructed, we must learn how to name alkyl groups.

PROBLEM 1 ♦

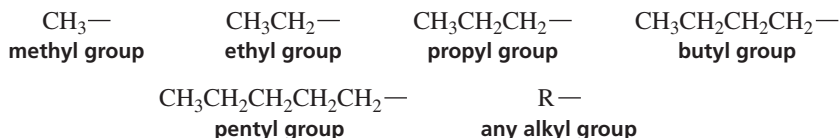
- How many hydrogens does an alkane with 17 carbons have?
- How many carbons does an alkane with 74 hydrogens have?

PROBLEM 2

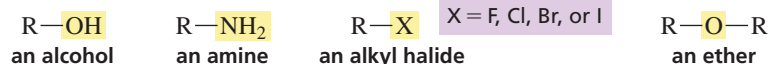
Draw the structures of octane and isooctane.

3.1 ALKYL GROUPS

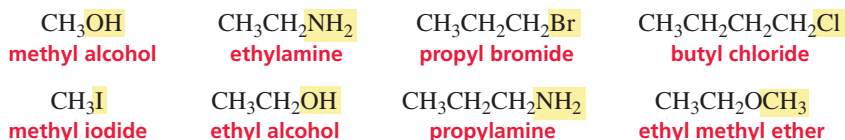
Removing a hydrogen from an alkane results in an **alkyl group** (or an **alkyl substituent**). Alkyl groups are named by replacing the “ane” ending of the alkane with “yl.” The letter “R” is used to indicate any alkyl group.



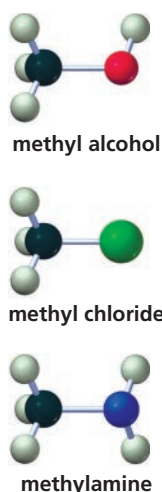
If a hydrogen in an alkane is replaced by an OH, the compound becomes an **alcohol**; if it is replaced by an NH_2 , the compound becomes an **amine**; if it is replaced by a halogen, the compound becomes an **alkyl halide**; and if it is replaced by an OR, the compound becomes an **ether**.



The alkyl group name followed by the name of the class of the compound (alcohol, amine, and so on) yields the common name of the compound. The two alkyl groups in ethers are listed in alphabetical order. The following examples show how alkyl group names are used to build common names:

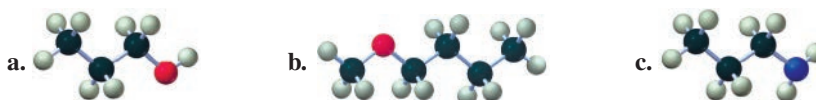


Notice that for most compounds, there is a space between the name of the alkyl group and the name of the class of compound. For amines, however, the entire name is written as one word.



PROBLEM 3 ♦

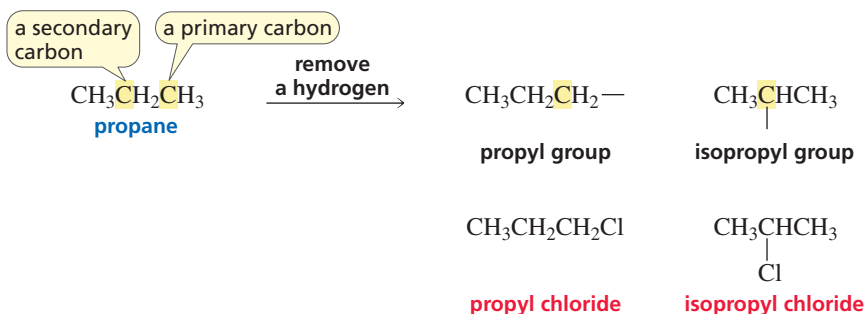
Name each of the following:



Three-Carbon Alkyl Groups

There are two alkyl groups—the propyl group and the isopropyl group—that contain three carbons.

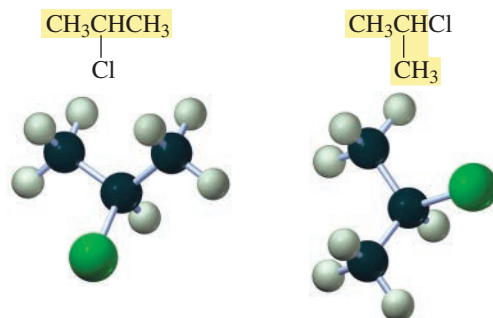
- A propyl group is obtained when a hydrogen is removed from a *primary carbon* of propane. A **primary carbon** is a carbon bonded to only one other carbon.
- An isopropyl group is obtained when a hydrogen is removed from the *secondary carbon* of propane. A **secondary carbon** is a carbon bonded to two other carbons.



Notice that an isopropyl group, as its name indicates, has three carbon atoms arranged as an iso structural unit—that is, a carbon bonded to a hydrogen and to two CH_3 groups.

Molecular structures can be drawn in different ways. For example, isopropyl chloride is drawn below in two ways. Both representations depict the same compound. Although the two-dimensional representations may appear at first to be different (the methyl groups are placed at opposite ends in one structure and at right angles in the other), the structures are identical because carbon is tetrahedral. The four groups bonded to the central carbon—a hydrogen, a chlorine, and two methyl groups—point to the corners of a tetrahedron. If you rotate the three-dimensional model on the right 90° in a clockwise direction, you should be able to see that the two models are the same.

two ways to draw isopropyl chloride

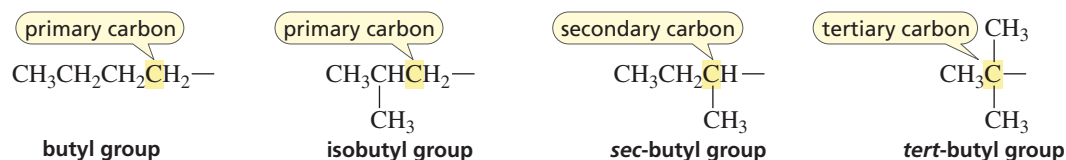


NOTE TO THE STUDENT

- Build models of the two representations of isopropyl chloride to see that they represent the same compound.

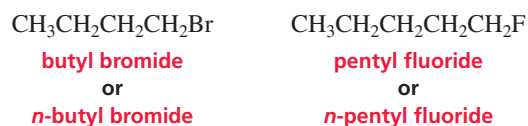
Four-Carbon Alkyl Groups

There are four alkyl groups that contain four carbons. Two of them, the butyl and isobutyl groups, have a hydrogen removed from a primary carbon. A *sec*-butyl group has a hydrogen removed from a secondary carbon (*sec*-, sometimes abbreviated *s*-, stands for secondary), and a *tert*-butyl group has a hydrogen removed from a tertiary carbon (*tert*-, often abbreviated *t*-, stands for tertiary). A **tertiary carbon** is bonded to three other carbons. Notice that the isobutyl group is the only one with an iso structural unit.

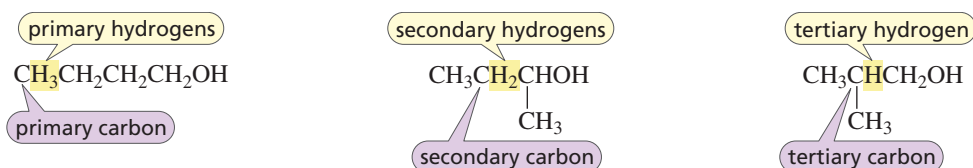


A primary carbon is bonded to one carbon, a secondary carbon is bonded to two carbons, and a tertiary carbon is bonded to three carbons.

The names of straight-chain alkyl groups often have the prefix “*n*” (for “normal”) to emphasize that the carbons are in an unbranched chain.



Like the carbons, the hydrogens in a molecule are also referred to as primary, secondary, and tertiary. **Primary hydrogens** are attached to a primary carbon, **secondary hydrogens** are attached to a secondary carbon, and **tertiary hydrogens** are attached to a tertiary carbon.



Primary hydrogens are attached to a primary carbon, secondary hydrogens to a secondary carbon, and tertiary hydrogens to a tertiary carbon.

A chemical name must specify one compound only. The prefix “*sec*,” therefore, can be used only for *sec*-butyl compounds. The name “*sec*-pentyl” cannot be used because pentane has two different secondary carbons. Thus, removing a hydrogen from a secondary carbon of pentane

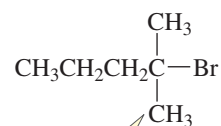
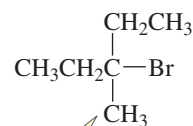
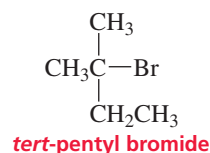
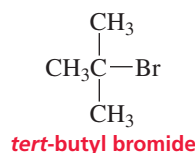
produces one of two different alkyl groups, depending on which hydrogen is removed. As a result, *sec*-pentyl chloride would specify two different alkyl chlorides, so it is *not* a correct name.

A name must specify one compound only.

Both alkyl halides have five carbon atoms with a chlorine attached to a secondary carbon, but two compounds cannot be named *sec*-pentyl chloride.

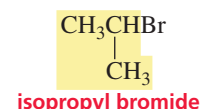
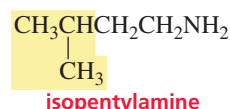
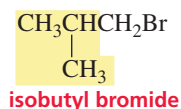
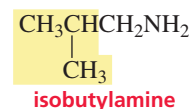
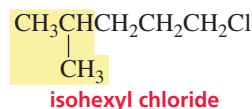
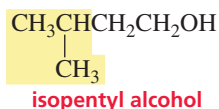


The prefix “*tert*” can be used for both *tert*-butyl and *tert*-pentyl compounds because each of these substituent names describes only one alkyl group. The name “*tert*-hexyl” cannot be used because it describes two different alkyl groups.



Both alkyl bromides have six carbon atoms with a bromine attached to a tertiary carbon, but two different compounds cannot be named *tert*-hexyl bromide.

Notice in the following structures that whenever the prefix “*iso*” is used, the *iso* structural unit is at one end of the molecule and the group replacing a hydrogen is at the other end:



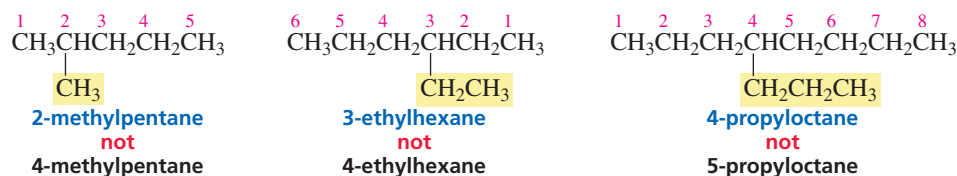
Notice that an *iso* group has a methyl group on the next-to-the-last carbon in the chain. Also notice that all *iso*alkyl compounds have the substituent (OH, Cl, NH₂, and so on) on a primary carbon, except for *isopropyl*, which has the substituent on a secondary carbon. Thus, the *isopropyl* group could have been called a *sec*-propyl group. Either name would have been appropriate because the group has an *iso* structural unit and a hydrogen has been removed from a secondary carbon. Chemists decided to call it *isopropyl*, however, which means that “*sec*” is used only for *sec*-butyl.

Alkyl group names are used so frequently that you need to learn them. Some of the most common alkyl group names are compiled in Table 3.2.

Table 3.2 Names of Some Common Alkyl Groups

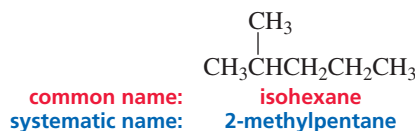
methyl	CH ₃ —	isobutyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2- \\ \\ \text{CH}_3 \end{array}$	pentyl	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ —
ethyl	CH ₃ CH ₂ —			isopentyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$
propyl	CH ₃ CH ₂ CH ₂ —	<i>sec</i> -butyl	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}- \\ \\ \text{CH}_3 \end{array}$		
isopropyl	$\begin{array}{c} \text{CH}_3\text{CH}- \\ \\ \text{CH}_3 \end{array}$			hexyl	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ —
butyl	CH ₃ CH ₂ CH ₂ CH ₂ —	<i>tert</i> -butyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}- \\ \\ \text{CH}_3 \end{array}$	isohexyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$

Number the chain in the direction that gives the substituent as low a number as possible.

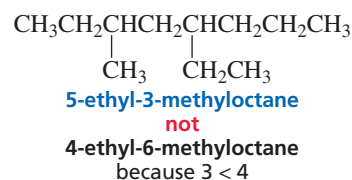


Only systematic names have numbers; common names *never* contain numbers.

Numbers are used only for systematic names, never for common names.

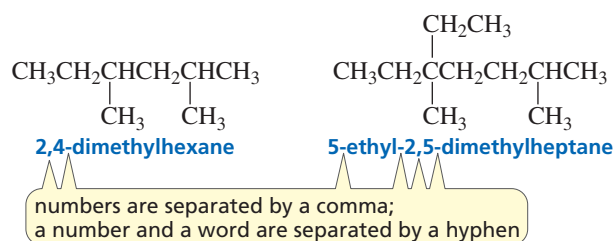


3. If more than one substituent is attached to the parent hydrocarbon, the chain is numbered in the direction that produces a name containing the lowest of the possible numbers. The substituents are listed in alphabetical order, with each substituent preceded by the appropriate number. In the following example, the correct name contains a 3 as its lowest number, whereas the incorrect name contains a 4 as its lowest number:



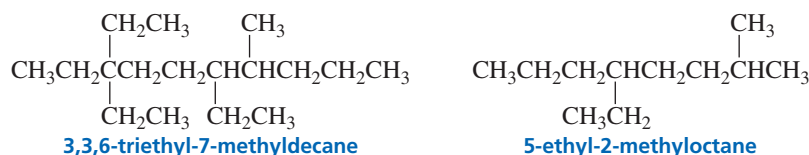
Substituents are listed in alphabetical order.

If two or more substituents are the same, the prefixes “di,” “tri,” and “tetra” are used to indicate how many identical substituents the compound has. The numbers indicating the locations of the identical substituents are listed together, separated by commas. There are no spaces on either side of a comma. There must be as many numbers in a name as there are substituents. The prefixes “di,” “tri,” “tetra,” “sec,” and “tert” are ignored in alphabetizing substituents.

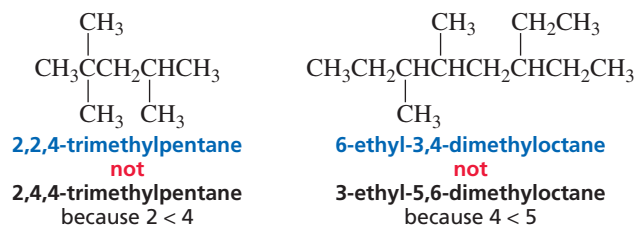


A number and a word are separated by a hyphen; numbers are separated by a comma.

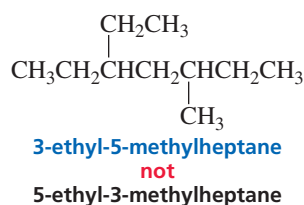
“di,” “tri,” “tetra,” “sec,” and “tert” are ignored in alphabetizing substituents.



4. When numbering in either direction leads to the same lowest number for one of the substituents, the chain is numbered in the direction that gives the lowest possible number to one of the remaining substituents.

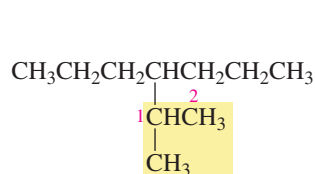


5. If the same substituent numbers are obtained in both directions, the first group listed receives the lower number.

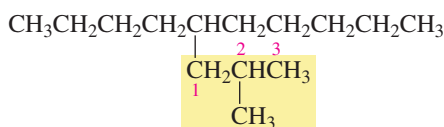


Only if the same set of numbers is obtained in both directions does the first group listed get the lower number.

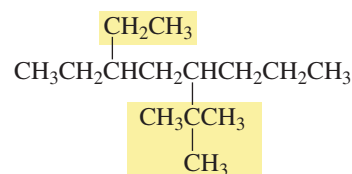
6. Systematic names for branched substituents are obtained by numbering the alkyl substituent starting at the carbon attached to the parent hydrocarbon. This means that the carbon attached to the parent hydrocarbon is always the number-1 carbon of the substituent. In a compound such as 4-(1-methylethyl)octane, the substituent name is in parentheses; the number inside the parentheses indicates a position on the substituent, whereas the number outside the parentheses indicates a position on the parent hydrocarbon. (If a prefix such as “di” is part of a branch name, it is included in the alphabetization.)



4-(1-methylethyl)heptane

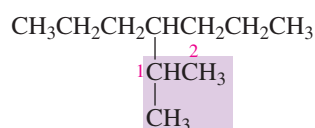


5-(2-methylpropyl)decane

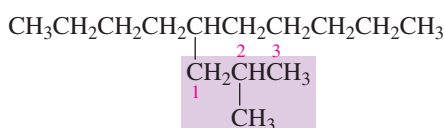


5-(1,1-dimethylethyl)-3-ethyloctane

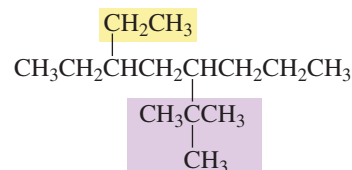
If the substituent has a common name, the common name can be used instead of the parenthetical name.



4-isopropylheptane

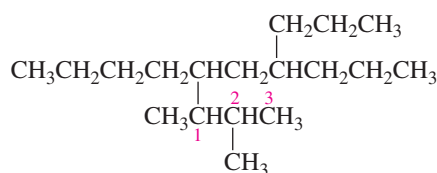


5-isobutyldecane

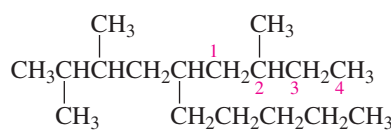


5-tert-butyl-3-ethyloctane

If the substituent does not have a common name, the parenthetical name must be used.

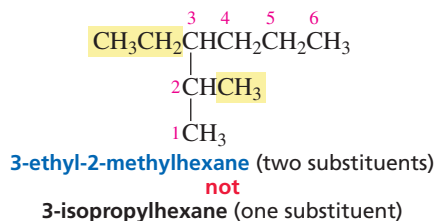


6-(1,2-dimethylpropyl)-4-propyldecane



2,3-dimethyl-5-(2-methylbutyl)decane

7. If a compound has two or more chains of the same length, the parent hydrocarbon is the chain with the greatest number of substituents.



In the case of two hydrocarbon chains with the same number of carbons, choose the one with the most substituents.