1

A Review of General Chemistry

ELECTRONS, BONDS, AND MOLECULAR PROPERTIES

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

DID YOU EVER **WONDER...**
what causes lightning?

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

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

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

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

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

1.1 Introduction to Organic Chemistry

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

Ammonium cyanate (Inorganic) **Urea** (Organic)

BY THE WAY

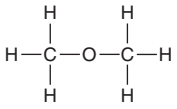
There are some carbon-containing compounds that are traditionally excluded from organic classification. For example, ammonium cyanate (seen on this page) is still classified as inorganic, despite the presence of a carbon atom. Other exceptions include sodium carbonate (Na_2CO_3) and potassium cyanide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

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

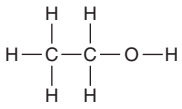
Organic chemistry occupies a central role in the world around us, as we are surrounded by organic compounds. The food that we eat and the clothes that we wear are comprised of organic compounds. Our ability to smell odors or see colors results from the behavior of organic compounds. Pharmaceuticals,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

1.2 The Structural Theory of Matter

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



Dimethyl ether
Boiling point = −23°C



Ethanol
Boiling point = 78.4°C

These compounds have the same molecular formula (C_2H_6O), yet they differ from each other in the way the atoms are connected—that is, they differ in their constitution. As a result, they are called **constitutional isomers**. Constitutional isomers have different physical properties and different names. The first compound is a colorless gas used as an aerosol spray propellant, while the second compound is a clear liquid, commonly referred to as "alcohol," found in alcoholic beverages.

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

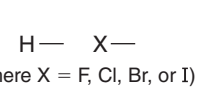
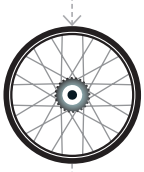
Tetravalent	*Trivalent*	*Divalent*	*Monovalent*
			 (where X = F, Cl, Br, or I)
Carbon generally forms ***four*** bonds.	Nitrogen generally forms ***three*** bonds.	Oxygen generally forms ***two*** bonds.	Hydrogen and halogens generally form ***one*** bond.

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

SKILLBUILDER



1.1 DRAWING CONSTITUTIONAL ISOMERS OF SMALL MOLECULES

LEARN the skill

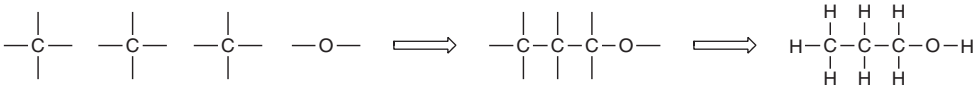
Draw all constitutional isomers that have the molecular formula C_3H_8O.

SOLUTION

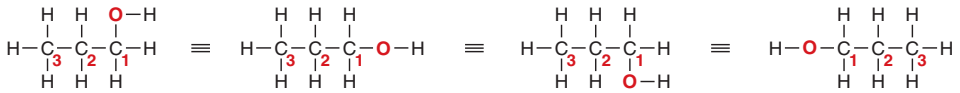
Begin by determining the valency of each atom that appears in the molecular formula. Carbon is tetravalent, hydrogen is monovalent, and oxygen is divalent. The atoms with the highest valency are connected first. So, in this case, we draw our first isomer by connecting the three carbon atoms, as well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

STEP 1
Determine the valency of each atom that appears in the molecular formula.

STEP 2
Connect the atoms of highest valency, and place the monovalent atoms at the periphery.



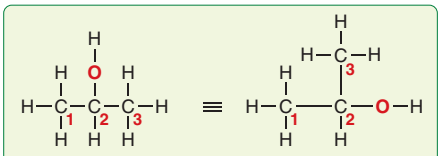
This isomer (called 1-propanol) can be drawn in many different ways, some of which are shown here:

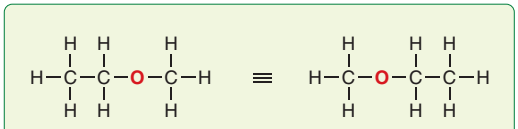


All of these drawings represent the same isomer. If we number the carbon atoms (C1, C2, and C3), with C1 being the carbon atom connected to oxygen, then all of the drawings above show the same connectivity: a three-carbon chain with an oxygen atom attached at one end of the chain.

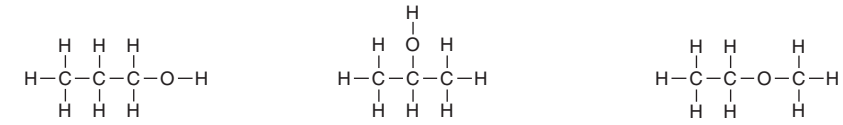
STEP 3
Consider other ways to connect the atoms.

Thus far, we have drawn just one isomer that has the molecular formula C_3H_8O. Other constitutional isomers can be drawn if we consider other possible ways of connecting the three carbon atoms and the oxygen atom. For example, the oxygen atom can be connected to C2 (rather than C1), giving a compound called 2-propanol (shown below). Alternatively, the oxygen atom can be inserted between two carbon atoms, giving a compound called ethyl methyl ether (also shown below). For each isomer, two of the many acceptable drawings are shown:

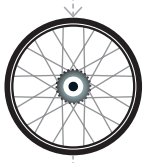




If we continue to search for alternate ways of connecting the three carbon atoms and the oxygen atom, we will not find any other ways of connecting them. So in summary, there are a total of three constitutional isomers with the molecular formula C_3H_8O, shown here:



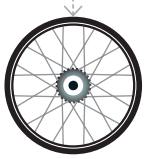
Additional skills (not yet discussed) are required to draw constitutional isomers of compounds containing a ring, a double bond, or a triple bond. Those skills will be developed in Section 14.16.



PRACTICE the skill

1.1 Draw all constitutional isomers with the following molecular formula.

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



APPLY the skill

1.2 Chlorofluorocarbons (CFCs) are gases that were once widely used as refrigerants and propellants. When it was discovered that these molecules contributed to the depletion of the ozone layer, their use was banned, but CFCs continue to be detected as contaminants in the environment.[1] Draw all of the constitutional isomers of CFCs that have the molecular formula $C_2Cl_3F_3$.

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

1.3 Electrons, Bonds, and Lewis Structures

What Are Bonds?

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

The existence of the electron was first proposed in 1874 by George Johnstone Stoney (National University of Ireland), who attempted to explain electrochemistry by suggesting the existence of

a particle bearing a unit of charge. Stoney coined the term *electron* to describe this particle. In 1897, J. J. Thomson (Cambridge University) demonstrated evidence supporting the existence of Stoney's mysterious electron and is credited with discovering the electron. In 1916, Gilbert Lewis (University of California, Berkeley) defined a **covalent bond** as the result of *two atoms sharing a pair of electrons*. As a simple example, consider the formation of a bond between two hydrogen atoms:

Each hydrogen atom has one electron. When these electrons are shared to form a bond, there is a decrease in energy, indicated by the negative value of ΔH. The energy diagram in Figure 1.2 plots the energy of the two hydrogen atoms as a function of the distance between them. Focus on the right side of the diagram, which represents the hydrogen atoms separated by a large distance. Moving toward the left on the diagram, the hydrogen atoms approach each other, and there are several forces that must be taken into account: (1) the force of repulsion between the two negatively charged electrons, (2) the force of repulsion between the two positively charged nuclei, and (3) the forces of attraction between the positively charged nuclei and the negatively charged electrons. As the hydrogen atoms get closer to each other, all of these forces get stronger. Under these circumstances, the electrons are capable of moving in such a way so as to minimize the repulsive forces between them while maximizing their attractive forces with the nuclei. This provides for a net force of attraction, which lowers the energy of the system. As the hydrogen atoms move still closer together, the energy continues to be lowered until the nuclei achieve a separation (internuclear distance) of 0.74 angstroms (Å). At that point, the force of repulsion between the nuclei begins to overwhelm the forces of attraction, causing the energy of the system to increase if the atoms are brought any closer together. The lowest point on the curve represents the lowest energy (most stable) state. This state determines both the bond length (0.74 Å) and the bond strength (436 kJ/mol).

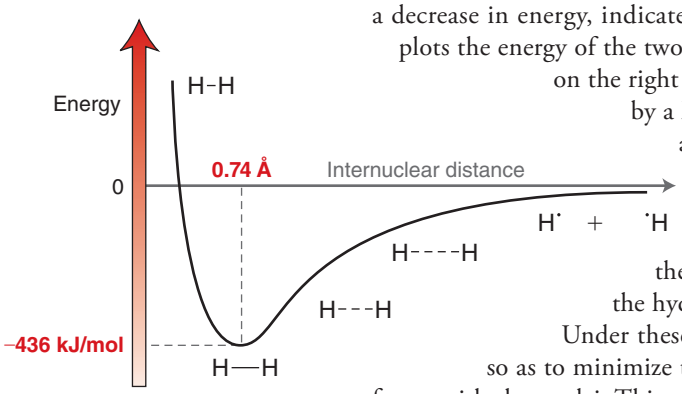


FIGURE 1.2
An energy diagram showing the energy as a function of the internuclear distance between two hydrogen atoms.

BY THE WAY
1 Å = 10^{-10} meters.

Drawing the Lewis Structure of an Atom

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

- The nucleus of an atom is comprised of protons and neutrons. Each proton has a charge of +1, and each neutron is electrically neutral.
- For a neutral atom, the number of protons is balanced by an equal number of electrons, which have a charge of −1 and exist in shells. The first shell, which is closest to the nucleus, can contain two electrons, and the second shell can contain up to eight electrons.
- The electrons in the outermost shell of an atom are called the valence electrons. The number of valence electrons in an atom is identified by its group number in the periodic table (Figure 1.3). So, for example, carbon (C) has four valence electrons because it is in group 4A of the periodic table.

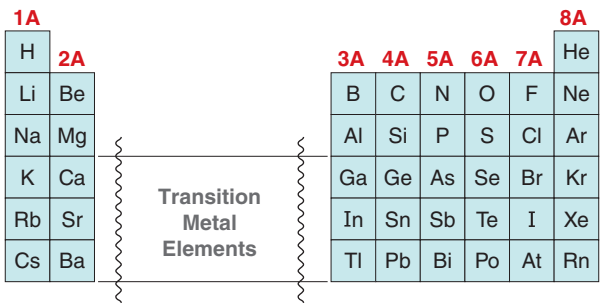
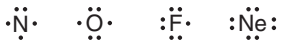


FIGURE 1.3
A periodic table showing group numbers.

The Lewis dot structure of an individual atom indicates the number of valence electrons, which are placed as dots around the periodic symbol of the atom (C for carbon, O for oxygen, etc.). For atoms

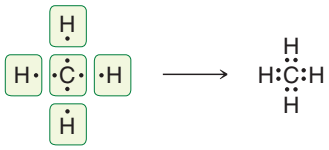
with four or fewer valence electrons, each valence electron is drawn by itself (unpaired), as seen in the following cases:

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

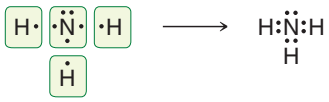


Drawing the Lewis Structure of a Small Molecule

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

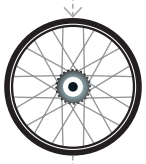


This observation, called the **octet rule**, explains why carbon is tetravalent. As just shown, it can achieve an octet of electrons by using each of its four valence electrons to form a bond. The octet rule also explains why nitrogen is trivalent. Specifically, it has five valence electrons and requires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



In Chapter 2, we will discuss the octet rule in more detail; in particular, we will explore when it can be violated and when it cannot be violated. For now, let's practice drawing Lewis structures.

SKILLBUILDER



1.2 DRAWING THE LEWIS STRUCTURE OF A SMALL MOLECULE

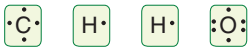
LEARN the skill

Draw the Lewis structure of CH_2O.

SOLUTION

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

STEP 1
Draw all individual atoms.



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

STEP 2
Connect atoms that form more than one bond.

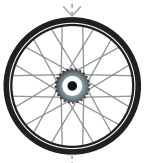
Next, connect all hydrogen atoms. We place the hydrogen atoms next to carbon, because carbon has more unpaired electrons than oxygen.

STEP 3
Connect the hydrogen atoms.

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

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

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



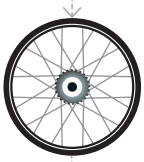
PRACTICE the skill

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

(a) C_2H_6 **(b)** C_2H_4 **(c)** C_2H_2 **(d)** C_3H_8 **(e)** CH_3OH

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

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



APPLY the skill

1.6 Smoking tobacco with a water pipe, or hookah, is often perceived as being less dangerous than smoking cigarettes, but hookah smoke has been found to contain the same variety of toxins and carcinogens (cancer-causing compounds) as cigarette smoke.[2] Draw a Lewis structure for each of the following dangerous compounds found in tobacco smoke:

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

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

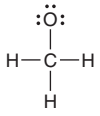
1.4 Identifying Formal Charges

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

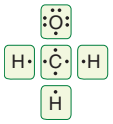
1. Determine the appropriate number of valence electrons for an atom.
2. Determine whether the atom exhibits the appropriate number of electrons.

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

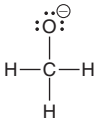
After identifying the appropriate number of electrons for each atom in a Lewis structure, the next task is to determine if any of the atoms exhibit an unexpected number of electrons. For example, consider the structure shown on the right:



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



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

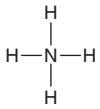


SKILLBUILDER

1.3 CALCULATING FORMAL CHARGE

LEARN the skill

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



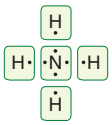
SOLUTION

STEP 1
Determine the appropriate number of valence electrons.

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

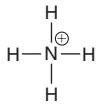
STEP 2
Determine the actual number of valence electrons in this case.

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



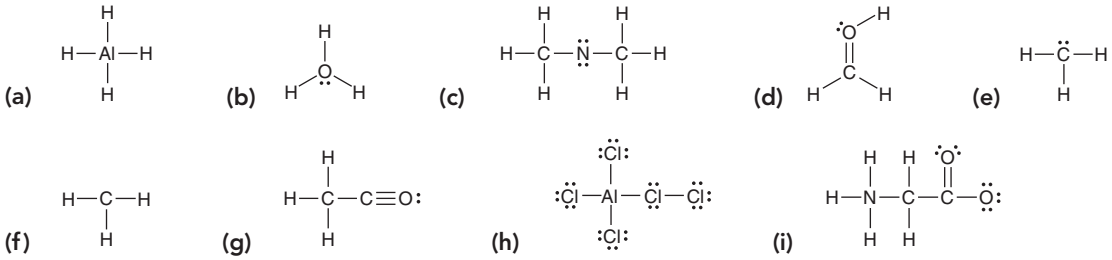
STEP 3
Assign a formal charge.

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



PRACTICE the skill

1.7 Identify any formal charges in the structures below:

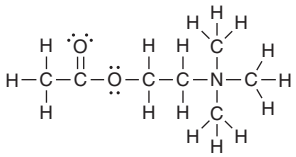


1.8 Draw a structure for each of the following ions; in each case, indicate which atom possesses the formal charge:

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

APPLY the skill

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



Acetylcholine

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

1.5 Induction and Polar Covalent Bonds

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

TABLE 1.1 ELECTRONEGATIVITY VALUES OF SOME COMMON ELEMENTS

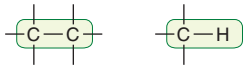
Increasing electronegativity →

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

↑ Increasing electronegativity

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

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



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

If the difference in electronegativity is between 0.5 and 1.7, the electrons are not shared equally between the atoms, resulting in a **polar covalent bond**. For example, consider a bond between carbon and oxygen (C—O). Oxygen is significantly more electronegative (3.5) than carbon (2.5), and therefore oxygen will more strongly attract the electrons of the bond. The withdrawal of electrons toward oxygen is called **induction**, which is often indicated with an arrow like this.

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

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

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

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

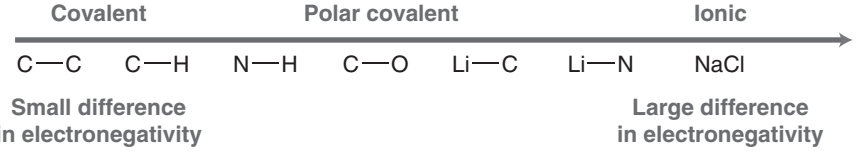
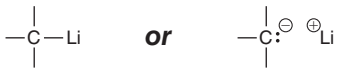


FIGURE 1.4
The nature of various bonds commonly encountered in organic chemistry.

This spectrum has two extremes: covalent bonds on the left and ionic bonds on the right. Between these two extremes are the polar covalent bonds. Some bonds fit clearly into one category, such as C—C bonds (covalent), C—O bonds (polar covalent), or NaCl bonds (ionic). However,

there are many cases that are not so clear-cut. For example, a C—Li bond has a difference in electronegativity of 1.5, and this bond is often drawn either as polar covalent or as ionic. Both drawings are acceptable:



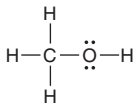
Another reason to avoid absolute cutoff numbers when comparing electronegativity values is that the electronegativity values shown above are obtained via one particular method developed by Linus Pauling. However, there are at least seven other methods for calculating electronegativity values, each of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

SKILLBUILDER

1.4 LOCATING PARTIAL CHARGES RESULTING FROM INDUCTION

LEARN the skill

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



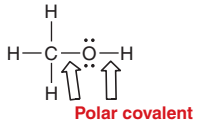
Methanol

SOLUTION

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

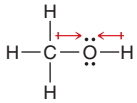
The C—O bond and the O—H bond are both polar covalent bonds:

STEP 1 Identify all polar covalent bonds.



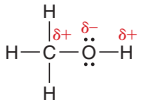
Now determine the direction of the inductive effects. Oxygen is more electronegative than C or H, so the inductive effects are shown like this:

STEP 2 Determine the direction of each dipole.



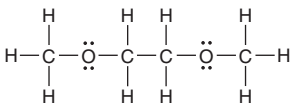
These inductive effects dictate the locations of the partial charges:

STEP 3 Indicate the location of partial charges.

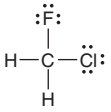


PRACTICE the skill

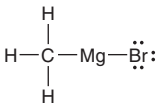
1.10 For each of the following compounds, identify any polar covalent bonds by drawing δ+ and δ− symbols in the appropriate locations:



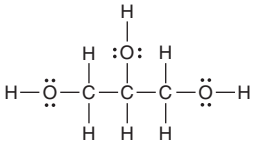
(a)



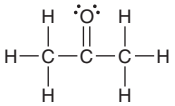
(b)



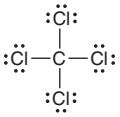
(c)



(d)



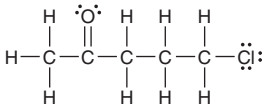
(e)



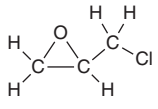
(f)

APPLY the skill

1.11 The regions of δ+ in a compound are the regions most likely to be attacked by an anion, such as hydroxide (HO^-). In the compound shown, identify the two carbon atoms that are most likely to be attacked by a hydroxide ion.



1.12 Plastics and synthetic fibers are examples of *polymers*, which are very large molecules made by joining repeating subunits of carbon-containing molecules (explored in more detail in Chapter 27). Although most synthetic polymers are prepared from fossil fuel sources, many researchers are exploring ways to make polymers from renewable sources instead. One example is the synthesis of an epoxy resin polymer using a by-product from cashew nut processing, another compound isolated from corn cobs, and epichlorohydrin, shown here.[4] Identify any polar covalent bonds in epichlorohydrin by drawing δ+ and δ− symbols in the appropriate locations.

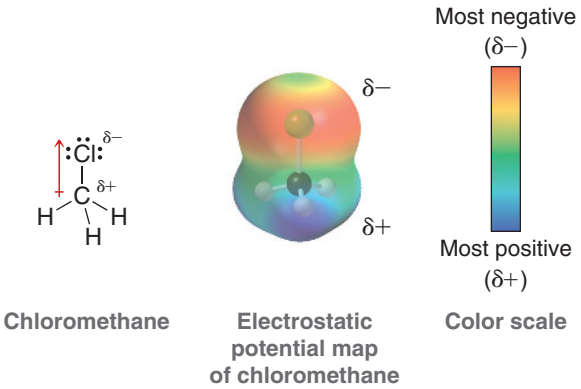


Epichlorohydrin

need more **PRACTICE?** **Try Problems 1.33, 1.34, 1.43, 1.54**

Electrostatic Potential Maps

Partial charges can be visualized with three-dimensional, rainbow-like images called **electrostatic potential maps**. As an example, consider the following electrostatic potential map of chloromethane:



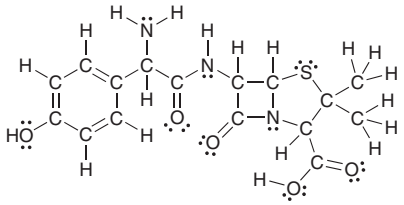
Chloromethane | Electrostatic potential map of chloromethane | Color scale

In the image, a color scale is used to represent areas of δ− and δ+. As indicated, red represents a region that is δ−, while blue represents a region that is δ+. In reality, electrostatic potential maps are rarely used by practicing organic chemists when they communicate with each other; however, these illustrations can often be helpful to students who are learning organic chemistry. Electrostatic potential maps are generated by performing a series of calculations. Specifically, an imaginary point positive charge is positioned at various locations, and for each location, we calculate the potential energy associated with the attraction between the point positive charge and the surrounding electrons. A large attraction indicates a position of δ−, while a small attraction indicates a position of δ+. The results are then illustrated using colors, as shown above.

A comparison of any two electrostatic potential maps is only valid if both maps were prepared using the same color scale. Throughout this book, care has been taken to use the same color scale whenever two maps are directly compared to each other. However, it will not be useful to compare two maps from different pages of this book (or any other book), as the exact color scales are likely to be different.

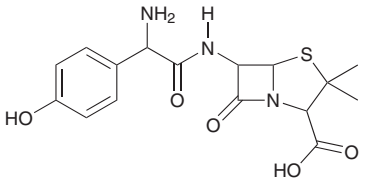
1.6 Reading Bond-Line Structures

It is not practical to draw Lewis structures for all compounds, especially large ones. As an example, consider the structure of amoxicillin, one of the most commonly used antibiotics in the penicillin family:



Amoxicillin

Previously fatal infections have been rendered harmless by antibiotics such as the one above. Amoxicillin is not a large compound, yet drawing this compound is time consuming. To deal with this problem, organic chemists have developed an efficient drawing style that can be used to draw molecules very quickly. **Bond-line structures** not only simplify the drawing process but also are easier to read. The following is a bond-line structure of amoxicillin.

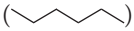


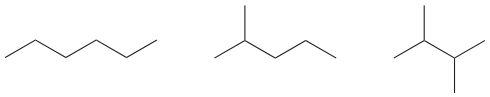
Most of the atoms are not drawn, but with practice, these drawings will become very user-friendly. Throughout the rest of this textbook, most compounds will be drawn in bond-line format, and therefore, it is absolutely critical that you are able to read these types of drawings. This section is designed to develop the skills necessary to read and interpret bond-line drawings.

BY THE WAY

You may find it worthwhile to purchase or borrow a molecular model set. There are several different kinds of molecular model sets on the market, and most of them are comprised of plastic pieces that can be connected to generate models of small molecules. Any one of these model sets will help you to visualize the relationship between molecular structures and the drawings used to represent them.

How to Read Bond-Line Structures

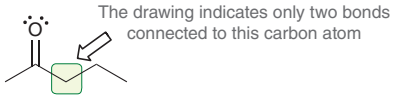
Bond-line structures are drawn in a zigzag format (), where each corner or endpoint represents a carbon atom. For example, each of the following compounds has six carbon atoms (count them!):



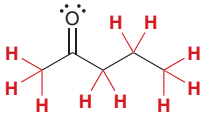
Double bonds are shown with two lines, and triple bonds are shown with three lines:

Notice that triple bonds are drawn in a linear fashion rather than in a zigzag format because triple bonds have linear geometry (as we will see in Section 1.10). The two carbon atoms of a triple bond and the two carbon atoms connected to them are drawn in a straight line. All other bonds are drawn in a zigzag format; for example, the following compound has eight carbon atoms:

Hydrogen atoms bonded to carbon are also not shown in bond-line structures, because it is assumed that each carbon atom will possess enough hydrogen atoms so as to achieve a total of four bonds (an octet of electrons). For example, the following highlighted carbon atom appears to have only two bonds:



Therefore, we can infer that there must be two more bonds to hydrogen atoms that have not been drawn (to give a total of four bonds). In this way, all hydrogen atoms are inferred by the drawing:



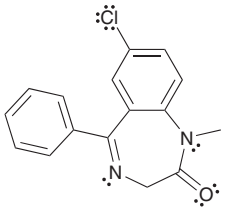
With a bit of practice, it will no longer be necessary to count bonds. Familiarity with bond-line structures will allow you to "see" all of the hydrogen atoms even though they are not drawn. This level of familiarity is absolutely essential, so let's get some practice.

SKILLBUILDER

1.5 READING BOND-LINE STRUCTURES

LEARN the skill

Consider the structure of diazepam, first marketed by the Hoffmann-La Roche Company under the trade name Valium. Diazepam is a sedative and muscle relaxant used in the treatment of anxiety, insomnia, and seizures. Identify the number of carbon atoms in diazepam, then fill in all the missing hydrogen atoms that are inferred by the drawing.

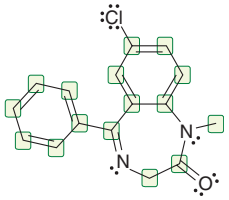


Diazepam (Valium)

SOLUTION

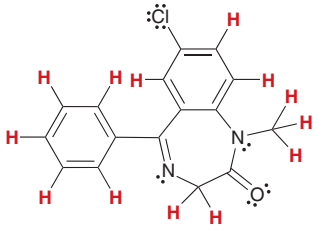
STEP 1
Count the carbon atoms, which are represented by corners or endpoints.

Remember that each corner and each endpoint represents a carbon atom. This compound therefore has 16 carbon atoms, highlighted here.



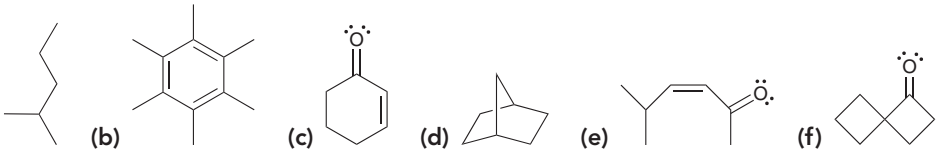
STEP 2
Count the hydrogen atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds.

Each carbon atom should have four bonds. We therefore draw enough hydrogen atoms in order to give each carbon atom a total of four bonds. Any carbon atoms that already have four bonds will not have any hydrogen atoms:



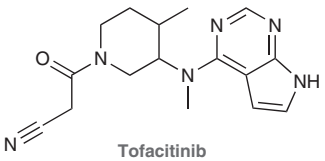
PRACTICE the skill

1.13 For each of the following molecules, determine the number of carbon atoms present and then determine the number of hydrogen atoms connected to each carbon atom:



APPLY the skill

1.14 Initially approved to treat psoriasis (a skin disorder) and rheumatoid arthritis, the drug tofacitinib has recently been found to also promote hair growth and restore hair loss.[5] Identify the number of carbon atoms in tofacitinib, and then fill in all of the missing hydrogen atoms that are inferred by the drawing.



Tofacitinib

need more **PRACTICE?** **Try Problems 1.46, 1.47, 1.71**

1.7 Atomic Orbitals

Quantum Mechanics

By the 1920s, vitalism had been discarded. Chemists were aware of constitutional isomerism and had developed the structural theory of matter. The electron had been discovered and identified as the source of bonding, and Lewis structures were used to keep track of shared and unshared electrons. But the understanding of electrons was about to change dramatically.

In 1924, French physicist Louis de Broglie suggested that electrons, heretofore considered as particles, also exhibited wavelike properties. Based on this assertion, a new theory of matter was born. In 1926, Erwin Schrödinger, Werner Heisenberg, and Paul Dirac independently proposed a mathematical description of the electron that incorporated its wavelike properties. This new theory, called *wave mechanics*, or **quantum mechanics**, radically changed the way we viewed the nature of matter and laid the foundation for our current understanding of electrons and bonds.

Quantum mechanics is deeply rooted in mathematics and represents an entire subject by itself. The mathematics involved is beyond the scope of our course, and we will not discuss it here. However, in order to understand the nature of electrons, it is critical to understand a few simple highlights from quantum mechanics:

- An equation is constructed to describe the total energy of a hydrogen atom (i.e., one proton plus one electron). This equation, called the **wave equation**, takes into account the wavelike behavior of an electron that is in the electric field of a proton.
- The wave equation is then solved to give a series of solutions called **wavefunctions**. The Greek symbol psi (ψ) is used to denote each wavefunction (ψ_1, ψ_2, ψ_3, etc.). Each of these wavefunctions corresponds to an allowed energy level for the electron. This result is incredibly important because it suggests that an electron, when contained in an atom, can only exist at discrete energy levels (ψ_1, ψ_2, ψ_3, etc.). In other words, the energy of the electron is *quantized*.
- Each wavefunction is a function of spatial location. It provides information that allows us to assign a numerical value for each location in three-dimensional space relative to the nucleus. The square of that value (ψ^2 for any particular location) has a special meaning. It indicates the probability of finding the electron in that location. Therefore, a three-dimensional plot of ψ^2 will generate an image of an atomic orbital (Figure 1.5).

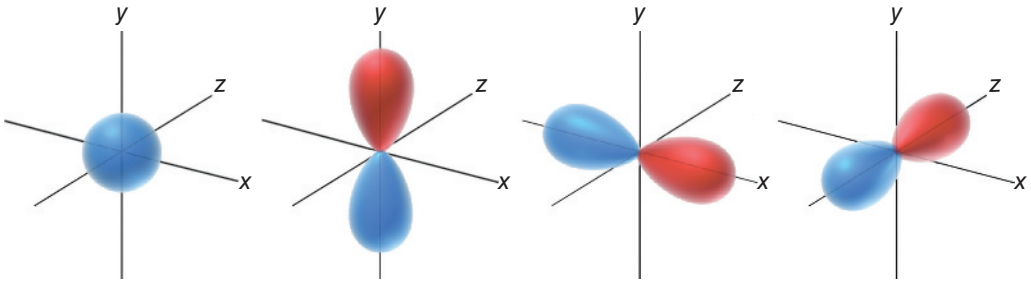


FIGURE 1.5
Illustrations of an *s* orbital and three *p* orbitals.

Electron Density and Atomic Orbitals

An *orbital* is a region of space that can be occupied by an electron. But care must be taken when trying to visualize this. There is a statement from earlier in this section that must be clarified because it is potentially misleading: "ψ^2 *represents the probability of finding an electron in a particular location.*" This statement seems to treat an electron as if it were a particle flying around within a specific region of space. But remember that an electron is not purely a particle—it has wavelike properties as well. Therefore, we must construct a mental image that captures both of these properties. That is not easy to do, but the following analogy might help. We will treat an occupied orbital as if it is a cloud—similar to a cloud in the sky. No analogy is perfect, and there are certainly features of clouds that are very different from orbitals. However, focusing on some of these differences between electron

clouds (occupied orbitals) and real clouds makes it possible to construct a better mental model of an electron in an orbital:

- Clouds in the sky can come in any shape or size. However, electron clouds have specific shapes and sizes (as defined by the orbitals).
- A cloud in the sky is comprised of billions of individual water molecules. An electron cloud is not comprised of billions of particles. We must think of an electron cloud as a single entity, even though it can be thicker in some places and thinner in other places. This concept is critical and will be used extensively throughout the course in explaining reactions.
- A cloud in the sky has edges, and it is possible to define a region of space that contains 100% of the cloud. In contrast, an electron cloud does not have defined edges. We frequently use the term **electron density**, which is associated with the probability of finding an electron in a particular region of space. The "shape" of an orbital refers to a region of space that contains 90–95% of the electron density. Beyond this region, the remaining 5–10% of the electron density tapers off but never ends. In fact, if we want to consider the region of space that contains 100% of the electron density, we must consider the entire universe.

In summary, we must think of an orbital as a region of space that can be occupied by electron density. An occupied orbital must be treated as a *cloud of electron density*. This region of space is called an **atomic orbital** (AO), because it is a region of space defined with respect to the nucleus of a single atom. Examples of atomic orbitals are the *s*, *p*, *d*, and *f* orbitals that were discussed in your general chemistry textbook.

Phases of Atomic Orbitals

Our discussion of electrons and orbitals has been based on the premise that electrons have wavelike properties. As a result, it will be necessary to explore some of the characteristics of simple waves in order to understand some of the characteristics of orbitals.

Consider a wave that moves across the surface of a lake (Figure 1.6). The wavefunction (ψ) mathematically describes the wave, and the value of the wavefunction is dependent on location. Locations above the average level of the lake have a positive value for ψ (indicated in red), and locations below the average level of the lake have a negative value for ψ (indicated in blue). Locations where the value of ψ is zero are called **nodes**.

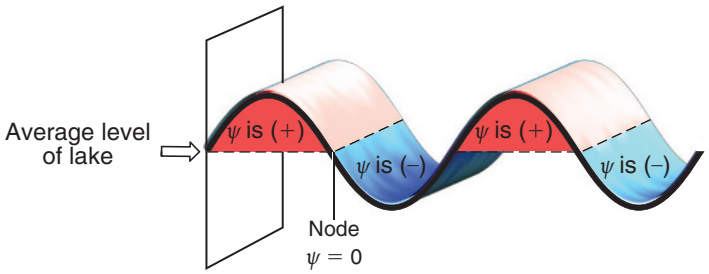


FIGURE 1.6
Phases of a wave moving across the surface of a lake.

Similarly, orbitals can have regions where the value of ψ is positive, negative, or zero. For example, consider a *p* orbital (Figure 1.7). Notice that the *p* orbital has two lobes: The top lobe is a region of space where the values of ψ are positive, while the bottom lobe is a region where the values of ψ are negative. Between the two lobes is a location where $\psi = 0$. This location represents a node.

Be careful not to confuse the sign of ψ (+ or −) with electrical charge. A positive value for ψ does not imply a positive charge. The value of ψ (+ or −) is a mathematical convention that refers to the *phase* of the wave (just like in the lake). Although ψ can have positive or negative values, nevertheless ψ^2 (which describes the electron density as a function of location) will always be a positive number. At a node, where $\psi = 0$, the electron density (ψ^2) will also be zero. This means that there is no electron density located at a node.

From this point forward, we will draw the lobes of an orbital with colors (red and blue) to indicate the phase of ψ for each region of space.

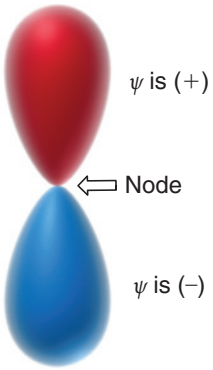


FIGURE 1.7
The phases of a *p* orbital.

Filling Atomic Orbitals with Electrons

The energy of an electron depends on the type of orbital that it occupies. Most of the organic compounds that we will encounter will be composed of first- and second-row elements (H, C, N, and O). These elements utilize the 1*s* orbital, the 2*s* orbital, and the three 2*p* orbitals. Our discussions will therefore focus primarily on these orbitals (Figure 1.8). Electrons are lowest in energy when they occupy a 1*s* orbital, because the 1*s* orbital is closest to the nucleus and it has no nodes (the more nodes that an orbital has, the greater its energy). The 2*s* orbital has one node and is farther away from the nucleus; it is therefore higher in energy than the 1*s* orbital. After the 2*s* orbital, there are three 2*p* orbitals that are all equivalent in energy to one another. Orbitals with the same energy level are called **degenerate orbitals**.

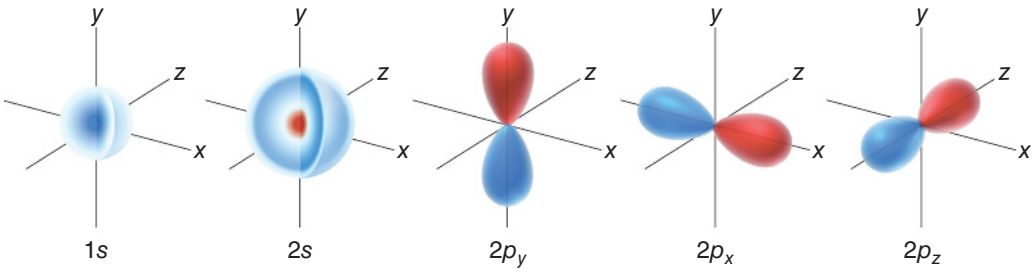


FIGURE 1.8
Illustrations of *s* orbitals and three *p* orbitals.

As we move across the periodic table, starting with hydrogen, each element has one more electron than the element before it (Figure 1.9). The order in which the orbitals are filled by electrons is determined by just three simple principles:

1. The **Aufbau principle.** The lowest energy orbital is filled first.
2. The **Pauli exclusion principle.** Each orbital can accommodate a maximum of two electrons that have opposite spin. To understand what "spin" means, we can imagine an electron spinning in space (although this is an oversimplified explanation of the term "spin"). For reasons that are beyond the scope of this course, electrons only have two possible spin states (designated by ↓ or ↑). In order for the orbital to accommodate two electrons, the electrons must have opposite spin states.
3. **Hund's rule.** When dealing with degenerate orbitals, such as *p* orbitals, one electron is placed in each degenerate orbital first, before electrons are paired up.

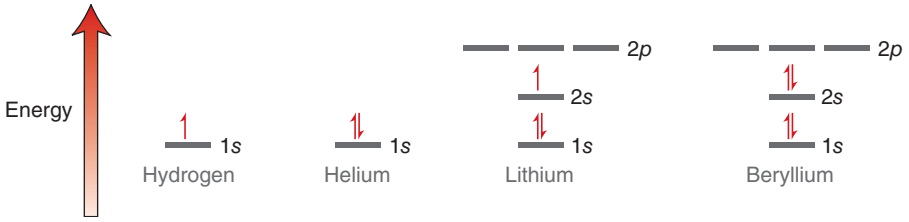


FIGURE 1.9
Energy diagrams showing the electron configurations for H, He, Li, and Be.

The application of the first two principles can be seen in the electron configurations shown in Figure 1.9 (H, He, Li, and Be). The application of the third principle can be seen in the electron configurations for the remaining second-row elements (Figure 1.10).

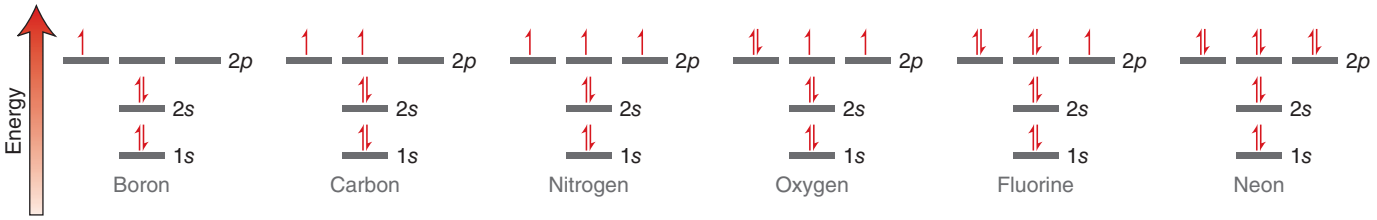


FIGURE 1.10
Energy diagrams showing the electron configurations for B, C, N, O, F, and Ne.

SKILLBUILDER

1.6 IDENTIFYING ELECTRON CONFIGURATIONS

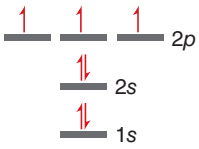
LEARN the skill

Identify the electron configuration of a nitrogen atom.

SOLUTION

STEP 1
Place the valence electrons in atomic orbitals using the Aufbau principle, the Pauli exclusion principle, and Hund's rule.

The electron configuration indicates which atomic orbitals are occupied by electrons. Nitrogen has a total of seven electrons. These electrons occupy atomic orbitals of increasing energy, with a maximum of two electrons in each orbital:



Nitrogen

STEP 2
Identify the number of valence electrons in each atomic orbital.

Two electrons occupy the 1*s* orbital, two electrons occupy the 2*s* orbital, and three electrons occupy the 2*p* orbitals. This is summarized using the following notation:

$$1s^2 2s^2 2p^3$$

PRACTICE the skill

1.15 Identify the electron configuration for each of the following atoms:

(a) Carbon **(b)** Oxygen **(c)** Boron **(d)** Fluorine **(e)** Sodium **(f)** Aluminum

1.16 Identify the electron configuration for each of the following ions:

(a) A carbon atom with a negative charge
(b) A carbon atom with a positive charge
(c) A nitrogen atom with a positive charge
(d) An oxygen atom with a negative charge

APPLY the skill

1.17 Silicon is the second most abundant element in the Earth's crust, and its compounds can be as ordinary as beach sand. However, silicon also plays an indispensable role in modern devices such as computers, cell phones, semiconductors, and solar panels. A recent technology incorporates silicon in nanometer-sized particles called quantum dots that act as luminescent labels for pancreatic cancer cells.[6] Identify the electron configuration of a silicon atom.

need more **PRACTICE?** **Try Problem 1.40**

1.8 Valence Bond Theory

With the understanding that electrons occupy regions of space called orbitals, we can now turn our attention to a deeper understanding of covalent bonds. Specifically, a covalent bond is formed from the overlap of atomic orbitals. There are two commonly used theories for describing the nature of atomic orbital overlap: valence bond theory and molecular orbital (MO) theory. The valence bond approach is more simplistic in its treatment of bonds, and therefore we will begin our discussion with valence bond theory.

If we are going to treat electrons as waves, then we must quickly review what happens when two waves interact with each other. Two waves that approach each other can interfere in one of two possible ways—constructively or destructively. Similarly, when atomic orbitals overlap, they can interfere either constructively (Figure 1.11) or destructively (Figure 1.12).

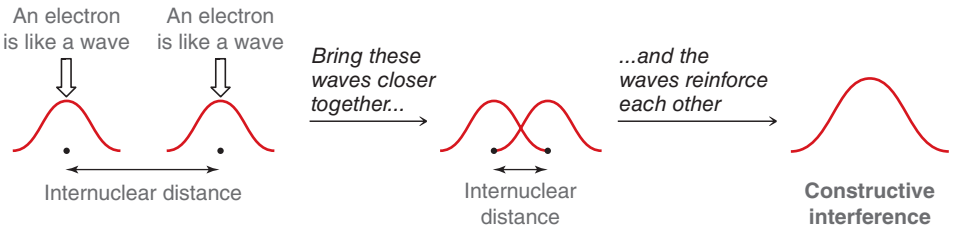


FIGURE 1.11
Constructive interference resulting from the interaction of two electrons.

Constructive interference produces a wave with larger amplitude. In contrast, destructive interference results in waves canceling each other, which produces a node (Figure 1.12).

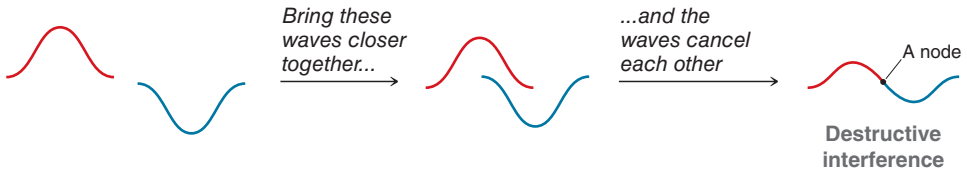


FIGURE 1.12
Destructive interference resulting from the interaction of two electrons.

According to **valence bond theory**, a bond is simply the sharing of electron density between two atoms as a result of the constructive interference of their atomic orbitals. Consider, for example, the bond that is formed between the two hydrogen atoms in molecular hydrogen (H_2). This bond is formed from the overlap of the 1*s* orbitals of each hydrogen atom (Figure 1.13).

The electron density of this bond is primarily located on the bond axis (the line that can be drawn between the two hydrogen atoms). This type of bond is called a **sigma (σ) bond** and is characterized by circular symmetry with respect to the bond axis. To visualize what this means, imagine a plane that is drawn perpendicular to the bond axis. This plane will carve out a circle (Figure 1.14). This is the defining feature of σ bonds and will be true of all purely single bonds. Therefore, *all single bonds are σ bonds*.

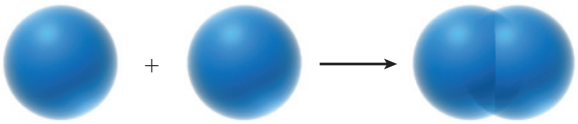


FIGURE 1.13
The overlap of the 1*s* atomic orbitals of two hydrogen atoms, forming molecular hydrogen (H_2).

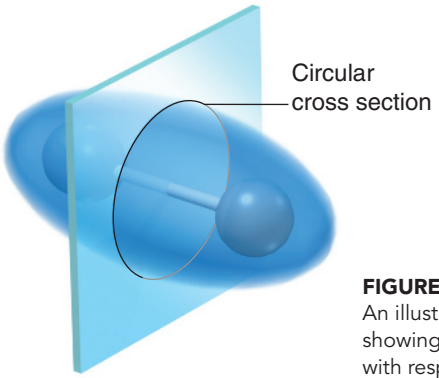


FIGURE 1.14
An illustration of a sigma bond, showing the circular symmetry with respect to the bond axis.

1.9 Molecular Orbital Theory

In most situations, valence bond theory will be sufficient for our purposes. However, there will be cases in the upcoming chapters where valence bond theory will be inadequate to describe the observations. In such cases, we will utilize molecular orbital theory, a more sophisticated approach to viewing the nature of bonds.

Molecular orbital (MO) theory uses mathematics as a tool to explore the consequences of atomic orbital overlap. The mathematical method is called the *linear combination of atomic orbitals (LCAO)*. According to this theory, atomic orbitals are mathematically combined to produce new orbitals, called **molecular orbitals**.

It is important to understand the distinction between atomic orbitals and molecular orbitals. Both types of orbitals are used to accommodate electrons, but an atomic orbital is a region of space associated with an individual atom, while a molecular orbital is associated with an entire molecule. That is, the molecule is considered to be a single entity held together by many electron clouds, some of which can actually span the entire length of the molecule. These molecular orbitals are filled with electrons in a particular order in much the same way that atomic orbitals are filled. Specifically, electrons first occupy the lowest energy orbitals, with a maximum of two electrons per orbital. In order to visualize what it means for an orbital to be associated with an entire molecule, we will explore two molecules: molecular hydrogen (H_2) and bromomethane (CH_3Br).

Consider the bond formed between the two hydrogen atoms in molecular hydrogen. This bond is the result of the overlap of two atomic orbitals (*s* orbitals), each of which is occupied by one electron. According to MO theory, when two atomic orbitals overlap, they cease to exist. Instead, they are replaced by two molecular orbitals, each of which is associated with the entire molecule (Figure 1.15).

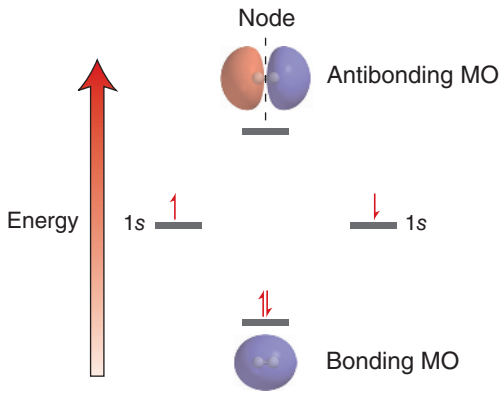


FIGURE 1.15
An energy diagram showing the relative energy levels of bonding and antibonding molecular orbitals.

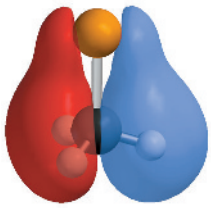


FIGURE 1.16
A low-energy molecular orbital of CH_3Br. Red and blue regions indicate the different phases, as described in Section 1.7. Notice that this molecular orbital is associated with the entire molecule, rather than being associated with two specific atoms.

In the energy diagram shown in Figure 1.15, the individual atomic orbitals are represented on the right and left, with each atomic orbital having one electron. These atomic orbitals are combined mathematically (using the LCAO method) to produce two molecular orbitals. The lower energy molecular orbital, or **bonding MO**, is the result of constructive interference of the original two atomic orbitals. The higher energy molecular orbital, or **antibonding MO**, is the result of destructive interference. Notice that the antibonding MO has one node, which explains why it is higher in energy. Both electrons occupy the bonding MO in order to achieve a lower energy state. This lowering in energy is the essence of the bond. For an H—H bond, the lowering in energy is equivalent to 436 kJ/mol. This energy corresponds with the bond strength of an H—H bond (as shown in Figure 1.2).

Now let's consider a molecule such as CH_3Br, which contains more than just one bond. Valence bond theory continues to view each bond separately, with each bond being formed from two overlapping atomic orbitals. In contrast, MO theory treats the bonding electrons as being associated with the entire molecule. The molecule has many molecular orbitals, each of which can be occupied by two electrons. Figure 1.16 illustrates one of the many molecular orbitals of CH_3Br. This molecular orbital is capable of accommodating up to two electrons. Red and blue regions indicate the different phases, as described in Section 1.7. As we saw with molecular hydrogen, not all molecular orbitals will be occupied. The bonding electrons will occupy the lower energy molecular orbitals (such as the one shown in Figure 1.16), while the higher energy molecular orbitals remain unoccupied. For every molecule, two of its molecular orbitals will be of particular interest: (1) the highest energy orbital from among the occupied orbitals is called the **highest occupied molecular orbital**, or **HOMO**, and (2) the lowest energy orbital from among the unoccupied orbitals is called the **lowest unoccupied molecular orbital**, or **LUMO**. For example, in Chapter 7, we will explore a reaction in which CH_3Br is attacked by a hydroxide ion (HO^-). In order for this process to occur, the hydroxide ion must transfer its electron density into the lowest energy, empty molecular orbital, or LUMO, of CH_3Br (Figure 1.17). The nature of the LUMO (i.e., number of nodes, location of nodes, etc.) will be useful in explaining the preferred direction from which the hydroxide ion will attack.

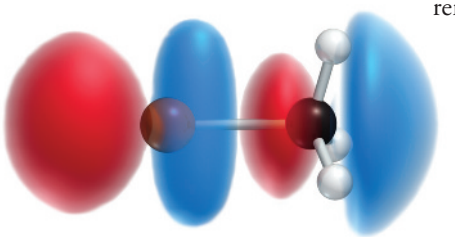


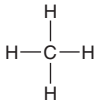
FIGURE 1.17
The LUMO of CH_3Br.

We will use MO theory several times in the chapters that follow. Most notably, in Chapter 16, we will investigate the structure of compounds containing several double bonds. For those compounds, valence bond theory will be inadequate, and MO theory will provide a more meaningful understanding of the bonding structure. Throughout this textbook, we will continue to develop both valence bond theory and MO theory.

1.10 Hybridized Atomic Orbitals

Methane and sp^3 Hybridization

Let us now apply valence bond theory to the bonds in methane:



Methane

Recall the electron configuration of carbon (Figure 1.18). This electron configuration cannot satisfactorily describe the bonding structure of methane (CH_4), in which the carbon atom has four separate C—H bonds, because the electron configuration shows only two atomic orbitals capable of forming bonds (each of these orbitals has one unpaired electron). This would imply that the carbon atom will form only two bonds, but we know that it forms four bonds. We can solve this problem by imagining an excited state of carbon (Figure 1.19): a state in which a 2*s* electron has been promoted

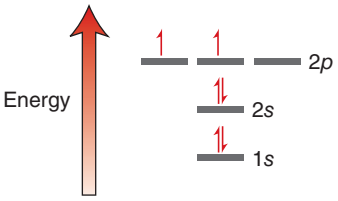


FIGURE 1.18
An energy diagram showing the electron configuration of carbon.

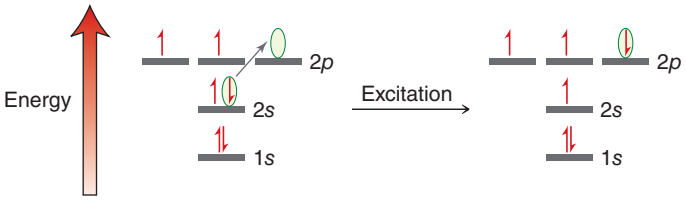


FIGURE 1.19
An energy diagram showing the electronic excitation of an electron in a carbon atom.

to a higher energy 2*p* orbital. Now the carbon atom has four atomic orbitals capable of forming bonds, but there is yet another problem here. The geometry of the 2*s* and three 2*p* orbitals does not satisfactorily explain the observed three-dimensional geometry of methane (Figure 1.20). All bond angles are 109.5°, and the four bonds point away from each other in a perfect tetrahedron. This geometry cannot be explained by an excited state of carbon because the *s* orbital and the three *p* orbitals do not occupy a tetrahedral geometry. The *p* orbitals are separated from each other by only 90° (as seen in Figure 1.5) rather than 109.5°.

This problem was solved in 1931 by Linus Pauling, who suggested that the electronic configuration of the carbon atom in methane does not necessarily have to be the same as the electronic configuration of a free carbon atom. Specifically, Pauling mathematically averaged, or *hybridized*, the 2*s* orbital and the three 2*p* orbitals, giving four degenerate hybridized atomic orbitals (Figure 1.21). The hybridization process in Figure 1.21 does not represent a real physical process that the orbitals

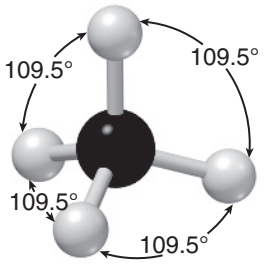


FIGURE 1.20
The tetrahedral geometry of methane. All bond angles are 109.5°.

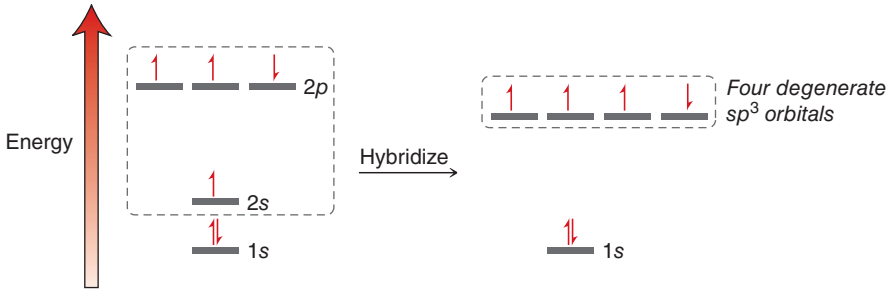


FIGURE 1.21
An energy diagram showing four degenerate hybridized atomic orbitals.

undergo. Rather, it is a mathematical procedure that is used to arrive at a satisfactory description of the observed bonding. This procedure gives us four orbitals that were produced by averaging one *s* orbital and three *p* orbitals, and therefore we refer to these atomic orbitals as ***sp*^{3}-hybridized orbitals**. Figure 1.22 shows an sp^3-hybridized orbital. If we use these hybridized atomic orbitals to describe the bonding of methane, we can successfully explain the observed geometry of the bonds. The four sp^3-hybridized orbitals are equivalent in energy (degenerate) and will therefore position themselves as far apart from each other as possible, achieving a tetrahedral geometry. Also notice that hybridized atomic orbitals are unsymmetrical. That is, hybridized atomic orbitals have a larger front lobe (shown

FIGURE 1.22
An illustration of an sp^3-hybridized atomic orbital.

in red in Figure 1.22) and a smaller back lobe (shown in blue). The larger front lobe enables hybridized atomic orbitals to be more efficient than *p* orbitals in their ability to form bonds.

Using valence bond theory, each of the four bonds in methane is represented by the overlap between an sp^3-hybridized atomic orbital from the carbon atom and an *s* orbital from a hydrogen atom (Figure 1.23). For purposes of clarity the back lobes (blue) have been omitted from the images in Figure 1.23.

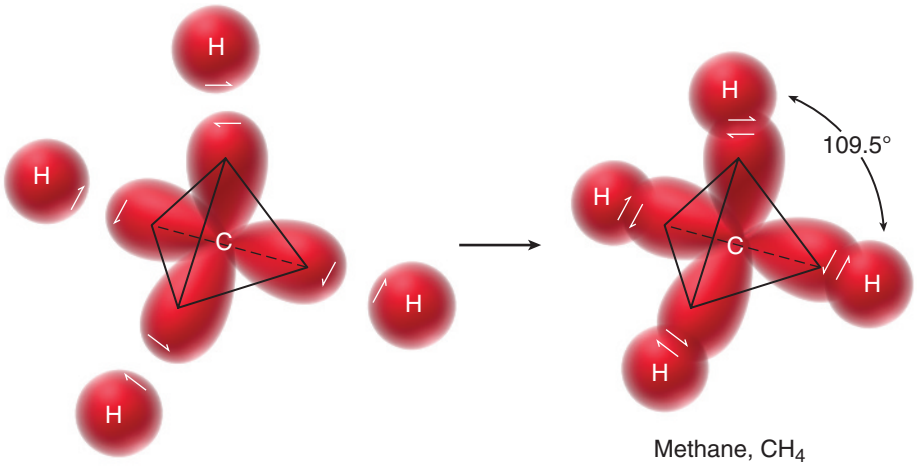
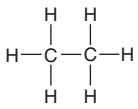


FIGURE 1.23
A tetrahedral carbon atom using each of its four sp^3-hybridized orbitals to form a bond.

The bonding in ethane is treated in much the same way:



Ethane

All bonds in this compound are single bonds, and therefore they are all σ bonds. Using the valence bond approach, each of the bonds in ethane can be treated individually and is represented by the overlap of atomic orbitals (Figure 1.24).

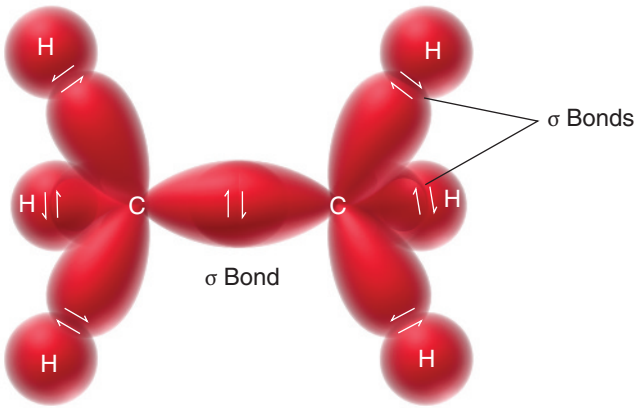
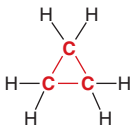


FIGURE 1.24
A valence bond picture of the bonding in ethane.

CONCEPTUAL CHECKPOINT

1.18 Cyclopropane is a compound in which the carbon atoms form a three-membered ring:

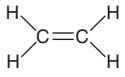


Cyclopropane

Each of the carbon atoms in cyclopropane is sp^3 hybridized. Cyclopropane is more reactive than other cyclic compounds (four-membered rings, five-membered rings, etc.). Analyze the bond angles in cyclopropane and explain why cyclopropane is so reactive.

Double Bonds and sp^2 Hybridization

Now let's consider the structure of a compound bearing a double bond. The simplest example is ethylene.



Ethylene

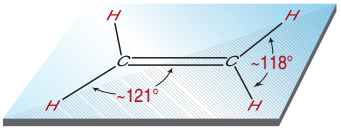


FIGURE 1.25
All six atoms of ethylene are in one plane.

Ethylene exhibits a planar geometry (Figure 1.25). A satisfactory model for explaining this geometry can be achieved by the mathematical maneuver of hybridizing the *s* and *p* orbitals of the carbon atom to obtain hybridized atomic orbitals. When we did this procedure earlier to explain the bonding in methane, we hybridized the *s* orbital and all three *p* orbitals to produce four equivalent sp^3-hybridized orbitals. However, in the case of ethylene, each carbon atom only needs to form bonds with three atoms, not four. Therefore, each carbon atom only needs three hybridized orbitals. So in this case we will mathematically average the *s* orbital with only two of the three *p* orbitals (Figure 1.26). The remaining *p* orbital will remain unaffected by our mathematical procedure.

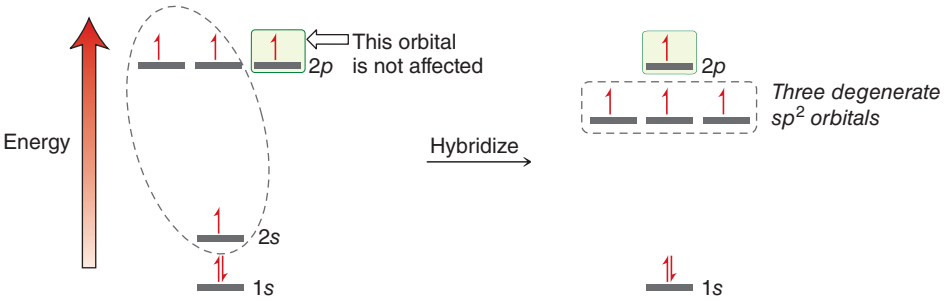


FIGURE 1.26
An energy diagram showing three degenerate sp^2-hybridized atomic orbitals.

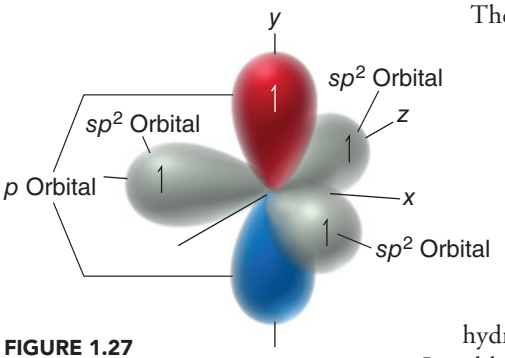


FIGURE 1.27
An illustration of an sp^2-hybridized carbon atom.

The result of this mathematical operation is a carbon atom with one *p* orbital and three ***sp^2*-hybridized orbitals** (Figure 1.27). In Figure 1.27 the *p* orbital is shown in red and blue, and the hybridized orbitals are shown in gray (for clarity, only the front lobe of each hybridized orbital is shown). They are called sp^2-hybridized orbitals to indicate that they were obtained by averaging one *s* orbital and two *p* orbitals. As shown in Figure 1.27, each of the carbon atoms in ethylene is sp^2 hybridized, and we can use this hybridization state to explain the bonding structure of ethylene.

Each carbon atom in ethylene has three sp^2-hybridized orbitals available to form σ bonds (Figure 1.28). One σ bond forms between the two carbon atoms, and then each carbon atom also forms a σ bond with each of its neighboring hydrogen atoms.

In addition, each carbon atom has one *p* orbital (shown in Figure 1.28 with blue and red lobes).

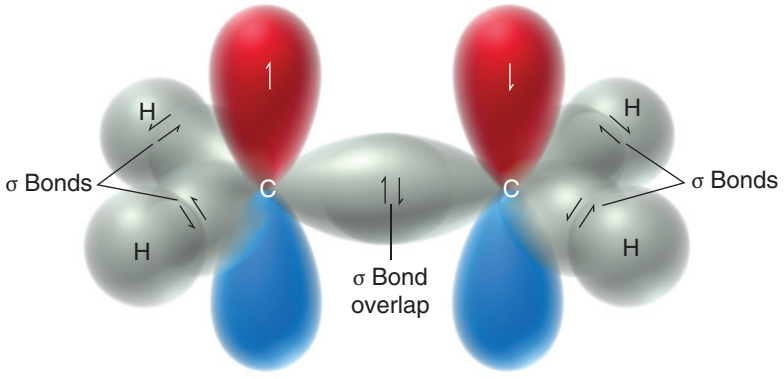


FIGURE 1.28
An illustration of the σ bonds in ethylene.

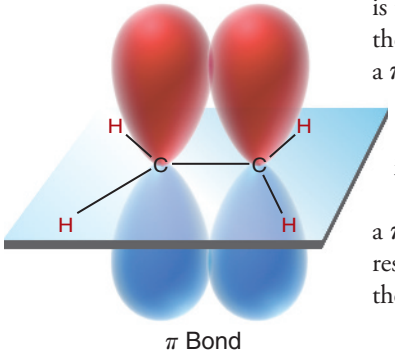


FIGURE 1.29
An illustration of the π bond in ethylene.

These *p* orbitals actually overlap with each other as well, which is a separate bonding interaction called a **pi (π) bond** (Figure 1.29). Do not be confused by the nature of this type of bond. It is true that the π overlap occurs in two places—above the plane of the molecule (in red) and below the plane (in blue). Nevertheless, these two regions of overlap represent only one interaction called a π bond.

The image of the π bond in Figure 1.29 is based on the valence bond approach (the *p* orbitals are simply drawn overlapping each other). Molecular orbital theory provides a fairly similar image of a π bond. Compare Figure 1.29 with the bonding MO in Figure 1.30.

To summarize, we have seen that the carbon atoms of ethylene are connected via a σ bond and a π bond. The σ bond results from the overlap of sp^2-hybridized atomic orbitals, while the π bond results from the overlap of *p* orbitals. These two separate bonding interactions (σ and π) comprise the double bond of ethylene.

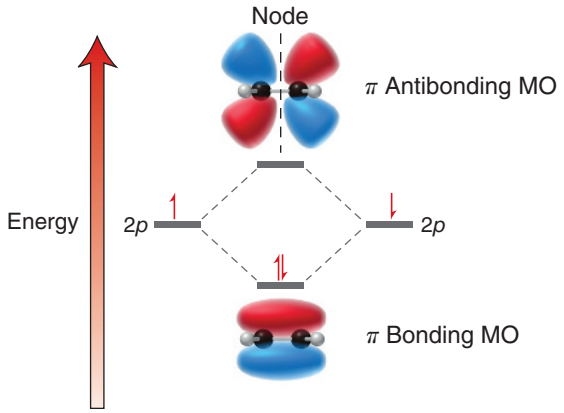


FIGURE 1.30
An energy diagram showing images of bonding and antibonding MOs in ethylene.

CONCEPTUAL CHECKPOINT

1.19 Consider the structure of formaldehyde:

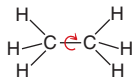
Formaldehyde

(a) Identify the type of bonds that form the C═O double bond.

(b) Identify the atomic orbitals that form each C—H bond.

(c) What type of atomic orbitals do the lone pairs occupy?

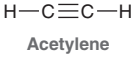
1.20 Sigma bonds experience free rotation at room temperature:



In contrast, π bonds do not experience free rotation. Explain. (**Hint:** Compare Figures 1.24 and 1.29, focusing on the orbitals used in forming a σ bond and the orbitals used in forming a π bond. In each case, what happens to the orbital overlap during bond rotation?)

Triple Bonds and *sp* Hybridization

Now let's consider the bonding structure of a compound bearing a triple bond, such as acetylene:



Acetylene

A triple bond is formed by ***sp*-hybridized** carbon atoms. To achieve *sp* hybridization, one *s* orbital is mathematically averaged with only one *p* orbital (Figure 1.31). This leaves two *p* orbitals unaffected by the mathematical operation. As a result, an *sp*-hybridized carbon atom has two *sp* orbitals and two *p* orbitals (Figure 1.32).

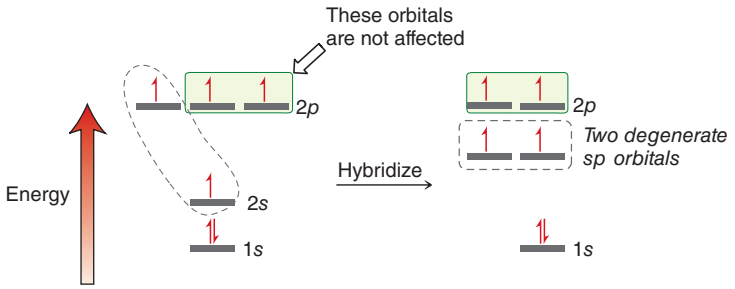


FIGURE 1.31
An energy diagram showing two degenerate *sp*-hybridized atomic orbitals.

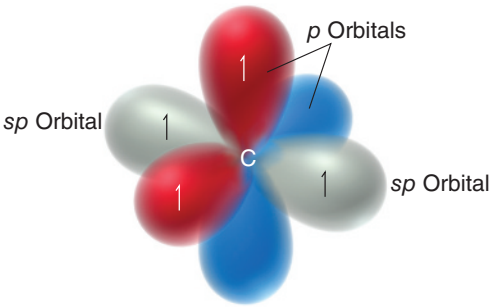


FIGURE 1.32
An illustration of an *sp*-hybridized carbon atom. The *sp*-hybridized orbitals are shown in gray.

The two *sp*-hybridized orbitals are available to form σ bonds (one on either side), and the two *p* orbitals are available to form π bonds, giving the bonding structure for acetylene shown in Figure 1.33. A triple bond between two carbon atoms is therefore the result of three separate bonding interactions: one σ bond and two π bonds. The σ bond results from the overlap of *sp* orbitals, while each of the two π bonds result from overlapping *p* orbitals. As shown in Figure 1.33, the geometry of the triple bond is linear.

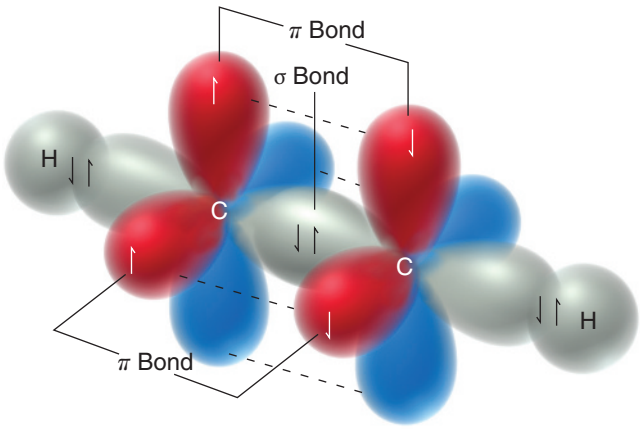


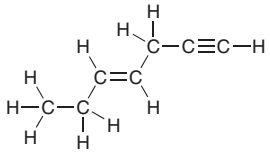
FIGURE 1.33
An illustration of the σ bonds and π bonds in acetylene.

SKILLBUILDER

1.7 IDENTIFYING HYBRIDIZATION STATES

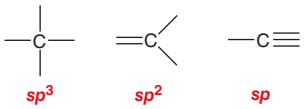
LEARN the skill

Identify the hybridization state of each carbon atom in the following compound:



SOLUTION

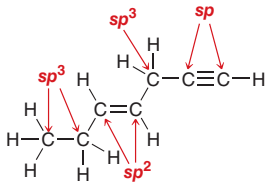
To determine the hybridization state of *an uncharged carbon atom*, simply count the number of σ bonds and π bonds:



A carbon atom with four single bonds (four σ bonds) will be sp^3 hybridized. A carbon atom with three σ bonds and one π bond will be sp^2 hybridized. A carbon atom with two σ bonds

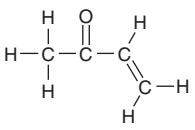
and two π bonds will be *sp* hybridized. Carbon atoms bearing a positive or negative charge will be discussed in more detail in Chapter 2.

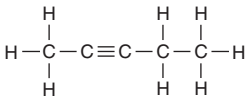
Using the simple scheme above, the hybridization state of most carbon atoms can be determined instantly:

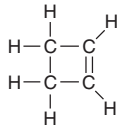


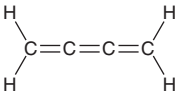
PRACTICE the skill

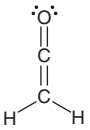
1.21 Determine the hybridization state of each carbon atom in the following compounds.


(a)


(b)

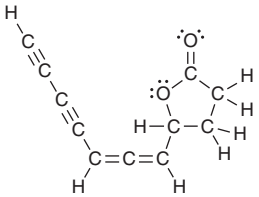

(c)


(d)


(e)

APPLY the skill

1.22 Nemotin is a compound that was first isolated from the fungi *Poria tenuis* and *Poria corticola* in the 1940s and was shown to possess potent antibacterial activity. However, its structure was not verified until it was made in the laboratory much more recently.[7] Determine the hybridization state of each carbon atom in nemotin.

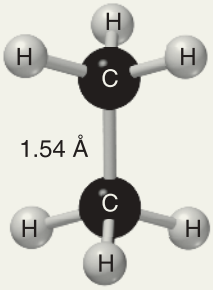
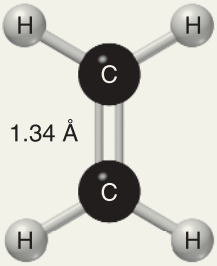
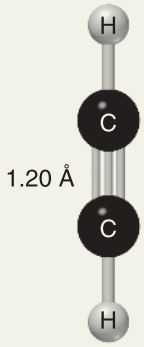

Nemotin

need more **PRACTICE?** **Try Problems 1.52, 1.53, 1.67, 1.73f, 1.73g, 1.74, 1.79a**

Bond Strength and Bond Length

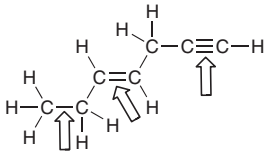
The information we have seen in this section allows us to compare single bonds, double bonds, and triple bonds. A single bond has only one bonding interaction (a σ bond), a double bond has two bonding interactions (one σ bond and one π bond), and a triple bond has three bonding interactions (one σ bond and two π bonds). Therefore, it is not surprising that a triple bond is stronger than a double bond, which in turn is stronger than a single bond. Compare the strengths and lengths of the C—C bonds in ethane, ethylene, and acetylene (Table 1.2).

TABLE 1.2 COMPARISON OF BOND LENGTHS AND BOND ENERGIES FOR ETHANE, ETHYLENE, AND ACETYLENE

	ETHANE	ETHYLENE	ACETYLENE
Structure			
C—C bond length	1.54 Å	1.34 Å	1.20 Å
Bond energy	368 kJ/mol	632 kJ/mol	820 kJ/mol

CONCEPTUAL CHECKPOINT

1.23 Rank the indicated bonds in terms of increasing bond length:



1.11 Predicting Molecular Geometry: VSEPR Theory

The shapes of small molecules can often be predicted if we presume that all electron pairs (whether bonding or nonbonding) repel each other, and as such, they arrange themselves in three-dimensional space so as to achieve maximal distance from each other. This approach, called **valence shell electron pair repulsion (VSEPR)** theory, enables us to make quick predictions about molecular geometry. In this section, we will encounter several different molecular shapes for small molecules, all of which are predicted accurately using the VSEPR model.

Tetrahedral Geometry

We begin our analysis with methane (CH_4), in which the carbon atom has four σ bonds and no lone pairs. VSEPR theory presumes that all four electron pairs will be positioned so as to achieve maximal distance from each other, suggesting a **tetrahedral** arrangement. That is, the VSEPR model predicts that the four hydrogen atoms should be positioned at the four corners of a tetrahedron (Figure 1.34a). This prediction is consistent with sp^3 hybridization, as described by valence bond theory (Section 1.10), and it is also consistent with the observed bond angles of 109.5° (Figure 1.34b).

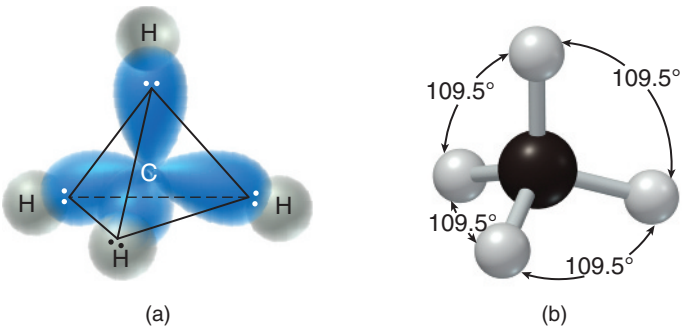


FIGURE 1.34
(a) The tetrahedral arrangement of electron pairs in CH_4.
(b) All bond angles in CH_4 are 109.5°.

Trigonal Pyramidal Geometry

Now let's apply the VSEPR model to ammonia (NH_3), in which the nitrogen atom has three σ bonds and one lone pair. The total number of electron pairs, also called the **steric number**, is four in this case (as it was in the previous case as well). VSEPR theory presumes that all four electron pairs will be positioned so as to achieve maximal distance from each other, suggesting once again a tetrahedral arrangement (Figure 1.35a). However, in this case, a lone pair is positioned at one corner of the tetrahedron. This predicted arrangement is observed to be accurate, and it is consistent with the valence bond approach, in which the nitrogen atom is sp^3 hybridized, and the lone pair occupies an sp^3-hybridized orbital.

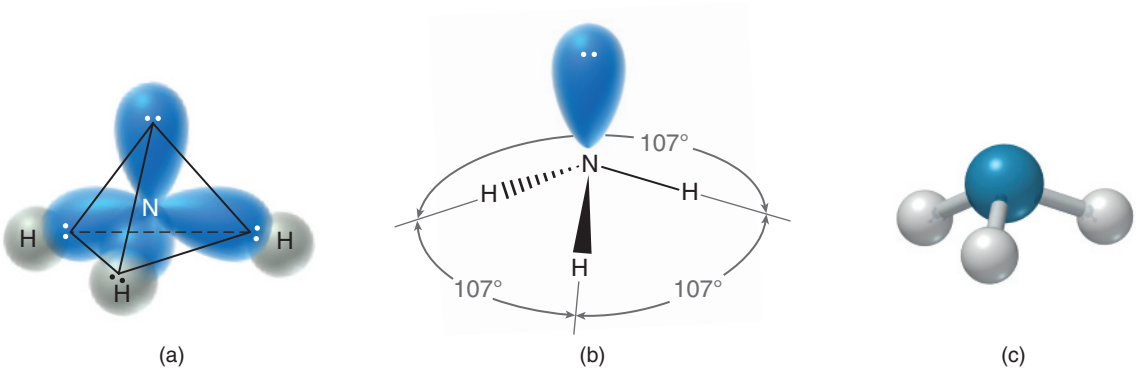


FIGURE 1.35
(a) The tetrahedral arrangement of electron pairs in NH_3.
(b) All bond angles in NH_3 are approximately 107°.
(c) NH_3 has trigonal pyramidal geometry.

As illustrated in Figure 1.35b, the bond angles for ammonia are observed to be 107°, rather than 109.5°. This shorter bond angle can be justified by VSEPR theory if we presume that lone pairs repel more strongly than σ bonds (lone pairs are not bound by another nucleus, so they occupy more space than bonding electron pairs). As such, the lone pair in ammonia repels the three bonds more strongly, causing the H—N—H bond angle to be less than 109.5°.

When we describe the geometry (or shape) of a molecule, we are generally referring to the arrangement of atoms. When we focus only on the positions of the atoms (ignoring the lone pair), the shape of ammonia is **trigonal pyramidal** (Figure 1.35c). "Trigonal" indicates the nitrogen atom is connected to three other atoms, and "pyramidal" indicates the compound is shaped like a pyramid, with the nitrogen atom sitting at the top of the pyramid.

Bent Geometry

Now let's apply the VSEPR model to water (H_2O), in which the oxygen atom has two σ bonds and two lone pairs. With a total of four electron pairs to consider (steric number = 4), VSEPR theory presumes that all four electron pairs will be positioned so as to achieve maximal distance from each other, suggesting once again a tetrahedral arrangement (Figure 1.36a). Notice that the VSEPR model predicts that the lone pairs should be positioned at two corners of the tetrahedral arrangement.

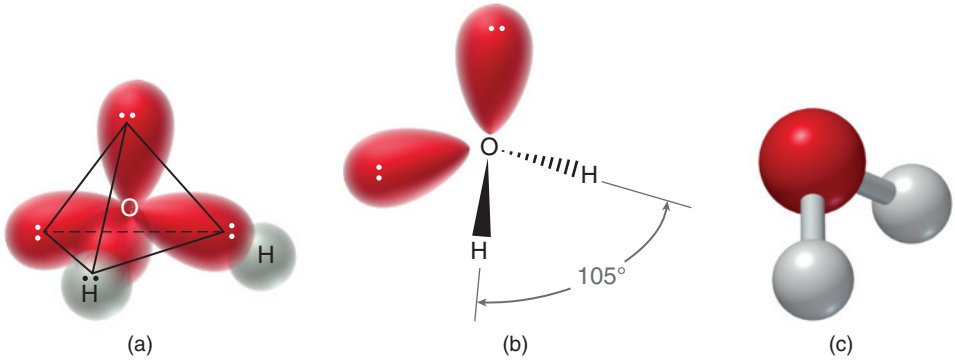


FIGURE 1.36
(a) The tetrahedral arrangement of electron pairs in H_2O, as predicted by VSEPR.
(b) The bond angle in H_2O is approximately 105°.
(c) H_2O has bent geometry.

Once again, VSEPR theory can explain the observed bond angle (105°) by considering the effect of two lone pairs (Figure 1.36b). Specifically, the lone pairs repel each other more strongly than σ bonds, causing the H—O—H bond angle to be even smaller than the bond angles in ammonia. In order to describe the geometry of H_2O, we focus on the arrangement of atoms, which gives a **bent** geometry (Figure 1.36c).

This analysis demonstrates that the VSEPR model correctly predicts the bent geometry of water, and the observed bond angle is even justified. However, VSEPR theory also predicts that the two lone pairs of H_2O should be degenerate (the same energy), and this has proven to be false. Experiments conducted over 30 years ago have revealed that the lone pairs of H_2O are indeed different (one lone pair is significantly higher in energy than the other). These observations strongly suggest that at least one lone pair occupies a *p* orbital, while the other lone pair occupies a lower-energy, hybridized orbital. Since one lone pair occupies a *p* orbital, the oxygen atom cannot be sp^3 hybridized, as we might expect from a classical interpretation of valence bond theory and VSEPR theory. In this case, the VSEPR model fails to explain why the lone pairs are different in hybridization, energy, and orientation. Indeed, this is compelling evidence that the VSEPR model does not take all of the relevant factors into account when predicting geometry. The VSEPR model assumes that steric repulsion of electrons is the only factor that determines electronic and molecular structures, but there are often additional relevant factors. In the case of H_2O, the lone pairs do *not* occupy the two corners of a tetrahedron, as predicted. Although VSEPR theory has correctly predicted the bent geometry of H_2O, it appears to have done so for the wrong reasons. This example illustrates that VSEPR is just a first approximation. It is just a model, incomplete and flawed (as most simple models are), but it is nevertheless useful, because it can be used to predict the molecular geometry of most small molecules with reasonable accuracy.

Thus far, we have seen three different molecular shapes: tetrahedral, trigonal pyramidal, and bent. We will now explore other common molecular shapes that are accurately predicted with VSEPR theory.

Trigonal Planar Geometry

Consider the structure of BF_3. Boron has three valence electrons, each of which is used to form a σ bond. Therefore, the boron atom requires the use of three hybridized orbitals (rather than four, as we have seen in previous examples). Applying valence bond theory, we expect the boron atom to be sp^2 hybridized (with three equivalent sp^2-hybridized orbitals and one empty *p* orbital). As we saw in Section 1.10, sp^2 hybridization is associated with **trigonal planar** geometry, in which all bond angles are 120° (Figure 1.37). The term "trigonal" indicates that the boron atom is connected to three other atoms, and the term "planar" indicates that all atoms lie in the same plane.

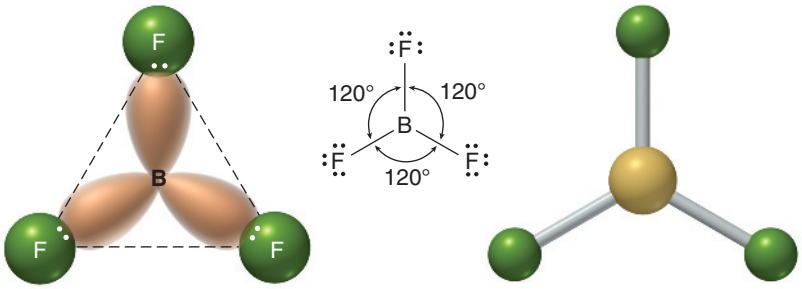


FIGURE 1.37
BF_3 has trigonal planar geometry, with bond angles of 120°.

Once again, the VSEPR model correctly predicts the trigonal planar geometry of BF_3. There are three electron pairs that are repelling each other (steric number = 3), and they are expected to position themselves in space so as to achieve maximal separation. This is only accomplished in a trigonal planar arrangement, with bond angles of 120°, exactly as observed.

Linear Geometry

Consider the structure of BeH_2. Beryllium has two valence electrons, each of which is used to form a σ bond. The beryllium atom therefore requires only two hybridized orbitals, and must be *sp* hybridized. Recall (Section 1.10) that *sp* hybridization is associated with **linear geometry** (Figure 1.38):

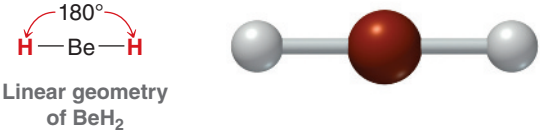


FIGURE 1.38
BeH_2 has linear geometry, with a bond angle of 180°.

Once again, the VSEPR model correctly predicts the linear geometry of BeH_2. There are two electron pairs that are repelling each other (steric number = 2), and they are expected to position themselves in space so as to achieve maximal separation. This is only accomplished in a linear arrangement, with a bond angle of 180°.

In summary, we have encountered five different molecular shapes, all of which are listed in Table 1.3.

TABLE 1.3 COMMON MOLECULAR SHAPES THAT CAN BE PREDICTED WITH VSEPR THEORY

EXAMPLE	BONDING ELECTRON PAIRS (BONDS)	NONBONDING ELECTRON PAIRS (LONE PAIRS)	STERIC NUMBER	PREDICTED ARRANGEMENT OF ELECTRON PAIRS	PREDICTED MOLECULAR GEOMETRY
CH_4	4	0	4	Tetrahedral	Tetrahedral
NH_3	3	1	4	Tetrahedral	Trigonal Pyramidal
H_2O	2	2	4	Tetrahedral	Bent
BF_3	3	0	3	Trigonal Planar	Trigonal Planar
BeH_2	2	0	2	Linear	Linear

SKILLBUILDER

1.8 PREDICTING GEOMETRY

LEARN the skill

Using VSEPR theory, predict the geometry of a hydronium ion (H_3O^+):

SOLUTION

STEP 1 Determine the steric number.

We begin by counting the number of electron pairs (bonding and nonbonding) on the oxygen atom. There are three sigma bonds and one lone pair, giving a total of four electron pairs (steric number = 4).

STEP 2 Identify the arrangement of electron pairs.

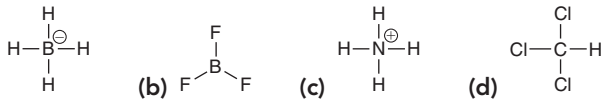
Next, identify the arrangement of the electron pairs in 3D space. According to VSEPR theory, we presume that all electron pairs will be positioned so as to achieve maximal distance from one another. Since there are four electron pairs, VSEPR theory predicts a tetrahedral arrangement of electron pairs.

STEP 3 Identify the geometry.

In this case, a lone pair is predicted to occupy one corner of the tetrahedron, giving rise to trigonal pyramidal geometry (just like NH_3).

PRACTICE the skill

1.24 Use VSEPR theory to predict the geometry for each of the following structures:



1.25 Compare the structures of a carbocation and a carbanion:

In one of these ions, the central carbon atom is trigonal planar, while the other is trigonal pyramidal. Using VSEPR theory, assign the correct geometry to each ion.

1.26 Ammonia (NH_3) will react with a strong acid, such as hydronium (H_3O^+), to give an ammonium ion, as shown below. This type of process is an acid-base reaction, which will be the topic of Chapter 3. Using VSEPR theory, determine whether you expect a change in bond angles when ammonia is converted into an ammonium ion. Explain.

APPLY the skill

1.27 When sand is coated with a layer of trimethylhydroxysilane, $(CH_3)_3SiOH$, it repels water and can no longer get wet. Hydrophobic sand (aka, magic sand) is fun to play with, but it can also have useful applications in agriculture to reduce water consumption.[8] Predict the geometry for the silicon atom in trimethylhydroxysilane.

need more **PRACTICE?** **Try Problems 1,37, 1.45, 1.52, 1.53, 1.55, 1.63, 1.68, 1.73b, 1.77c, 1.77f, 1.82b, 1.82c**

1.12 Dipole Moments and Molecular Polarity

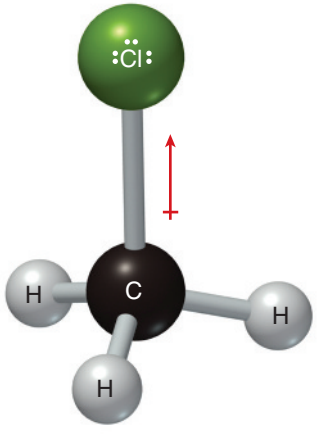
Recall that induction is caused by the presence of an electronegative atom, as we saw earlier in the case of chloromethane. In Figure 1.39a the arrow shows the inductive effect of the chlorine atom. Figure 1.39b is a map of the electron density, revealing that the molecule is polarized. Chloromethane is said to exhibit a dipole moment, because *the center of negative charge and the center of positive charge are separated from one another by a certain distance*. The **dipole moment** (μ) is used as an indicator of polarity, where μ is defined as the amount of partial charge (δ) on either end of the dipole multiplied by the distance of separation (d):

$$\mu = \delta \times d$$

Partial charges ($\delta+$ and $\delta-$) are generally on the order of 10^{-10} esu (electrostatic units) and the distances are generally on the order of 10^{-8} cm. Therefore, for a polar compound, the dipole moment (μ) will generally have an order of magnitude of around 10^{-18} esu · cm. The dipole moment of chloromethane, for example, is 1.87×10^{-18} esu · cm. Since most compounds will have a dipole moment on this order of magnitude (10^{-18}), it is more convenient to report dipole moments with a new unit, called a **debye (D)**, where

$$1 \text{ debye} = 10^{-18} \text{ esu} \cdot \text{cm}$$

Using these units, the dipole moment of chloromethane is reported as 1.87 D. The debye unit is named after Dutch scientist Peter Debye, whose contributions to the fields of chemistry and physics earned him a Nobel Prize in 1936.



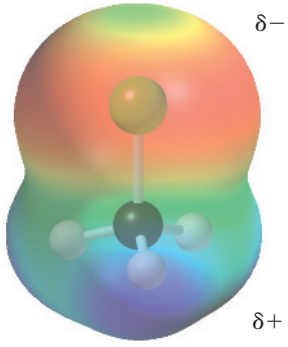


FIGURE 1.39
(a) Ball-and-stick model of chloromethane showing the dipole moment.
(b) An electrostatic potential map of chloromethane.

Measuring the dipole moment of a particular bond allows us to calculate the percent ionic character of that bond. As an example, let's analyze a C—Cl bond. This bond has a bond length of 1.772×10^{-8} cm, and an electron has a charge of 4.80×10^{-10} esu. If the bond were 100% ionic, then the dipole moment would be

$$\begin{aligned}\mu &= e \times d \\ &= (4.80 \times 10^{-10}\ \text{esu}) \times (1.772 \times 10^{-8}\ \text{cm}) \\ &= 8.51 \times 10^{-18}\ \text{esu} \cdot \text{cm}\end{aligned}$$

or 8.51 D. In reality, the bond is not 100% ionic. The experimentally observed dipole moment is measured at 1.87 D, and we can use this value to calculate the percent ionic character of a C—Cl bond:

$$\frac{1.87\ \text{D}}{8.51\ \text{D}} \times 100\% = \boxed{22\%}$$

Table 1.4 shows the percent ionic character for a few of the bonds that we will frequently encounter in this text. Take special notice of the C═O bond. It has considerable ionic character, rendering it extremely reactive. Chapters 19–21 are devoted exclusively to the reactivity of compounds containing C═O bonds.

TABLE 1.4 PERCENT IONIC CHARACTER FOR SEVERAL BONDS

BOND	BOND LENGTH ($\times 10^{-8}$ CM)	OBSERVED μ (D)	PERCENT IONIC CHARACTER
C—O	1.41	0.7 D	$\frac{(0.7 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})(1.41 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{10\%}$
O—H	0.96	1.5 D	$\frac{(1.5 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})(0.96 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{33\%}$
C═O	1.227	2.4 D	$\frac{(2.4 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})(1.23 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{41\%}$

Chloromethane was a simple example, because it has only one polar bond. When dealing with a compound that has more than one polar bond, it is necessary to take the vector sum of the individual dipole moments. The vector sum is called the **molecular dipole moment**, and it takes into account both the magnitude and the direction of each individual dipole moment. For example, consider the structure of dichloromethane (Figure 1.40). The individual dipole moments partially cancel, but not completely. The vector sum produces a dipole moment of 1.14 D, which is significantly smaller than the dipole moment of chloromethane because the two dipole moments here partially cancel each other.

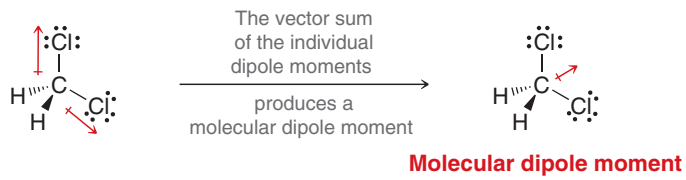


FIGURE 1.40
The molecular dipole moment of dichloromethane is the net sum of all dipole moments in the compound.

The presence of a lone pair has a significant effect on the molecular dipole moment. The two electrons of a lone pair are balanced by two positive charges in the nucleus, but the lone pair is separated from the nucleus by some distance. There is, therefore, a dipole moment associated with every lone pair. A common example is ammonia (Figure 1.41). In this way, the lone pair contributes

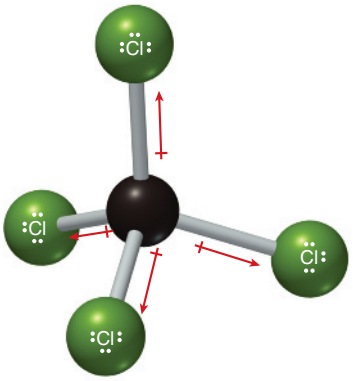


FIGURE 1.42
A ball-and-stick model of carbon tetrachloride. The individual dipole moments cancel to give a zero net dipole moment.

significantly to the magnitude of the molecular dipole moment, although its direction is not altered. That is, the direction of the molecular dipole moment would be the same with or without the contribution of the lone pair.

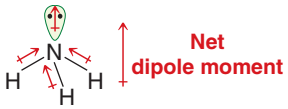
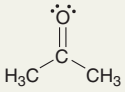
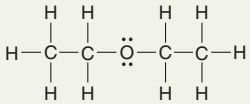
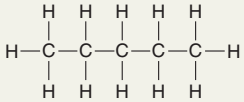
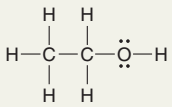


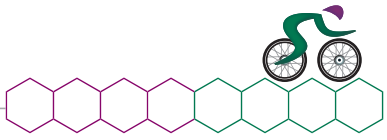
FIGURE 1.41
The net dipole moment of ammonia.

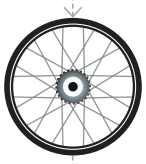
Table 1.5 shows experimentally observed molecular dipole moments for several common solvents. Notice that carbon tetrachloride (CCl_4) has no molecular dipole moment. In this case, the individual dipole moments cancel each other completely to give the molecule a zero net dipole moment ($\mu = 0$). This example (Figure 1.42) demonstrates that we must take geometry into account when assessing molecular dipole moments.

TABLE 1.5 DIPOLE MOMENTS FOR SOME COMMON SOLVENTS (AT 20°C)

COMPOUND	STRUCTURE	DIPOLE MOMENT	COMPOUND	STRUCTURE	DIPOLE MOMENT
Acetone		2.69 D	Ammonia	NH_3	1.47 D
Chloromethane	CH_3Cl	1.87 D	Diethyl ether		1.15 D
Water	H_2O	1.85 D	Methylene chloride	CH_2Cl_2	1.14 D
Methanol	CH_3OH	1.69 D	Pentane		0 D
Ethanol		1.66 D	Carbon tetrachloride	CCl_4	0 D

SKILLBUILDER





1.9 IDENTIFYING THE PRESENCE OF MOLECULAR DIPOLE MOMENTS

LEARN the skill

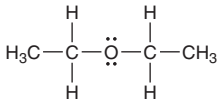
Identify whether each of the following compounds exhibits a molecular dipole moment. If so, indicate the direction of the net molecular dipole moment:

(a) $CH_3CH_2OCH_2CH_3$ **(b)** CO_2

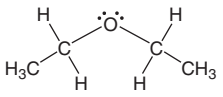
SOLUTION

(a) In order to determine whether the individual dipole moments cancel each other completely, we must first predict the molecular geometry. Specifically, we need to know if the geometry around the oxygen atom is linear or bent:

STEP 1
Predict the molecular geometry.



Linear



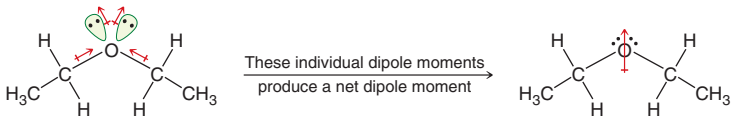
Bent

To make this determination, we use the method described in the previous SkillBuilder. The oxygen atom has two σ bonds and two lone pairs, so the steric number is 4. Since there are two lone pairs, VSEPR theory predicts bent geometry.

After determining the molecular geometry, now draw all dipole moments and determine whether they cancel each other. In this case, they do not fully cancel each other:

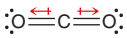
STEP 2
Identify the direction of all dipole moments.

STEP 3
Draw the net dipole moment.



This compound does in fact have a net molecular dipole moment, and the direction of the moment is shown above.

(b) Carbon dioxide (CO_2) has two C═O bonds, each of which exhibits a dipole moment. In order to determine whether the individual dipole moments cancel each other completely, we must first predict the molecular geometry. Once again, we use the method described in the previous SkillBuilder. The carbon atom has two σ bonds and no lone pairs, so the steric number is two. Accordingly, VSEPR theory predicts linear geometry. Therefore, we expect the dipole moments to fully cancel each other:

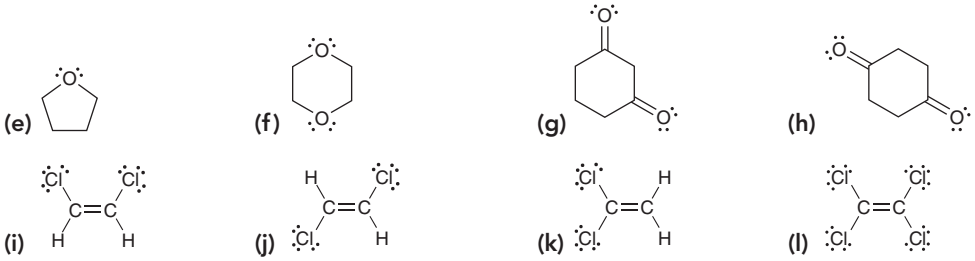


In a similar way, the dipole moments associated with the lone pairs also cancel each other, and therefore CO_2 does not have a net molecular dipole moment.

PRACTICE the skill

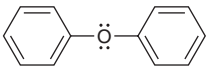
1.28 Identify whether each of the following compounds exhibits a molecular dipole moment. For compounds that do, indicate the direction of the net molecular dipole moment:

(a) $CHCl_3$ **(b)** CH_3OCH_3 **(c)** NH_3 **(d)** CCl_2Br_2



APPLY the skill

1.29 Volatile organic compounds (VOCs) contribute to the aroma of plants and can also be used for communication between plants. Diphenyl ether was identified as a minor VOC found in tomato plants.[9] Identify whether diphenyl ether exhibits a molecular dipole moment. If so, indicate the direction of the net molecular dipole moment.



Diphenyl ether

need more **PRACTICE?** **Try Problems 1.34, 1.36, 1.39, 1.58–1.61**

1.13 Intermolecular Forces and Physical Properties

The physical properties of a compound are determined by the attractive forces between the individual molecules, called **intermolecular forces**. It is often difficult to use the molecular structure alone to predict a precise melting point or boiling point for a compound. However, a few simple trends will allow us to compare compounds to each other in a relative way, for example, to predict which compound will boil at a higher temperature.

All intermolecular forces are *electrostatic*—that is, these forces occur as a result of the attraction between opposite charges. The electrostatic interactions for neutral molecules (with no formal charges) are often classified as (1) **dipole-dipole interactions**, (2) hydrogen bonding, and (3) fleeting dipole-dipole interactions.

Dipole-Dipole Interactions

Compounds with net dipole moments can either attract each other or repel each other, depending on how they approach each other in space. In the solid phase, the molecules align so as to attract each other (Figure 1.43).

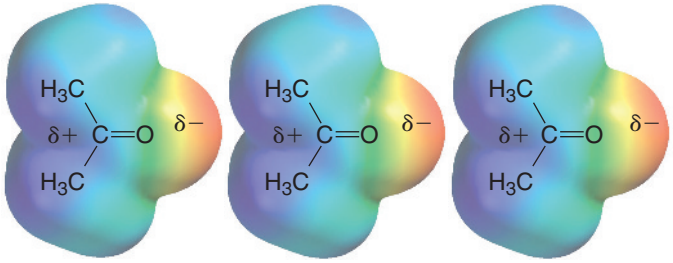


FIGURE 1.43
In solids, molecules align themselves so that their dipole moments experience attractive forces.

In the liquid phase, the molecules are free to tumble in space, but they do tend to move in such a way so as to attract each other more often than they repel each other. The resulting net attraction between the molecules results in an elevated melting point and boiling point. To illustrate this, compare the physical properties of isobutylene and acetone:

Isobutylene
Melting point = −140.3°C
Boiling point = −6.9°C

Acetone
Melting point = −94.9°C
Boiling point = 56.3°C

Isobutylene lacks a significant dipole moment, but acetone does have a strong net dipole moment. Therefore, acetone molecules will experience greater attractive interactions than isobutylene molecules. As a result, acetone has a higher melting point and higher boiling point than isobutylene.

Hydrogen Bonding

The term **hydrogen bonding** is misleading. A hydrogen bond is not actually a "bond" but rather, it is a type of attractive interaction. When a hydrogen atom is connected to an electronegative atom (usually O or N), the hydrogen atom will bear a partial positive charge (δ+) as a result of induction. This δ+ can then interact with a lone pair from an electronegative atom of another molecule or ion. This can be illustrated with water or ammonia (Figure 1.44).

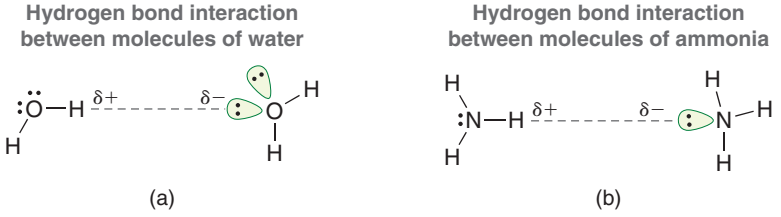


FIGURE 1.44
(a) Hydrogen bonding between molecules of water. **(b)** Hydrogen bonding between molecules of ammonia.

This attractive interaction is common among compounds that have an O—H bond or an N—H bond. For example, ethanol has an O—H bond, so it exhibits the same kind of attractive interaction (Figure 1.45).

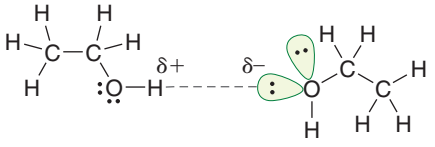
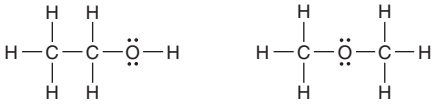


FIGURE 1.45
Hydrogen bonding between molecules of ethanol.

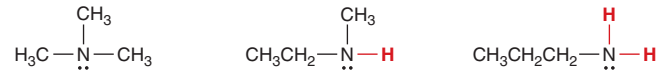
This type of interaction is quite strong because hydrogen is a relatively small atom, and as a result, the partial charges can get very close to each other. In fact, the effect of hydrogen bonding on physical properties is quite dramatic. In Section 1.2, we briefly mentioned the difference in properties between the following two constitutional isomers:



Ethanol
Boiling point = 78.4°C

Methoxymethane
Boiling point = –23°C

These compounds have the same molecular formula, but they have very different boiling points. Ethanol experiences intermolecular hydrogen bonding, giving rise to a very high boiling point. Methoxymethane does not experience intermolecular hydrogen bonding, giving rise to a relatively lower boiling point. A similar trend can be seen in a comparison of the following amines:



Trimethylamine
Boiling point = 3.5°C

Ethylmethylamine
Boiling point = 37°C

Propylamine
Boiling point = 49°C

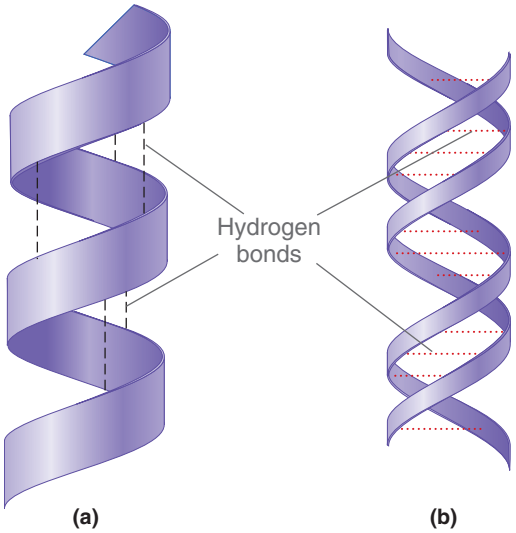


FIGURE 1.46
(a) An alpha helix of a protein. (b) The double helix in DNA.

LOOKING AHEAD
The structure of DNA is explored in more detail in Section 24.9.

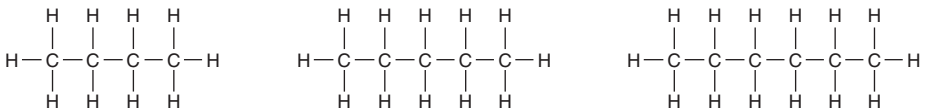
Once again, all three compounds have the same molecular formula (C_3H_9N), but they have very different properties as a result of the extent of hydrogen bonding. Trimethylamine does not exhibit any hydrogen bonding and has a relatively low boiling point. Ethylmethylamine does exhibit hydrogen bonding and therefore has a higher boiling point. Finally, propylamine, which has the highest boiling point of the three compounds, has two N—H bonds and therefore exhibits even more hydrogen-bonding interactions.

Hydrogen bonding is incredibly important in determining the shapes and interactions of biologically important compounds. Chapter 25 will focus on proteins, which are long molecules that coil up into specific shapes under the influence of hydrogen bonding (Figure 1.46a). These shapes ultimately determine their biological function. Similarly, hydrogen bonds hold together individual strands of DNA to form the familiar double-helix structure.

As mentioned earlier, hydrogen "bonds" are not really bonds. To illustrate this, compare the energy of a real bond with the energy of a hydrogen-bonding interaction. A typical single bond (C—H, N—H, O—H) has a bond strength of approximately 400 kJ/mol. In contrast, a hydrogen-bonding interaction has an average strength of approximately 20 kJ/mol. This leaves us with the obvious question: Why do we call them hydrogen *bonds* instead of just hydrogen *interactions*? To answer this question, consider the double-helix structure of DNA (Figure 1.46b). The two strands are joined by hydrogen-bonding interactions that function like rungs of a very long, twisted ladder. The net sum of these interactions contributes to the structure of the double helix, in which the hydrogen-bonding interactions appear *as if* they were actually bonds. Nevertheless, it is relatively easy to "unzip" the double helix and retrieve the individual strands.

Fleeting Dipole-Dipole Interactions

Some compounds have no permanent dipole moments, and yet analysis of boiling points indicates that they must have fairly strong intermolecular attractions. To illustrate this point, consider the following compounds:



Butane
(C_4H_{10})
Boiling point = 0°C

Pentane
(C_5H_{12})
Boiling point = 36°C

Hexane
(C_6H_{14})
Boiling point = 69°C

LOOKING AHEAD
Hydrocarbons will be discussed in more detail in Chapters 4, 16, and 17.

These three compounds are hydrocarbons, compounds that contain only carbon and hydrogen atoms. If we compare the properties of the hydrocarbons above, an important trend becomes apparent. Specifically, the boiling point appears to increase with increasing molecular weight. This trend can be justified by considering the fleeting, or transient, dipole moments that are more prevalent in larger hydrocarbons. To understand the source of these temporary dipole moments, we consider the electrons to be in constant motion, and therefore, the center of negative charge is also constantly moving around within the molecule. On average, the center of negative charge coincides with the center of positive charge, resulting in a zero dipole moment. However, at any given instant, the center of negative charge and the center of positive charge might not coincide. The resulting transient dipole moment can then induce a separate transient dipole moment in a neighboring molecule, initiating a fleeting attraction between the two molecules (Figure 1.47). These attractive forces are called **London dispersion forces,** named after German-American physicist Fritz London. Large hydrocarbons have more surface area than smaller hydrocarbons and therefore experience these attractive forces to a larger extent.

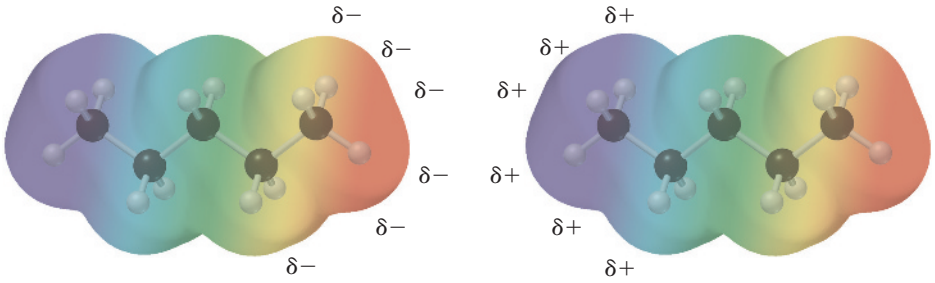
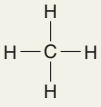
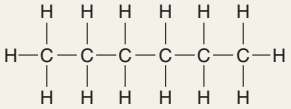
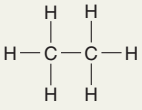
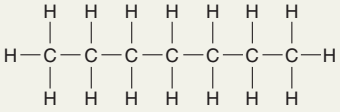
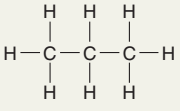
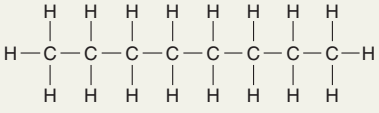
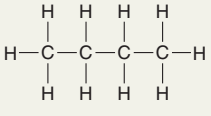
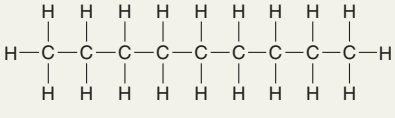
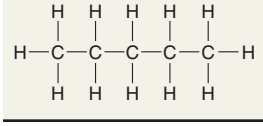
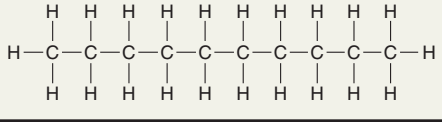


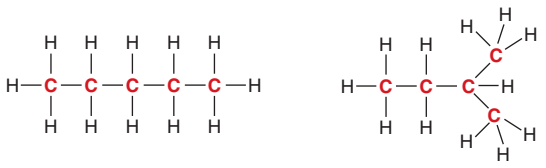
FIGURE 1.47
The fleeting attractive forces between two molecules of pentane.

London dispersion forces are stronger for higher molecular weight hydrocarbons because these compounds have larger surface areas that can accommodate more interactions. As a result, compounds of higher molecular weight will generally boil at higher temperatures. Table 1.6 illustrates this trend.

TABLE 1.6 BOILING POINTS FOR HYDROCARBONS OF INCREASING MOLECULAR WEIGHT

STRUCTURE	BOILING POINT (°C)	STRUCTURE	BOILING POINT (°C)
	−164		69
	−89		98
	−42		126
	0		151
	36		174

A branched hydrocarbon generally has a smaller surface area than its corresponding straight-chain isomer, and therefore, branching causes a decrease in boiling point. This trend can be seen by comparing the following constitutional isomers of C_5H_{12}:



Pentane
Boiling point = 36°C

2-Methylbutane
Boiling point = 28°C

2,2-Dimethylpropane
Boiling point = 10°C

WorldLinks Biomimicry and Gecko Feet

The term biomimicry describes the notion that scientists often draw creative inspiration from studying nature. By investigating some of nature's processes, it is possible to mimic those processes and to develop new technology. One such example is based on the way that geckos can scurry up walls and along ceilings. Until recently, scientists were baffled by the curious ability of geckos to walk upside down, even on very smooth surfaces such as polished glass.

As it turns out, geckos do not use any chemical adhesives, nor do they use suction. Instead, their abilities arise from the intermolecular forces of attraction between the molecules in their feet and the molecules in the surface on which they are walking. When you place your hand on a surface, there are certainly intermolecular forces of attraction between the molecules of your hand and the surface, but the microscopic topography of your hand is quite bumpy. As a result, your hand only makes contact with the surface at perhaps a few thousand points. In contrast, the foot of a gecko has approximately half a million microscopic flexible hairs, called *setae*, each of which has even smaller hairs.

When a gecko places its foot on a surface, the flexible hairs allow the gecko to make extraordinary contact with the surface, and the resulting London dispersion forces are collectively strong enough to support the gecko.

In the last decade, many research teams have drawn inspiration from geckos and have created materials with densely packed microscopic hairs. For example, some scientists are developing adhesive bandages that could be used in the healing of surgical wounds, while other scientists are developing special gloves and boots that would enable people to climb up walls (and perhaps walk upside down on ceilings). Imagine the possibility of one day being able to walk on walls and ceilings like Spiderman.

There are still many challenges that we must overcome before these materials will show their true potential. It is a technical challenge to design microscopic hairs that are strong enough to prevent the hairs from becoming tangled but flexible enough to allow the hairs to stick to any surface. Many researchers believe that these challenges can be overcome, and if they are right, we might have the opportunity to see the world turned literally upside down.

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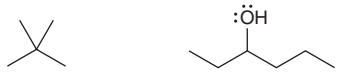
Eye of Science/Science Source

SKILLBUILDER

1.10 PREDICTING PHYSICAL PROPERTIES OF COMPOUNDS BASED ON THEIR MOLECULAR STRUCTURE

LEARN the skill

Determine which compound has the higher boiling point, neopentane or 3-hexanol:



Neopentane **3-Hexanol**

SOLUTION

STEP 1
Identify all dipole-dipole interactions in both compounds.

When comparing boiling points of compounds, we look for the following factors:

1. Are there any dipole-dipole interactions in either compound?
2. Will either compound form hydrogen bonds?

STEP 2
Identify all H-bonding interactions in both compounds.

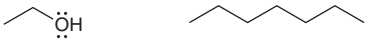
STEP 3
Identify the number of carbon atoms and extent of branching in both compounds.

3a. How many carbon atoms are in each compound?

3b. How much branching is in each compound?

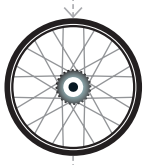
The second compound above (3-hexanol) is the winner in all of these categories. It has a dipole moment, while neopentane does not. It will experience hydrogen bonding, while neopentane will not. It has six carbon atoms, while neopentane only has five. And, finally, it has a straight chain, while neopentane is highly branched. Each of these factors alone would suggest that 3-hexanol should have a higher boiling point. When we consider all of these factors together, we expect that the boiling point of 3-hexanol will be significantly higher than neopentane.

When comparing two compounds, it is important to consider all four factors. However, it is not always possible to make a clear prediction because in some cases there may be competing factors. For example, compare ethanol and heptane:



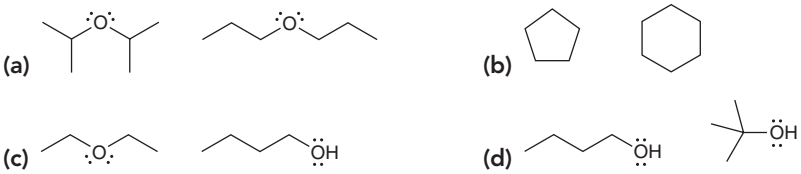
Ethanol Heptane

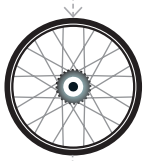
Ethanol will exhibit hydrogen bonding, but heptane has many more carbon atoms. Which factor dominates? It is not easy to predict. In this case, heptane has the higher boiling point, which is perhaps not what we would have guessed. In order to use the trends to make a prediction, there must be a clear winner.



PRACTICE the skill

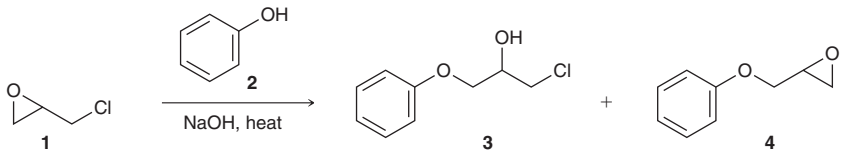
1.30 For each of the following pairs of compounds, identify the higher boiling compound and justify your choice:





APPLY the skill

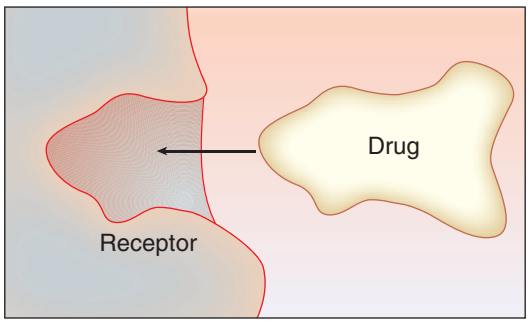
1.31 Epichlorohydrin (**1**) is an epoxide used in the production of plastic, epoxy glues, and resins (reactions of epoxides will be discussed in Chapter 13). When epichlorohydrin is treated with phenol (**2**), two products are formed (**3** and **4**).[10] These two products can be separated from each other via distillation, a process which exploits the difference in their boiling points. Which product (**3** or **4**) is expected to have the lower boiling point?



need more **PRACTICE?** **Try Problems 1.49, 1.50, 1.57, 1.62, 1.65, 1.70**

BioLinks Drug-Receptor Interactions

In most situations, the physiological response produced by a drug is attributed to the interaction between the drug and a biological receptor site. A *receptor* is a region within a biological macromolecule that can serve as a pouch in which the drug molecule can fit:

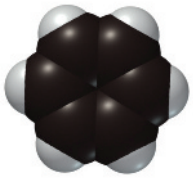


Initially, this mechanism was considered to work much like a lock and key. That is, a drug molecule would function as a key, either fitting or not fitting into a particular receptor. Extensive research on drug-receptor interactions has forced us to modify this simple lock-and-key model. It is now understood that both the drug and the receptor are flexible, constantly changing their shapes. As such, drugs can bind to receptors with various levels of efficiency, with some drugs binding more strongly and other drugs binding more weakly.

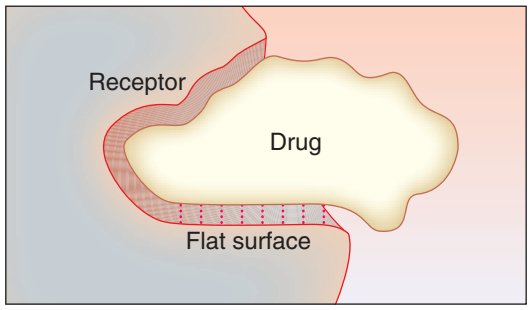
How does a drug bind to a receptor? In some cases, the drug molecule forms covalent bonds with the receptor. In such cases, the binding is indeed very strong (approximately 400 kJ/mol for each covalent bond) and therefore irreversible. We will see an example of irreversible binding when we explore a class of anticancer agents called nitrogen mustards (Chapter 7). For most drugs, however, the desired physiological response is meant to be temporary, which can only be accomplished if a drug can bind *reversibly* with its target receptor. This requires a weaker interaction between the drug and the receptor (at least weaker than a covalent bond). Examples of weak interactions include hydrogen-bonding interactions (20 kJ/mol) and London dispersion forces (approximately 4 kJ/mol for each carbon atom participating in the interaction). As an example, consider the structure of a benzene ring, which is incorporated as a structural subunit in many drugs:

Benzene

In a benzene ring, each carbon is sp^2 hybridized and therefore trigonal planar. As a result, a benzene ring represents a flat surface:



If the receptor also has a flat surface, the resulting London dispersion forces can contribute to the reversible binding of the drug to the receptor site:



This interaction is roughly equivalent to the strength of a single hydrogen-bonding interaction. The binding of a drug to a receptor is the result of the sum of the intermolecular forces of attraction between a portion of the drug molecule and the receptor site. We will have more to say about drugs and receptors in the upcoming chapters. In particular, we will see how drugs make their journey to the receptor, and we will explore how drugs flex and bend when interacting with a receptor site.

1.14 Solubility

Solubility is based on the principle that "like dissolves like." In other words, polar compounds are soluble in polar solvents, while nonpolar compounds are soluble in nonpolar solvents. Why is this so? A polar compound experiences dipole-dipole interactions with the molecules of a polar solvent, allowing the compound to dissolve in the solvent. Similarly, a nonpolar compound experiences London dispersion forces with the molecules of a nonpolar solvent. Therefore, if an article of clothing is stained with a polar compound, the stain can generally be washed away with water (like dissolves like). However, water will be insufficient for cleaning clothing stained with nonpolar compounds, such as oil or grease. In a situation like this, the clothes can be cleaned with soap or by dry cleaning.

Soap

Soaps are compounds that have a polar group on one end of the molecule and a nonpolar group on the other end (Figure 1.48).

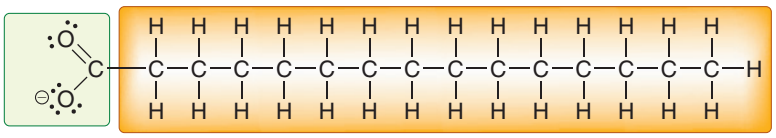


FIGURE 1.48
The hydrophilic and hydrophobic ends of a soap molecule.

The polar group represents the **hydrophilic** region of the molecule (literally, "loves water"), while the nonpolar group represents the **hydrophobic** region of the molecule (literally, "afraid of water"). Oil molecules are surrounded by the hydrophobic tails of the soap molecules, forming a **micelle** (Figure 1.49).

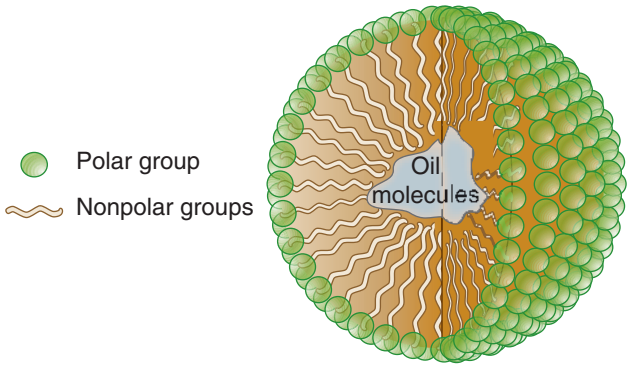
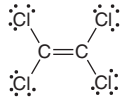


FIGURE 1.49
A micelle is formed when the hydrophobic tails of soap molecules surround the nonpolar oil molecules.

The surface of the micelle is comprised of all of the polar groups, rendering the micelle water soluble. This is a clever way to dissolve the oil in water, but this technique only works for clothing that can be subjected to water and soap. Some clothes will be damaged in soapy water, and in those situations, dry cleaning is the preferred method.

Dry Cleaning

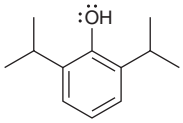
Rather than surrounding the nonpolar compound with a micelle so that it will be water soluble, it is actually conceptually simpler to use a nonpolar solvent. This is just another application of the principle of "like dissolves like." Dry cleaning utilizes a nonpolar solvent, such as tetrachloroethylene, to dissolve the nonpolar compounds. This compound is nonflammable, making it an ideal choice as a solvent. Dry cleaning allows clothes to be cleaned without coming into contact with water or soap.



Tetrachloroethylene

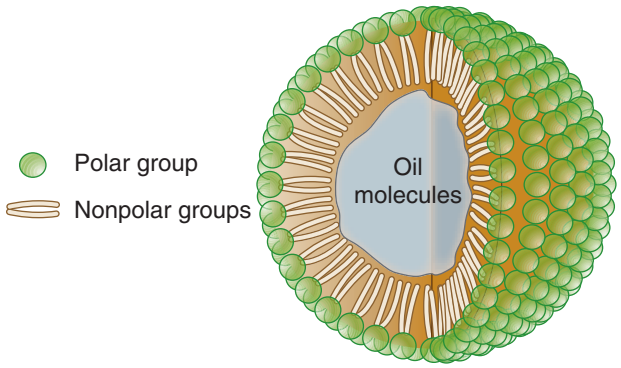
BioLinks Propofol: The Importance of Drug Solubility

The drug propofol received a lot of publicity in 2009 as one of the drugs implicated in the death of Michael Jackson:



Propofol

Propofol is normally used for initiating and maintaining anesthesia during surgery. It is readily soluble in the hydrophobic membranes of the brain, where it inhibits the firing (or excitation) of brain neurons. To be effective, propofol must be administered through intravenous injection, yet this poses a solubility problem. Specifically, the hydrophobic region of the drug is much larger than the hydrophilic region, and consequently, the drug does not readily dissolve in water (or in blood). Propofol does dissolve very well in soybean oil (a complex mixture of hydrophobic compounds, discussed in Section 26.3), but injecting a dose of soybean oil into the bloodstream would result in an oil globule, which could be fatal. To overcome this problem, a group of compounds called lecithins (discussed in Section 26.5) are added to the mixture. Lecithins are compounds that exhibit hydrophobic regions as well as a hydrophilic region. As such, lecithins form micelles, analogous to soap (as described in Section 1.14), which encapsulate the mixture of propofol and soybean oil. This solution of micelles can then be injected into the bloodstream. The propofol readily passes out of the micelles, crosses the hydrophobic membranes of the brain, and reaches the target neurons.



The high concentration of micelles results in a solution that looks very much like milk, and ampules of propofol are sometimes referred to as "milk of amnesia."

Julia Hiebaum/Alamy Stock Photo

REVIEW OF CONCEPTS AND VOCABULARY

SECTION 1.1

- **Organic** compounds contain carbon atoms, while **inorganic** compounds generally lack carbon atoms.

SECTION 1.2

- **Constitutional isomers** share the same molecular formula but have different connectivity of atoms and different physical properties.
- Each element will generally form a predictable number of bonds. Carbon is generally **tetravalent**, nitrogen **trivalent**, oxygen **divalent**, and hydrogen and the halogens **monovalent**.

SECTION 1.3

- A **covalent bond** results when two atoms share a pair of electrons.
- Covalent bonds are illustrated using **Lewis structures**, in which electrons are represented by dots.
- Second-row elements generally obey the **octet rule**, bonding to achieve noble gas electron configuration.
- A pair of unshared electrons is called a **lone pair**.

SECTION 1.4

- A **formal charge** occurs when atoms do not exhibit the appropriate number of valence electrons; formal charges must be drawn in Lewis structures.

SECTION 1.5

- Bonds are classified as (1) **covalent**, (2) **polar covalent**, or (3) **ionic.**
- Polar covalent bonds exhibit **induction**, causing the formation of partial positive charges ($\delta+$) and partial negative charges ($\delta-$). **Electrostatic potential maps** present a visual illustration of partial charges.

SECTION 1.6

- In **bond-line structures**, carbon atoms and most hydrogen atoms are not drawn.

SECTION 1.7

- **Quantum mechanics** describes electrons in terms of their wavelike properties.
- A **wave equation** describes the total energy of an electron when in the vicinity of a proton. Solutions to wave equations are called **wavefunctions** (ψ), where ψ^2 represents the probability of finding an electron in a particular location.
- **Atomic orbitals** are represented visually by generating three-dimensional plots of ψ^2; **nodes** indicate that the value of ψ is zero.
- An occupied orbital can be thought of as a cloud of **electron density**.
- Electrons fill orbitals following three principles: (1) the **Aufbau principle**, (2) the **Pauli exclusion principle**, and (3) **Hund's rule**. Orbitals with the same energy level are called **degenerate orbitals**.

SECTION 1.8

- **Valence bond theory** treats every bond as the sharing of electron density between two atoms as a result of the constructive interference of their atomic orbitals.
- **Sigma** (σ) **bonds** are formed when the electron density is located primarily on the bond axis.

SECTION 1.9

- **Molecular orbital theory** uses a mathematical method called the linear combination of atomic orbitals (LCAO) to form **molecular orbitals**. Each molecular orbital is associated with the entire molecule, rather than just two atoms.
- The **bonding MO** of molecular hydrogen results from constructive interference between its two atomic orbitals. The **antibonding MO** results from destructive interference.
- An **atomic orbital** is a region of space associated with an individual atom, while a molecular orbital is associated with an entire molecule.

- Two molecular orbitals are the most important to consider: (1) the **highest occupied molecular orbital**, or **HOMO**, and (2) the **lowest unoccupied molecular orbital**, or **LUMO**.

SECTION 1.10

- Methane's tetrahedral geometry can be explained using four degenerate ***sp*^{3}-hybridized orbitals** to achieve its four single bonds.
- Ethylene's planar geometry can be explained using three degenerate ***sp*^{2}-hybridized orbitals**. The remaining *p* orbitals overlap to form a separate bonding interaction, called a **pi (π) bond**. The carbon atoms of ethylene are connected via a σ bond, resulting from the overlap of *sp*^{2}-hybridized atomic orbitals, and via a π bond, resulting from the overlap of *p* orbitals, both of which comprise the double bond of ethylene.
- Acetylene's linear geometry is achieved via ***sp*-hybridized** carbon atoms in which a triple bond is created from the bonding interactions of one σ bond, resulting from overlapping *sp* orbitals, and two π bonds, resulting from overlapping *p* orbitals.
- Triple bonds are stronger and shorter than double bonds, which are stronger and shorter than single bonds.

SECTION 1.11

- The geometry of small compounds can be predicted using valence shell electron pair repulsion (**VSEPR**) theory, which focuses on the number of σ bonds and lone pairs exhibited by each atom. The total, called the **steric number**, indicates the number of electron pairs that repel each other.
- A compound's geometry depends on the number of lone pairs and can be **tetrahedral, trigonal pyramidal, bent, trigonal planar**, or **linear**.

SECTION 1.12

- **Dipole moments** (μ) occur when the center of negative charge and the center of positive charge are separated from one another by a certain distance; the dipole moment is used as an indicator of polarity (measured in **debyes**).
- The percent ionic character of a bond is determined by measuring its **dipole moment**. The vector sum of individual dipole moments in a compound determines the **molecular dipole moment**.

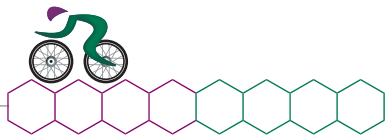
SECTION 1.13

- The physical properties of compounds are determined by **intermolecular forces**, the attractive forces between molecules.
- **Dipole-dipole interactions** occur between two molecules that possess permanent dipole moments. **Hydrogen bonding**, a type of attractive interaction, occurs when the lone pairs of an electronegative atom interact with an electron-poor hydrogen atom. Compounds that exhibit hydrogen bonding have higher boiling points than similar compounds that lack hydrogen bonding.
- **London dispersion forces** result from the interaction between transient dipole moments and are stronger for larger alkanes due to their larger surface area and ability to accommodate more interactions.

SECTION 1.14

- Polar compounds are soluble in polar solvents; nonpolar compounds are soluble in nonpolar solvents.
- Soaps are compounds that contain both **hydrophilic** and **hydrophobic** regions. The hydrophobic tails surround nonpolar compounds, forming a water-soluble **micelle**.

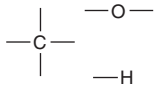
SKILLBUILDER REVIEW



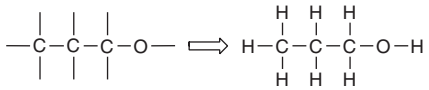
1.1 DRAWING CONSTITUTIONAL ISOMERS OF SMALL MOLECULES

EXAMPLE Draw all constitutional isomers that have the molecular formula C_3H_8O.

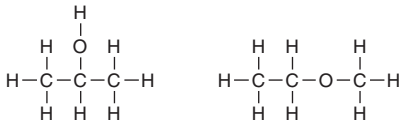
STEP 1 Determine the valency of each atom.



STEP 2 Connect the atoms of highest valency, and place the monovalent atoms at the periphery.



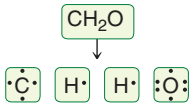
STEP 3 Consider other ways to connect the atoms.



Try Problems 1.1, 1.2, 1.32, 1.42, 1.51

1.2 DRAWING THE LEWIS STRUCTURE OF A SMALL MOLECULE

STEP 1 Draw all individual atoms.



STEP 2 Connect atoms that form more than one bond.

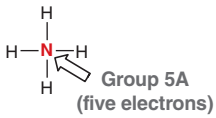
STEP 3 Connect hydrogen atoms.

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

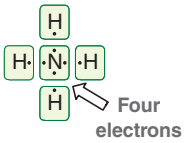
Try Problems 1.3–1.6, 1.35

1.3 CALCULATING FORMAL CHARGE

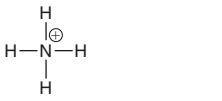
STEP 1 Determine appropriate number of valence electrons.



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



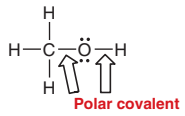
STEP 3 Assign a formal charge.



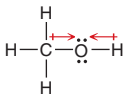
Try Problems 1.7–1.9, 1.66, 1.81a

1.4 LOCATING PARTIAL CHARGES RESULTING FROM INDUCTION

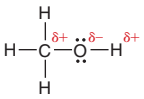
STEP 1 Identify all polar covalent bonds.



STEP 2 Determine the direction of each dipole.



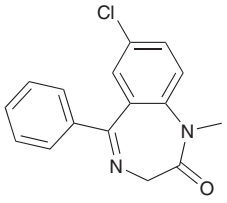
STEP 3 Indicate location of partial charges.



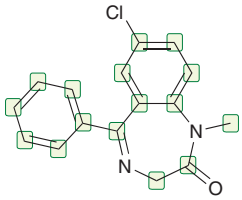
Try Problems 1.10–1.12, 1.33, 1.34, 1.43, 1.54

1.5 READING BOND-LINE STRUCTURES

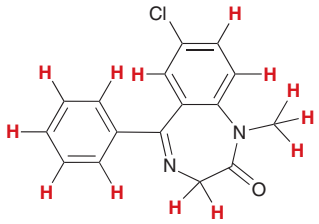
Identify all carbon atoms and hydrogen atoms.



STEP 1 The end of every line represents a carbon atom.



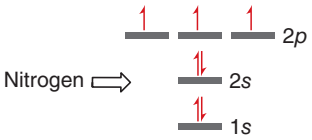
STEP 2 Each carbon atom will possess enough hydrogen atoms in order to achieve four bonds.



Try Problems 1.13, 1.14, 1.46, 1.47, 1.71

1.6 IDENTIFYING ELECTRON CONFIGURATIONS

STEP 1 Fill orbitals using the Aufbau principle, the Pauli exclusion principle, and Hund's rule.



STEP 2 Summarize using the following notation:

$1s^2 2s^2 2p^3$

Try Problems 1.15–1.17, 1.40

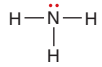
1.7 IDENTIFYING HYBRIDIZATION STATES

Four single bonds	A double bond	A triple bond
		
sp^3	sp^2	sp

Try Problems 1.21, 1.22, 1.52, 1.53, 1.67, 1.73f, 1.73g, 1.74, 1.79a

1.8 PREDICTING GEOMETRY

STEP 1 Determine the steric number by adding the number of σ bonds and lone pairs.



# of σ bonds = 3

# of lone pairs = 1

***Steric number* = 4**

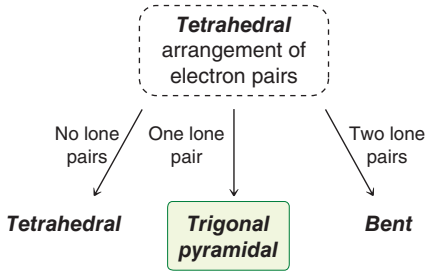
STEP 2 Use steric number to identify the arrangement of electron pairs.

4 → Tetrahedral

3 → Trigonal planar

2 → Linear

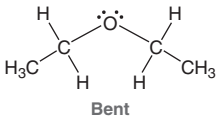
STEP 3 Identify the geometry.



Try Problems 1.24–1.27, 1,37, 1.45, 1.52, 1.53, 1.55, 1.63, 1.68, 1.73b, 1.77c, 1.77f, 1.82b, 1.82c

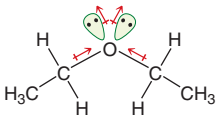
1.9 IDENTIFYING THE PRESENCE OF MOLECULAR DIPOLE MOMENTS

STEP 1 Predict geometry.

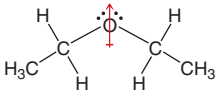


Bent

STEP 2 Identify direction of all dipole moments.



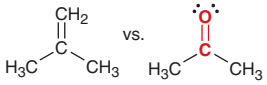
STEP 3 Draw net dipole moment.



Try Problems 1.28, 1.29, 1.34, 1.36, 1.39, 1.58–1.61

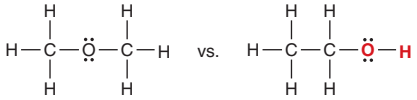
1.10 PREDICTING PHYSICAL PROPERTIES OF COMPOUNDS BASED ON THEIR MOLECULAR STRUCTURE

STEP 1 Identify dipole-dipole interactions.



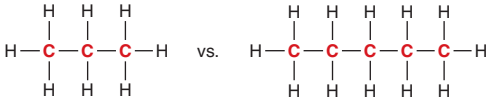
Higher boiling point

STEP 2 Identify H-bonding interactions.



Higher boiling point

STEP 3 Identify number of carbon atoms and extent of branching.



Higher boiling point

Try Problems 1.30, 1.31, 1.49, 1.50, 1.57, 1.62, 1.65, 1.70

PRACTICE PROBLEMS

• Included in Answers section

1.32 • Draw structures for all constitutional isomers with the following molecular formulas:

(a) C_2H_5Cl (b) $C_2H_4Cl_2$ (c) $C_2H_3Cl_3$ (d) C_6H_{14}

1.33 For each compound below, identify any polar covalent bonds and indicate the direction of the dipole moment using the symbols δ+ and δ−:

(a) HBr (b) HCl (c) H_2O (d) CH_4O

1.34 For each pair of compounds below, identify the one that would be expected to have more ionic character. Explain your choice.

(a) NaBr or HBr (b) BrCl or FCl

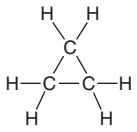
1.35 Draw a Lewis dot structure for each of the following compounds:

(a) CH_3CH_2OH (b) CH_3CN

1.36 Draw a Lewis structure for a compound with the molecular formula $C_4H_{11}N$ in which three of the carbon atoms are bonded to the nitrogen atom. What is the geometry of the nitrogen atom in this compound? Does this compound exhibit a molecular dipole moment? If so, indicate the direction of the dipole moment.

1.37 • Draw a Lewis structure of the anion $AlBr_4^-$ and determine its geometry.

1.38 Draw the structure for the only constitutional isomer of cyclopropane:



Cyclopropane

1.39 Determine whether each compound below exhibits a molecular dipole moment:

(a) CH_4 (b) NH_3 (c) H_2O

(d) CO_2 (e) CCl_4 (f) CH_2Br_2

1.40 Identify the neutral element that corresponds with each of the following electron configurations:

(a) $1s^2 2s^2 2p^4$ (b) $1s^2 2s^2 2p^5$ (c) $1s^2 2s^2 2p^2$

(d) $1s^2 2s^2 2p^3$ (e) $1s^2 2s^2 2p^6 3s^2 3p^5$

1.41 In the compounds below, classify each bond as covalent, polar covalent, or ionic:

(a) NaBr (b) NaOH (c) $NaOCH_3$

(d) CH_3OH (e) CH_2O

1.42 Draw structures for all constitutional isomers with the following molecular formulas:

(a) C_2H_6O (b) $C_2H_6O_2$ (c) $C_2H_4Br_2$

1.43 For each type of bond below, determine the direction of the expected dipole moment:

(a) C—O (b) C—Mg (c) C—N (d) C—Li

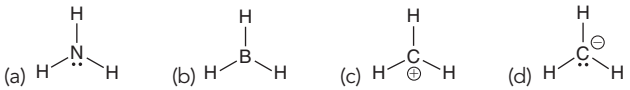
(e) C—Cl (f) C—Si (g) O—H (h) N—H

1.44 Predict the bond angles for all bonds in the following compounds:

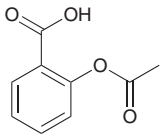
(a) CH_3CH_2OH (b) CH_2O (c) C_2H_4 (d) C_2H_2

(e) CH_3OCH_3 (f) CH_3NH_2 (g) C_3H_8 (h) CH_3CN

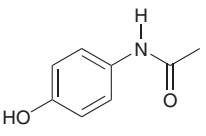
1.45 Identify the expected hybridization state and geometry for the central atom in each of the following structures:



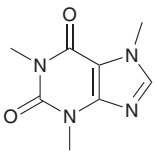
1.46 Draw all carbon atoms and hydrogen atoms for the following compounds.



Acetylsalicylic acid (aspirin)

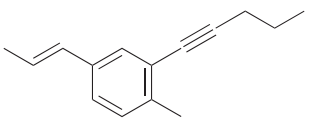


Acetaminophen (Tylenol)

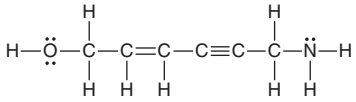


Caffeine

1.47 Identify the number of carbon atoms and hydrogen atoms in the compound below:



1.48 • Count the total number of σ bonds and π bonds in the compound below:

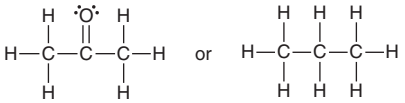


1.49 For each pair of compounds below, predict which compound will have the higher boiling point and explain your choice:

(a) $CH_3CH_2CH_2OCH_3$ or $CH_3CH_2CH_2CH_2OH$

(b) $CH_3CH_2CH_2CH_3$ or $CH_3CH_2CH_2CH_2CH_3$

(c)



1.50 Which of the following pure compounds will exhibit hydrogen bonding?

(a) CH_3CH_2OH (b) CH_2O

(c) C_2H_4 (d) C_2H_2

(e) CH_3OCH_3 (f) CH_3NH_2

(g) C_3H_8 (h) NH_3

1.51 For each case below, identify the most likely value for *x*:

(a) BH_x (b) CH_x

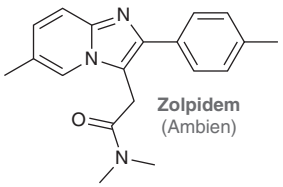
(c) NH_x (d) CH_2Cl_x

1.52 Identify the hybridization state and geometry of each carbon atom in the following compounds:

(a)

(b)

1.53 • Zolpidem, sold under the trade name Ambien, is a sedative used in the treatment of insomnia. It was discovered in 1982 and brought to market in 1992 (it takes a long time for new drugs to undergo the extensive testing required to receive approval from the Food and Drug Administration). Identify the hybridization state and geometry of each carbon atom in the structure of this compound:

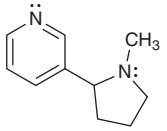


Zolpidem (Ambien)

1.54 Identify the most electronegative element in each of the following compounds:

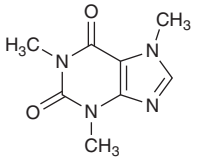
(a) $CH_3OCH_2CH_2NH_2$ (b) CH_2ClCH_2F (c) CH_3Li

1.55 Nicotine is an addictive substance found in tobacco. Identify the hybridization state and geometry of each of the nitrogen atoms in nicotine:



Nicotine

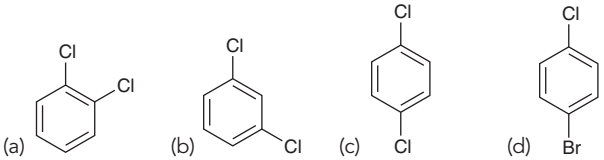
1.56 Below is the structure of caffeine, but its lone pairs are not shown. Identify the location of all lone pairs in this compound:



Caffeine

1.57 There are two different compounds with the molecular formula C_2H_6O. One of these isomers has a much higher boiling point than the other. Explain why.

1.58 Identify which compounds below possess a molecular dipole moment and indicate the direction of that dipole moment:



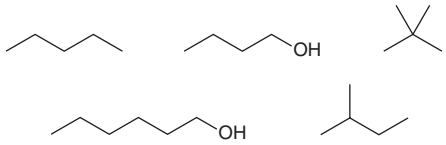
1.59 Methylene chloride (CH_2Cl_2) has fewer chlorine atoms than chloroform ($CHCl_3$). Nevertheless, methylene chloride has a larger molecular dipole moment than chloroform. Explain.

1.60 Which of the following compounds has the larger dipole moment? Explain your choice:

$CHCl_3$ or $CBrCl_3$

1.61 Bonds between carbon and oxygen (C—O) are more polar than bonds between sulfur and oxygen (S—O). Nevertheless, sulfur dioxide (SO_2) exhibits a dipole moment while carbon dioxide (CO_2) does not. Explain this apparent anomaly.

1.62 • Arrange the following compounds in order of increasing boiling point:



ACS-STYLE PROBLEMS (Multiple Choice)

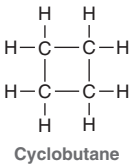
Problems 1.63–1.72 follow the style of the ACS organic chemistry exam. For each of these problems, there will be one correct answer and three distractors.

1.63 • Which is the correct hybridization state and geometry for the carbon atom in HCN?

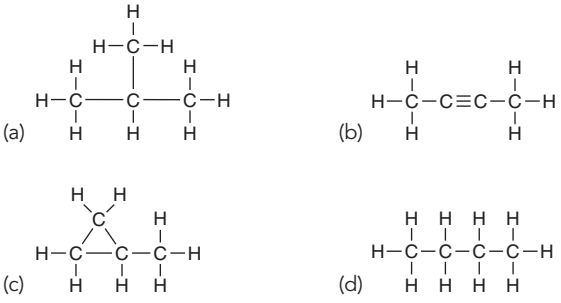
(a) *sp*, linear (b) sp^2, trigonal planar

(c) sp^3, tetrahedral (d) None of the above

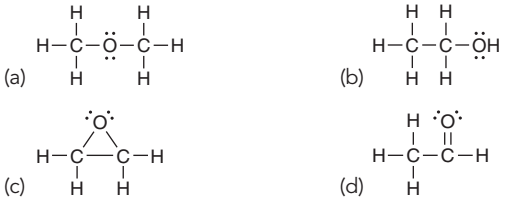
1.64 • Which of the following is a constitutional isomer of cyclobutane?



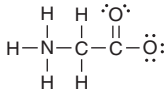
Cyclobutane



1.65 • Which of the following is expected to have the highest boiling point?



1.66 • The following structure has been drawn without formal charges. Which statement describes the missing formal charge(s)?



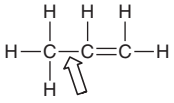
(a) This structure has one positive charge and one negative charge.

(b) This structure has one positive charge but no negative charges.

(c) This structure has one negative charge but no positive charges.

(d) This structure has no formal charges.

1.67 • The indicated σ bond results from the overlap of which orbitals?



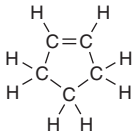
(a) sp^2–sp^2 (b) *sp*–sp^3 (c) *sp*–sp^2 (d) sp^2–sp^3

1.68 • Of the following molecular geometries, which has the largest bond angle?

(a) Pyramidal (b) Tetrahedral

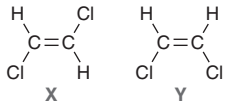
(c) Trigonal planar (d) Bent

1.69 • How many σ bonds are in the following compound?



(a) 8 (b) 9 (c) 13 (d) 14

1.70 • Which compound has the higher boiling point? Explain briefly.



X Y

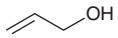
(a) **X**, because the dipole moments are far apart.

(b) **Y**, because the dipole moments do not fully cancel.

(c) **Y**, because it is less branched.

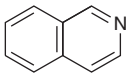
(d) **X**, because it is more linear.

1.71 • How many hydrogen atoms are in the compound represented by the following bond-line drawing?



(a) 5 (b) 6 (c) 7 (d) 8

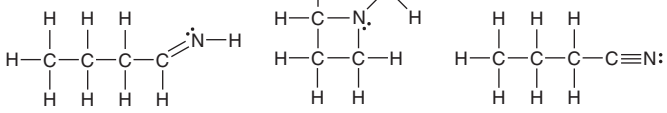
1.72 • The compound represented by the following bond-line drawing has how many carbon atoms and how many π bonds?



	C atoms	π bonds
(a)	10	6
(b)	10	5
(c)	9	6
(d)	9	5

INTEGRATED PROBLEMS

1.73 • Consider the three compounds shown below and then answer the questions that follow:



Compound A Compound B Compound C

(a) Which two compounds are constitutional isomers?

(b) Which compound contains a nitrogen atom with trigonal pyramidal geometry?

(c) Identify the compound with the greatest number of σ bonds.

(d) Identify the compound with the fewest number of σ bonds.

(e) Which compound contains more than one π bond?

(f) Which compound contains an sp^2-hybridized carbon atom?

(g) Which compound contains only sp^3-hybridized atoms (in addition to hydrogen atoms)?

(h) Which compound do you predict will have the highest boiling point? Explain.

1.74 Propose at least two different structures for a compound with six carbon atoms that exhibits the following features:

(a) All six carbon atoms are sp^2 hybridized.

(b) Only one carbon atom is *sp* hybridized, and the remaining five carbon atoms are all sp^3 hybridized (remember that your compound can have elements other than carbon and hydrogen).

(c) There is a ring, and all of the carbon atoms are sp^3 hybridized.

(d) All six carbon atoms are *sp* hybridized, and the compound contains no hydrogen atoms (remember that a triple bond is linear and therefore cannot be incorporated into a ring of six carbon atoms).

1.75 With current spectroscopic techniques (discussed in Chapters 14–16), chemists are generally able to determine the structure of an unknown organic compound in just one day. These techniques have only been available for the last several decades. In the first half of the twentieth century, structure determination was a very slow and painful process in which the compound under investigation would be subjected to a variety of chemical reactions. The results of those reactions would provide chemists with clues about the structure of the compound. With enough clues, it was sometimes (but not always) possible to determine the structure. As an example, try to determine the structure of an unknown compound, using the following clues:

- The molecular formula is $C_4H_{10}N_2$.
- There are no π bonds in the structure.
- The compound has no net dipole moment.
- The compound exhibits very strong hydrogen bonding.

You should find that there are at least two constitutional isomers that are consistent with the information above. (**Hint:** Consider incorporating a ring in your structure.)

1.76 A compound with the molecular formula $C_5H_{11}N$ has no π bonds. Every carbon atom is connected to exactly two hydrogen atoms. Determine the structure of the compound.

1.77 Isonitriles (**A**) are an important class of compounds because of the versatile reactivity of the functional group, enabling the preparation of numerous new compounds and natural products. Isonitriles can be

converted to isonitrile dihalides (**B**), which represents a useful procedure for temporarily hiding the reactivity of an isonitrile.[11]

A **B**

(a) Identify the hybridization state for each highlighted atom in **A**.

(b) One of the carbon atoms in **A** exhibits a lone pair. In what type of hybridized atomic orbital does this lone pair reside?

(c) Predict the C—N—C bond angle in compound **A**.

(d) Identify the hybridization state for each highlighted atom in **B**.

(e) The nitrogen atom in **B** exhibits a lone pair. In what type of hybridized atomic orbital does this lone pair reside?

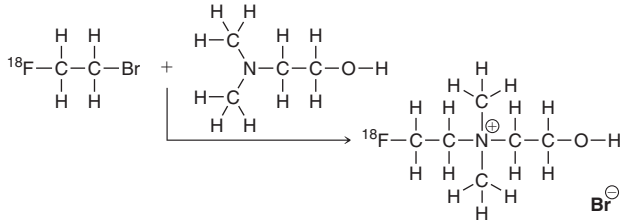
(f) Predict the C—N—C bond angle in compound **B**.

1.78 Consider the following table that provides bond lengths for a variety of C—X bonds (measured in Å).

	X = F	X = Cl	X = Br	X = I
—C—X	1.40	1.79	1.97	2.16
C—X	1.34		1.88	2.10
≡C—X	1.27	1.63	1.79	

Two trends emerge when we compare these data. First, notice that the bond length increases as the size of the halogen increases. This should make sense, since the valence electrons in iodine are farther away from the nucleus than the valence electrons in Br, so a C—I bond is longer than a C—Br bond. For the same reason, a C—Br bond is longer than a C—Cl bond, which in turn is longer than a C—F bond. Notice also that bond length decreases as the hybridization state goes from sp^3 to sp^2 to sp. This should also make sense, because sp-hybridized atoms hold their valence electrons closer to the nucleus (as seen in Table 1.2), and therefore form shorter bonds. These two trends are in conflict with each other when we compare a C_{sp^2}—Cl bond with a C_{sp}—I bond. The former bond is expected to be shorter because of the first trend (size of halogen), while the latter bond is expected to be shorter because of the second trend (hybridization state). Use the data provided to determine which bond is actually shorter, and explain your choice.

1.79 Positron emission tomography (PET) is a medical imaging technique that produces a three-dimensional picture of functional processes in the body, such as the brain uptake of glucose. PET imaging requires the introduction of [^{18}F]-fluorine (a radioactive isotope of fluorine) into molecules and can be achieved by several routes, such as the following:[12]

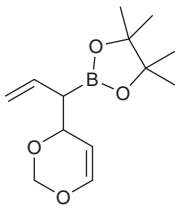


(a) Identify the hybridization for all atoms except for C, H, and O in the three compounds. Note: Throughout this chapter, all lone pairs were drawn. We will soon see (Chapter 2) that lone pairs are often omitted from structural drawings, because they can be inferred by the presence or absence of formal charges. In this problem, none of the lone pairs have been drawn.

(b) Predict the bond angle of each C—N—C bond in the product.

CHALLENGE PROBLEMS

1.80 Phenalamide A_2 belongs to a class of natural products that are of interest because of their antibiotic, antifungal, and antiviral activity. In the first total synthesis of this compound, the following boronate ester was utilized:[13]

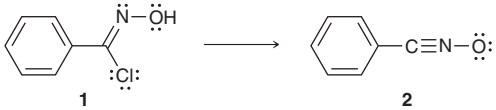


(a) Determine the hybridization state of the boron atom.

(b) Predict the O—B—O bond angle and then suggest a reason why the actual bond angle might deviate from the predicted value in this case.

(c) The lone pairs have not been drawn. Draw all of them. (**Hint:** Note that the structure has no formal charges.)

1.81 The formation of a variety of compounds called oxazolidinones is important for the synthesis of many different natural products and other compounds that have potential use as future medicines. One method[14] for preparing oxazolidinones involves the conversion of a hydroximoyl chloride, such as compound **1**, into a nitrile oxide, such as compound **2**:



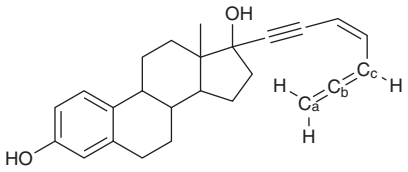
1 **2**

(a) Identify any formal charges that are missing from the structures of **1** and **2**.

(b) Determine which compound is expected to be more soluble in a polar solvent, and justify your choice.

(c) Determine the amount by which the C—C—N bond angle increases as a result of the conversion from **1** to **2**.

1.82 The following compound belongs to a class of compounds, called estradiol derivatives, which show promise in the treatment of breast cancer:[15]



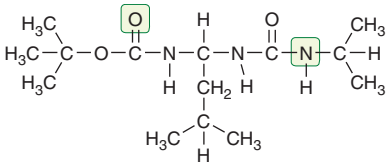
(a) Determine the hybridization state of C_a, C_b, and C_c.

(b) Determine the H—C_a—C_b bond angle.

(c) Determine the C_a—C_b—C_c bond angle.

(d) C_b exhibits two π bonds: one to C_a, and the other to C_c. Draw a picture of C_a, C_b, and C_c that shows the relative orientation of the two different *p* orbitals that C_b is utilizing to form its two π bonds. Also show the *p* orbitals on C_a and C_c that are being used by each of those atoms. Describe the relative orientation of the *p* orbitals on C_a and C_c.

1.83 The following structure shows promise for studying how enzymes (nature's catalysts) coil up into very discrete shapes that endow them with catalytic function:[16]



(a) This compound has two N—C—N units, with differing bond angles. Predict the difference in bond angles between these two units and explain the source of the difference.

(b) When this compound was prepared and investigated, it demonstrated a preference for adopting a three-dimensional shape in which the two highlighted regions were in close proximity. Describe the interaction that occurs and create a drawing that illustrates this interaction.

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