#### ATOMS AND MOLECULES

This file contains: Chapter 10: pages 442-495 Chapter 10 Answers to Exercises: pages 496-497 Chapter 10 Answers to Selected Study Questions: pages 498-502 Answers to Chapter-Opener Puzzler and Case Study: page 503

Camphor was also used as a treatment during the yellow fever epidemic in 1793 that killed thousands in Philadelphia. Benjamin Rush, a Philadelphia physician, chemist (who published the first American chemistry textbook), and signer of the Declaration of Independence, recommended a mixture of vinegar and camphor to

ward off the yellow fever. It did not cure the disease, but it did keep

away mosquitoes, the carrier of yellow fever.

# 10

# Carbon: More Than Just Another Element



### **Camphor, an "Aromatic" Molecule**

You might know just what this compound smells like! When you were a child and had a cold or cough, your mother might have smeared some Vick's<sup>®</sup> VapoRub on your chest. This home remedy, now more than 100 years old, contains camphor (5% by weight) as well as eucalyptus oil, turpentine oil, and menthol as active ingredients.

Camphor is said to be the first pure chemical that humans isolated and purified. Beginning in about 3000 BC, it was isolated from the camphor tree (*Cinnamomum camphora*), a native of China, Japan, and Indonesia, by chipping the wood from the tree and then steaming it. Camphor, being quite volatile, readily sublimes, and the solid is collected by cooling the resulting vapor.

An early use for camphor was as a wine additive, but the compound is toxic when taken internally, so this was clearly not a healthy practice. In the Middle Ages, it was said to be an aphrodisiac, but later it was declared an antiaphrodisiac.

### Questions:

- 1. The structure of camphor is interesting, although it was not known until 1893.
  - a) The O atom is attached to a structurally unique C atom. What is the geometry around this atom? What is its hybridization? What are the geometry and hybridization of the other C atoms in the molecule?
  - b) The five- and six-carbon rings in the molecule are not flat. Why is this so?
  - c) Is there a chiral center in this molecule? (See page 446.)
- Organic compounds are often classified by their "functional group." To what class does this molecule belong?

Answers to these questions are in Appendix Q.

### **Chapter Goals**

See Chapter Goals Revisited (page 488) for Study Questions keyed to these goals and assignable in OWL.

- Classify organic compounds based on formula and structure.
- Recognize and draw structures of structural isomers and stereoisomers for carbon compounds.
- Name and draw structures of common organic compounds.
- Know the common reactions of organic functional groups.
- Relate properties to molecular structure.
- Identify common polymers.

### **Chapter Outline**

- **10.1** Why Carbon?
- **10.2** Hydrocarbons
- 10.3 Alcohols, Ethers, and Amines
- **10.4** Compounds with a Carbonyl Group
- 10.5 Polymers

The vast majority of the millions of chemical compounds currently known are organic; that is, they are compounds built on a carbon framework. Organic compounds vary greatly in size and complexity, from the simplest hydrocarbon, methane, to molecules made up of many thousands of atoms. As you read this chapter, you will see why the range of possible materials is huge.

### 10.1 Why Carbon?

We begin this discussion of organic chemistry with a question: What features of carbon lead to both the abundance and the complexity of organic compounds? Answers fall into two categories: structural diversity and stability.

### **Structural Diversity**

With four electrons in its outer shell, carbon will form four bonds to reach an octet configuration. In contrast, the elements boron and nitrogen form three bonds in molecular compounds; oxygen forms two bonds; and hydrogen and the halogens form one bond. With a larger number of bonds comes the opportunity to create more complex structures. This will become increasingly evident in this brief tour of organic chemistry.

A carbon atom can reach an octet of electrons in various ways (Figure 10.1):

- *By forming four single bonds.* A carbon atom can bond to four other atoms, which can be either atoms of other elements (often H, N, or O) or other carbon atoms.
- By forming a double bond and two single bonds. The carbon atoms in ethylene, H<sub>2</sub>C==CH<sub>2</sub>, are linked to other atoms in this way.
- By forming two double bonds, as in carbon dioxide (O=C=O).
- By forming a triple bond and a single bond, an arrangement seen in acetylene, HC=CH.

Recognize, with each of these arrangements, the various possible geometries around carbon: tetrahedral, trigonal planar, and linear. Carbon's tetrahedral

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(a) Acetic acid. One carbon atom in this compound is attached to four other atoms by single bonds and has tetrahedral geometry. The second carbon atom, connected by a double bond to one oxygen and by single bonds to the other oxygen and to carbon, has trigonal-planar geometry. (b) Benzonitrile. Six trigonal-planar carbon atoms make up the benzene ring. The seventh C atom, bonded by a single bond to carbon and a triple bond to nitrogen, has a linear geometry.





(c) Carbon is linked by double bonds to two other carbon atoms in  $C_3H_4,$  a linear molecule commonly called allene.

#### FIGURE 10.1 Ways that carbon atoms bond.

geometry is of special significance because it leads to three-dimensional chains and rings of carbon atoms, as in propane and cyclopentane.



The ability to form multiple bonds leads to families of compounds with double and triple bonds.

#### Isomers

A hallmark of carbon chemistry is the remarkable array of isomers that can exist. **Isomers** are compounds that have identical composition but different structures. Two broad categories of isomers exist: structural isomers and stereoisomers.

**Structural isomers** are compounds having the same elemental composition, but the atoms are linked together in different ways. Ethanol and dimethyl ether are structural isomers, as are 1-butene and 2-methylpropene.





Ethylene, H<sub>2</sub>C==CH<sub>2</sub>



Ethylene and acetylene. These two-carbon hydrocarbons can be the building blocks of more complex molecules. These are their common names, but their systematic names are ethene and ethyne.

### A Closer Look

In Chapter 2, you learned that there are various ways of presenting structures (page 68). It is appropriate to return to this topic as we look at organic compounds. Consider methane and ethane, for example. We can represent these molecules in several ways:

- Molecular formula: CH<sub>4</sub> or C<sub>2</sub>H<sub>6</sub>. This type of formula gives information on composition only.
- Condensed formula: For ethane, this would be written CH<sub>3</sub>CH<sub>3</sub> (or as H<sub>3</sub>CCH<sub>3</sub>). This method of writing the formula gives some information on the way atoms are connected.
- Structural formula: You will recognize this formula as the Lewis structure. An elaboration on the condensed formula in (2), this representation defines more clearly how the atoms are connected,

#### Writing Formulas and Drawing Structures

but it fails to describe the shapes of molecules.



4. Perspective drawings: These drawings are used to convey the three-dimensional nature of molecules. Bonds extending out of the plane of the paper are drawn with wedges, and bonds behind the plane of the paper are represented as dashed wedges (page 70). Using these guidelines, the structures of methane and ethane could be drawn as follows:



5. Computer-drawn ball-and-stick and spacefilling models.



**Stereoisomers** are compounds with the same formula and in which there is a similar attachment of atoms. However, the atoms have different orientations in space. Two types of stereoisomers exist: geometric isomers and optical isomers.

*Cis*- and *trans*-2-butene are **geometric isomers**. Geometric isomerism in these compounds occurs as a result of the C==C double bond. Recall that the carbon atom and the attached groups cannot rotate around a double bond (page 420). Thus, the geometry around the C==C double bond is fixed in space. If identical groups occur on the adjacent carbon atoms and on the same side of the double bond, a *cis* isomer is produced. If those groups appear on opposite sides, a *trans* isomer is produced.



**Optical isomerism** is a second type of stereoisomerism. Optical isomers are molecules that have nonsuperimposable mirror images (Figure 10.2). Molecules (and other objects) that have nonsuperimposable mirror images are termed **chiral**. Pairs of nonsuperimposable molecules are called **enantiomers**.

Pure samples of enantiomers have the same physical properties, such as melting point, boiling point, density, and solubility in common solvents. They differ in one significant way, however: When a beam of plane-polarized light passes through a solution of a pure enantiomer, the plane of polarization rotates. The two enantiomers rotate polarized light to an equal extent, but in opposite directions (Figure 10.3). The term "optical isomerism" is used because this effect involves light.

#### Active Figure 10.2 Optical

**isomers.** (a) Optical isomerism occurs if a molecule and its mirror image cannot be superimposed. The situation is seen if four different groups are attached to carbon. (b) Lactic acid is a chiral molecule because four different groups (H, OH,  $CH_3$ , and  $CO_2H$ ) are attached to the central carbon atom.

Lactic acid is produced from milk when milk is fermented to make cheese. It is also found in other sour foods such as sauerkraut and is a preservative in pickled foods such as onions and olives. In our bodies, it is produced by muscle activity and normal metabolism.

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**FIGURE 10.3** Rotation of planepolarized light by an optical isomer.

Monochromatic light (light of only one wavelength) is produced by a sodium lamp. After it passes through a polarizing filter, the light vibrates in only one direction—it is polarized. A solution of an optical isomer placed between the first and second polarizing filters causes rotation of the plane of polarized light. The angle of rotation can be determined by rotating the second filter until maximum light transmission occurs. The magnitude and direction of rotation are unique physical properties of the optical isomer being tested.



(a) Lactic acid enantiomers are nonsuperimposable

(b) Lactic acid, CH<sub>3</sub>CH(OH)CO<sub>2</sub>H

The most common examples of chiral compounds are those in which four different atoms (or groups of atoms) are attached to a tetrahedral carbon atom. Lactic acid, found in milk and a product of normal human metabolism, is an example of one such chiral compound (Figure 10.2). Optical isomerism is particularly important in the amino acids (▶ *The Chemistry of Life: Biochemistry*) and other biologically important molecules. Among the many interesting examples is a compound, frontalin, produced naturally by male elephants (see "Chemical Perspectives: Chirality and Elephants").

### Stability of Carbon Compounds

Carbon compounds are notable for their resistance to chemical change. This resistance is a result of two things: strong bonds and slow reactions.

Strong bonds are needed for molecules to survive in their environment. Molecular collisions in gases, liquids, and solutions often provide enough energy to break some chemical bonds, and bonds can be broken if the energy associated with photons of visible and ultraviolet light exceeds the bond energy. Carbon-carbon bonds are relatively strong, however, as are the bonds between carbon and most other atoms. The average C—C bond energy is 346 kJ/mol; the C—H bond energy is 413 kJ/mol; and carbon-carbon double and triple bond energies are even higher (◄ Section 8.9). Contrast these values with bond energies for the Si—H bond (328 kJ/mol) and the Si—Si bond (222 kJ/mol). The consequence of high



### **Chemical Perspectives**

During a period known as musth, male elephants undergo a time of heightened sexual activity. They can become more aggressive and can work themselves into a frenzy. Aside from these physical changes, the males also produce chemical signals. A secretion containing the enantiomers of frontalin ( $C_8H_{14}O_2$ ) is emitted from a gland between the eye and the ear. Young males produce mixtures containing more of one enantiomer than the other, whereas older elephants produce a more balanced and more concentrated mixture. When that occurs in older elephants, other males

#### **Chirality and Elephants**

are repelled, but ovulating female elephants are more highly attracted.





An African elephant in musth. Fluid containing the enantiomers of frontalin flows from a gland between the elephant's eye and ear.

bond energies for bonds to carbon is that, for the most part, organic compounds do not degrade under normal conditions.

Oxidation of most organic compounds is strongly product-favored, but most organic compounds survive contact with  $O_2$ . The reason is that these reactions occur slowly. Most organic compounds burn only if their combustion is initiated by heat or by a spark. As a consequence, oxidative degradation is not a barrier to the existence of organic compounds.

### **10.2** Hydrocarbons

**Hydrocarbons**, compounds made of carbon and hydrogen only, are classified into several subgroups: alkanes, cycloalkanes, alkenes, alkynes, and aromatic compounds (Table 10.1). We begin our discussion by considering compounds that have carbon atoms with four single bonds, the alkanes and cycloalkanes.

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Type of Hydrocarbon	Characteristic Features	General Formula	Example
alkanes	C—C single bonds and all C atoms have four single bonds	$C_nH_{2n+2}$	CH4, methane C2H6, ethane
cycloalkanes	C—C single bonds and all C atoms have four single bonds	C <sub>n</sub> H <sub>2n</sub>	$C_6H_{12}$ , cyclohexane
alkenes	C=C double bond	$C_nH_{2n}$	$H_2C = CH_2$ , ethylene
alkynes	C≡C triple bond	$C_nH_{2n-2}$	HC≡CH, acetylene
aromatics	rings with $\pi$ bonding extending over several C atoms	_	benzene, $C_6H_6$

#### TABLE 10.1 Some Types of Hydrocarbons





Name	Molecular Formula	State at Room Temperature
methane	CH <sub>4</sub>	
ethane	$C_2H_6$	gas
propane	C <sub>3</sub> H <sub>8</sub>	
butane	$C_4H_{10}$	
pentane	$C_{5}H_{12}$ (pent- = 5)	
hexane	$C_6H_{14}$ (hex- = 6)	
heptane	$C_{7}H_{16}$ (hept- = 7)	liquid
octane	$C_8H_{18} (oct- = 8)$	
nonane	$C_{9}H_{20}$ (non- = 9)	
decane	$C_{10}H_{22}$ (dec- = 10)	
octadecane	$C_{18}H_{38}$ (octadec- = 18)	solid
eicosane	$C_{20}H_{42}$ (eicos- = 20)	

**TABLE 10.2** Selected Hydrocarbons of the Alkane Family,  $C_n H_{2n+2}^*$ 

\* This table lists only selected alkanes. Liquid compounds with 11 to 16 carbon atoms are also known. Many solid alkanes with more than 20 carbon atoms also exist.

### Alkanes

Alkanes have the general formula  $C_nH_{2n+2}$ , with *n* having integer values (Table 10.2). Formulas of specific compounds can be generated from this general formula, the first four of which are CH<sub>4</sub> (methane),  $C_2H_6$  (ethane),  $C_3H_8$  (propane), and  $C_4H_{10}$  (butane) (Figure 10.4). Methane has four hydrogen atoms arranged tetrahedrally around a single carbon atom. Replacing a hydrogen atom in methane by a  $-CH_3$  group gives ethane. If an H atom of ethane is replaced by yet another  $-CH_3$  group, propane results. Butane is derived from propane by replacing an H atom of one of the chain-ending carbon atoms with a  $-CH_3$  group. In all of these compounds, each C atom is attached to four other atoms, either C or H, so alkanes are often called **saturated compounds**.

#### **Structural Isomers**

Structural isomers are possible for all alkanes larger than propane. For example, there are two structural isomers for  $C_4H_{10}$  and three for  $C_5H_{12}$ . As the number of carbon atoms in an alkane increases, the number of possible structural isomers









CH₃

Structural isomers of butane, C<sub>4</sub>H<sub>10</sub>.

greatly increases; there are five isomers possible for  $C_6H_{14}$ , nine isomers for  $C_7H_{16}$ , 18 for  $C_8H_{18}$ , 75 for  $C_{10}H_{22}$ , and 366,319 for  $C_{20}H_{42}$ .

To recognize the isomers corresponding to a given formula, keep in mind the following points:

- Each alkane is built upon a framework of tetrahedral carbon atoms, and each carbon must have four single bonds.
- An effective approach is to create a framework of carbon atoms and then fill the remaining positions around carbon with H atoms so that each C atom has four bonds.
- Nearly free rotation occurs around carbon–carbon single bonds. Therefore, when atoms are assembled to form the skeleton of an alkane, the emphasis is on how carbon atoms are attached to one another and not on how they might lie relative to one another in the plane of the paper.



**Problem** Draw structures of the five isomers of C<sub>6</sub>H<sub>14</sub>. Are any of these isomers chiral?

**Strategy** Focus first on the different frameworks that can be built from six carbon atoms. Having created a carbon framework, fill hydrogen atoms into the structure so that each carbon has four bonds.

#### Solution

**Step 1.** Placing six carbon atoms in a chain gives the framework for the first isomer. Now fill in hydrogen atoms: three on the carbons on the ends of the chain, two on each of the carbons in the middle. You have created the first isomer, hexane.



**Step 2.** Draw a chain of five carbon atoms; then add the sixth carbon atom to one of the carbons in the middle of this chain. (Adding it to a carbon at the end of the chain gives a six-carbon chain, the same framework drawn in Step 1.) Two different carbon frameworks can be built from the five-carbon chain, depending on whether the sixth carbon is linked to the 2 or 3 position. For each of these frameworks, fill in the hydrogens.





Structural isomers of pentane, C<sub>5</sub>H<sub>12</sub>.

■ Chirality in Alkanes To be chiral, a compound must have at least one C atom attached to four different groups. Thus, the C<sub>7</sub>H<sub>16</sub> isomer here is chiral.



We often designate the center of chirality with an asterisk.

**Step 3.** Draw a chain of four carbon atoms. Add in the two remaining carbons, again being careful not to extend the chain length. Two different structures are possible: one with the remaining carbon atoms in the 2 and 3 positions, and another with both extra carbon atoms attached at the 2 position. Fill in the 14 hydrogens. You have now drawn the fourth and fifth isomers.



None of the isomers of  $C_6H_{14}$  is chiral. To be chiral, a compound must have at least one C atom with four different groups attached. This condition is not met in any of these isomers.

**Comment** Should we look for structures in which the longest chain is three carbon atoms? Try it, but you will see that it is not possible to add the three remaining carbons to a three-carbon chain without creating one of the carbon chains already drawn in a previous step. Thus, we have completed the analysis, with five isomers of this compound being identified.

Names have been given to each of these compounds. See the text that follows this Example, and see Appendix E for guidelines on nomenclature.

#### **EXERCISE 10.1** Drawing Structural Isomers of Alkanes

(a) Draw the nine isomers having the formula  $C_7H_{16}$ . (Hint: There is one structure with a sevencarbon chain, two structures with six-carbon chains, five structures in which the longest chain has five carbons [one is illustrated in the margin], and one structure with a four-carbon chain.)

(b) Identify the isomers of  $C_7H_{16}$  that are chiral.

#### Naming Alkanes

With so many possible isomers for a given alkane, chemists need a systematic way of naming them. The guidelines for naming alkanes and their derivatives follow:

- The names of alkanes end in "-ane."
- The names of alkanes with chains of one to 10 carbon atoms are given in Table 10.2. After the first four compounds, the names are derived from Latin numbers—pentane, hexane, heptane, octane, nonane, decane—and this regular naming continues for higher alkanes.
- When naming a specific alkane, the root of the name corresponds to the longest carbon chain in the compound. One isomer of  $C_5H_{12}$  has a three—



One possible isomer of an alkane with the formula  $C_7H_{16}$ .

 Naming Guidelines For more details on naming organic compounds, see Appendix E.

#### Problem Solving Tip 10.1

An error students sometimes make is to suggest that the three carbon skeletons drawn here are different. They are, in fact, the same. All are five-carbon chains with another C atom in the 2 position.





Remember that Lewis structures do not indicate the geometry of molecules.

carbon chain with two  $-CH_3$  groups on the second C atom of the chain. Thus, its name is based on propane.



- Substituent groups on a hydrocarbon chain are identified by a name and the position of substitution in the carbon chain; this information precedes the root of the name. The position is indicated by a number that refers to the carbon atom to which the substituent is attached. (Numbering of the carbon atoms in a chain should begin at the end of the carbon chain that allows the substituent groups to have the lowest numbers.) Both —CH<sub>3</sub> groups in 2,2-dimethylpropane are located at the 2 position.
- Names of hydrocarbon substituents, called **alkyl groups**, are derived from the name of the hydrocarbon. The group –-CH<sub>3</sub>, derived by taking a hydrogen from methane, is called the methyl group; the C<sub>2</sub>H<sub>5</sub> group is the ethyl group.
- If two or more of the same substituent groups occur, the prefixes di-, tri-, and tetra- are added. When different substituent groups are present, they are generally listed in alphabetical order.

#### **EXAMPLE 10.2** Naming Alkanes

Problem Give the systematic name for

**Strategy** Identify the longest carbon chain and base the name of the compound on that alkane. Identify the substituent groups on the chain and their locations. When there are two or more substituents (the groups attached to the chain), number the parent chain from the end that gives the lower number to the substituent encountered first. If the substituents are different, list them in alphabetical order. (For more on naming compounds, see Appendix E.)

**Solution** Here, the longest chain has seven C atoms, so the root of the name is *heptane*. There is a methyl group on C-2 and an ethyl group on C-5. Giving the substituents in alphabetic order and numbering the chain from the end having the methyl group, the systematic name is 5-ethyl-2-methylheptane.

■ Systematic and Common Names The IUPAC (International Union of Pure and Applied Chemistry) has formulated rules for systematic names, which are generally used in this book. (See Appendix E.) However, many organic compounds are known by common names. For example, 2,2-dimethyl-propane is also called neopentane.



FIGURE 10.5 Paraffin wax and mineral oil. These common consumer products are mixtures of alkanes.

#### EXERCISE 10.2 Naming Alkanes

Name the nine isomers of  $C_7H_{16}$  in Exercise 10.1.

#### **Properties of Alkanes**

Methane, ethane, propane, and butane are gases at room temperature and pressure, whereas the higher-molar-mass compounds are liquids or solids (Table 10.2). An increase in melting point and boiling point with molar mass is a general phenomenon that reflects the increased forces of attraction between molecules ( $\triangleright$  Section 12.2).

You already know about alkanes in a nonscientific context because several are common fuels. Natural gas, gasoline, kerosene, fuel oils, and lubricating oils are all mixtures of various alkanes. White mineral oil is also a mixture of alkanes, as is paraffin wax (Figure 10.5).

Pure alkanes are colorless. (The colors seen in gasoline and other petroleum products are due to additives.) The gases and liquids have noticeable but not unpleasant odors. All of these substances are insoluble in water, which is typical of compounds that are nonpolar or nearly so. Low polarity is expected for alkanes because the electronegativities of carbon ( $\chi = 2.5$ ) and hydrogen ( $\chi = 2.2$ ) are not greatly different ( $\blacktriangleleft$  Section 8.8).

All alkanes burn readily in air to give  $CO_2$  and  $H_2O$  in very exothermic reactions. This is, of course, the reason they are widely used as fuels.

$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(\ell)$$
  $\Delta_r H^\circ = -890.3 \text{ kJ/mol-rxn}$ 

Other than in combustion reactions, alkanes exhibit relatively low chemical reactivity. One reaction that does occur, however, is the replacement of the hydrogen atoms of an alkane by chlorine atoms on reaction with  $Cl_2$ . It is formally an oxidation because  $Cl_2$ , like  $O_2$ , is a strong oxidizing agent. These reactions, which can be initiated by ultraviolet radiation, are free radical reactions. Highly reactive Cl atoms are formed from  $Cl_2$  under UV radiation. Reaction of methane with  $Cl_2$  under these conditions proceeds in a series of steps, eventually yielding  $CCl_4$ , commonly known as carbon tetrachloride. (HCl is the other product of these reactions.)



The last three compounds are used as solvents, albeit less frequently today because of their toxicity. Carbon tetrachloride was also once widely used as a dry cleaning fluid and, because it does not burn, in fire extinguishers.

#### Cycloalkanes, C<sub>n</sub>H<sub>2n</sub>

**Cycloalkanes** are constructed with tetrahedral carbon atoms joined together to form a ring. For example, cyclopentane,  $C_5H_{10}$ , consists of a ring of five carbon atoms. Each carbon atom is bonded to two adjacent carbon atoms and to two hydrogen atoms. Notice that the five carbon atoms fall very nearly in a plane because



Cyclohexane, Cyclopentane, top and front views top and front views

The structures of cyclopentane,  $C_5H_{10}$ , and cyclohexane,  $C_6H_{12}$ . The  $C_5$  ring is nearly planar. In contrast, the tetrahedral geometry around carbon means that the  $C_6$  ring is decidedly puckered.

### A Closer Look

#### **Flexible Molecules**

Most organic molecules are flexible; that is, they can twist and bend in various ways. Few molecules better illustrate this behavior than cyclohexane. Two structures are possible: "chair" and "boat" forms. These forms can interconvert by partial rotation of several bonds. The more stable structure is the chair form, which allows the hydrogen atoms to remain as far apart as possible. A side view of this form of cyclohexane reveals two sets of hydrogen atoms in this molecule. Six hydrogen atoms, called the equatorial hydrogens, lie in a plane around the carbon ring. The other six hydrogens are positioned above and below the plane and are called axial hydrogens. Flexing the ring (a rotation around the C—C single bonds) moves the hydrogen atoms between axial and equatorial environments.



the internal angles of a pentagon, 108°, closely match the tetrahedral angle of 109.5°. The small distortion from planarity allows hydrogen atoms on adjacent carbon atoms to be a little farther apart.

Cyclohexane has a nonplanar ring with six  $-CH_2$  groups. If the carbon atoms were in the form of a regular hexagon with all carbon atoms in one plane, the C-C-C bond angles would be 120°. To have tetrahedral bond angles of 109.5° around each C atom, the ring has to pucker. The C<sub>6</sub> ring is flexible, however, and exists in two interconverting forms (see *A Closer Look: Flexible Molecules*).

Interestingly, cyclobutane and cyclopropane are also known, although the bond angles in these species are much less than 109.5°. These compounds are examples of **strained hydrocarbons**, so named because an unfavorable geometry is imposed around carbon. One of the features of strained hydrocarbons is that the C—C bonds are weaker and the molecules readily undergo ring-opening reactions that relieve the bond angle strain.

#### Alkenes and Alkynes

The diversity seen for alkanes is repeated with **alkenes**, hydrocarbons with one or more C=C double bonds. The presence of the double bond adds two features missing in alkanes: the possibility of geometric isomerism and increased reactivity.

The general formula for alkenes is  $C_nH_{2n}$ . The first two members of the series of alkenes are ethene,  $C_2H_4$  (common name, ethylene), and propene,  $C_3H_6$  (common name, propylene). Only a single structure can be drawn for these compounds. As with alkanes, the occurrence of isomers begins with species containing four carbon atoms. Four alkene isomers have the formula  $C_4H_8$ , and each has distinct chemical and physical properties (Table 10.3).





Cyclobutane, C<sub>4</sub>H<sub>8</sub> Cyclopropane, C<sub>3</sub>H<sub>6</sub> Cyclopropane and cyclobutane. Cyclopropane was at one time used as a general anesthetic in surgery. However, its explosive nature when mixed with oxygen soon eliminated this application. The Columbia Encyclopedia states that "cyclopropane allowed the transport of more oxygen to the tissues than did other common anesthetics and also produced greater skeletal muscle relaxation. It is not irritating to the respiratory tract. Because of the low solubility of cyclopropane in the blood, postoperative recovery was usually rapid but nausea and vomiting were common."



#### TABLE 10.3 Properties of Butene Isomers

Name	<b>Boiling Point</b>	Melting Point	Dipole Moment (D)	∆ <sub>f</sub> H° (gas) (kJ/mol)
1-butene	-6.26 °C	-185.4 °C	_	-20.5
2-methylpropene	-6.95 °C	-140.4 °C	0.503	-37.5
cis-2-butene	3.71 °C	-138.9 °C	0.253	-29.7
trans-2-butene	0.88 °C	-105.5 °C	0	-33.0

Alkene names end in "-ene." As with alkanes, the root name for alkenes is that of the longest carbon chain that contains the double bond. The position of the double bond is indicated with a number, and, when appropriate, the prefix *cis* or *trans* is added. Three of the  $C_4H_8$  isomers have four-carbon chains and so are butenes. One has a three-carbon chain and is a propene. Notice that the carbon chain is numbered from the end that gives the double bond the lowest number. In the first isomer at the left, the double bond is between C atoms 1 and 2, so the name is 1-butene and not 3-butene.

#### EXAMPLE 10.3 Determining Isomers of Alkenes from a Formula

**Problem** Draw structures for the six possible alkene isomers with the formula  $C_5H_{10}$ . Give the systematic name of each.

**Strategy** A procedure that involved drawing the carbon skeleton and then adding hydrogen atoms served well when drawing structures of alkanes (Example 10.1), and a similar approach can be used here. It will be necessary to put one double bond into the framework and to be alert for *cis-trans* isomerism.

#### Solution

1. A five-carbon chain with one double bond can be constructed in two ways. *Cis-trans* isomers are possible for 2-pentene.



**2.** Draw the possible four-carbon chains containing a double bond. Add the fifth carbon atom to either the 2 or 3 position. When all three possible combinations are found, fill in the hydrogen atoms. This results in three more structures:





H<sub>2</sub>C=CHCH=CH<sub>2</sub>

1,3-Butadiene,  $C_4H_6$ **Cycloalkenes and dienes.** Cyclohexene,  $C_6H_{10}$  (*top*), and 1,3-butadiene ( $C_4H_6$ ) (*bottom*).

**EXERCISE 10.3 Determining Structural Isomers of Alkenes from a Formula** There are 17 possible alkene isomers with the formula  $C_6H_{12}$ . Draw structures of the five isomers in which the longest chain has six carbon atoms, and give the name of each. Which of these isomers is chiral? (There are also eight isomers in which the longest chain has five carbon atoms, and four isomers in which the longest chain has four carbon atoms. How many can you find?)

More than one double bond can be present in a hydrocarbon. Butadiene, for example, has two double bonds and is known as a *diene*. Many natural products have numerous double bonds (Figure 10.6). There are also cyclic hydrocarbons, such as cyclohexene, with double bonds.



Charles D. Winters

**FIGURE 10.6 Carotene**, a naturally occurring compound with 11 C=C bonds. The  $\pi$  electrons can be excited by visible light in the blue-violet region of the spectrum. As a result, carotene appears orange-yellow to the observer. Carotene or carotene-like molecules are partnered with chlorophyll in nature in the role of assisting in the harvesting of sunlight. Green leaves have a high concentration of carotene. In autumn, green chlorophyll molecules are destroyed, and the yellows and reds of carotene and related molecules are seen. The red color of tomatoes, for example, comes from a molecule very closely related to carotene. As a tomato ripens, its chlorophyll disintegrates, and the green color is replaced by the red of the carotene-like molecule.



An oxy-acetylene torch. The reaction of ethyne (acetylene) with oxygen produces a very high temperature. Oxy-acetylene torches, used in welding, take advantage of this fact.

<b>TABLE 10.4</b>	Some Simple Alkynes $C_n H_{2n-2}$		
Structure	Systematic Name	Common Name	BP (°C)
HC≡CH	ethyne	acetylene	-85
CH₃C≡CH	propyne	methylacetylene	-23
CH₃CH₂C≡CH	1-butyne	ethylacetylene	9

**Alkynes**, compounds with a carbon–carbon triple bond, have the general formula  $(C_nH_{2n-2})$ . Table 10.4 lists alkynes that have four or fewer carbon atoms. The first member of this family is ethyne (common name, acetylene), a gas used as a fuel in metal cutting torches.

dimethylacetylene

27

#### Properties of Alkenes and Alkynes

2-butvne

 $CH_3C \equiv CCH_3$ 

Like alkanes, alkenes and alkynes are colorless. Low-molar-mass compounds are gases, whereas compounds with higher molecular weights are liquids or solids. Alkanes, alkenes, and alkynes are also oxidized by  $O_2$  to give  $CO_2$  and  $H_2O$ .

In contrast to alkanes, alkenes and alkynes have an elaborate chemistry. We gain an insight into their chemical behavior by noting that they are called **unsaturated compounds.** Carbon atoms are capable of bonding to a maximum of four other atoms, and they do so in alkanes and cycloalkanes. In alkenes, however, the carbon atoms linked by a double bond are bonded to only three atoms; in alkynes, they bond to two atoms. It is possible to increase the number of groups attached to carbon by **addition reactions**, in which molecules with the general formula X—Y (such as hydrogen, halogens, hydrogen halides, and water) add across the carbon–carbon double bond (Figure 10.7). The result is a compound with four groups bonded to each carbon.



The products of addition reactions are often substituted alkanes. For example, the addition of bromine to ethylene forms 1,2-dibromoethane.



The addition of 2 mol of chlorine to acetylene gives 1,1,2,2-tetrachloroethane.



During the 1860s, a Russian chemist, Vladimir Markovnikov, examined a large number of alkene addition reactions. In cases in which two isomeric products were



possible, he found that one was more likely to predominate. Based on these results, Markovnikov formulated a rule (now called *Markovnikov's rule*) stating that, when a reagent HX adds to an unsymmetrical alkene, the hydrogen atom in the reagent becomes attached to the carbon that already has the largest number of hydrogens. An example of Markovnikov's rule is the reaction of 2-methylpropene with HCl that results in formation of 2-chloro-2-methylpropane rather than 1-chloro-2-methylpropane.



If the reagent added to a double bond is hydrogen  $(X-Y = H_2)$ , the reaction is called **hydrogenation.** Hydrogenation is usually a very slow reaction, but it can be speeded up in the presence of a catalyst, often a specially prepared form of a metal, such as platinum, palladium, and rhodium. You may have heard the term hydrogenation because certain foods contain "hydrogenated" or "partially hydrogenated" ingredients. One brand of crackers has a label that says, "Made with 100% pure vegetable shortening . . . (partially hydrogenated soybean oil with hydrogenated cottonseed oil)." One reason for hydrogenating an oil is to make it less susceptible to spoilage; another is to convert it from a liquid to a solid.

#### Chemistry , Oow™

Sign in at **www.thomsonedu.com/login** and go to Chapter 10 Contents to see Screen 10.4 for a simulation and tutorial on **alkene addition reactions.** 

#### **EXAMPLE 10.4** Reaction of an Alkene

**Problem** Draw the structure of the compound obtained from the reaction of  $Br_2$  with propene, and name the compound.

**Strategy** Bromine adds across the C==C double bond. The name includes the name of the carbon chain and indicates the positions of the Br atoms.

Solution



#### FIGURE 10.7 Bacon fat and addi-

tion reactions. The fat in bacon is partially unsaturated. Like other unsaturated compounds, bacon fat reacts with  $Br_2$  in an addition reaction. Here, you see the color of  $Br_2$  vapor fade when a strip of bacon is introduced.

#### Nomenclature of Substituted

**Alkanes** The substituent groups in substituted alkanes are identified by the name and position of the substituent on the alkane chain.

Catalysts A catalyst is a substance that causes a reaction to occur at a faster rate without itself being permanently changed in the reaction. We will describe catalysts in more detail in Chapter 15.

#### **EXERCISE 10.4** Reactions of Alkenes

(a) Draw the structure of the compound obtained from the reaction of HBr with ethylene, and name the compound.

(b) Draw the structure of the product of the reaction of  $Br_2$  with *cis*-2-butene, and name this compound.

### **Aromatic Compounds**

Benzene,  $C_6H_6$ , is a key molecule in chemistry. It is the simplest **aromatic compound**, a class of compounds so named because they have significant, and usually not unpleasant, odors. Other members of this class, which are all based on benzene, include toluene and naphthalene. A source of many aromatic compounds is coal. These compounds, and many other volatile substances, are released when coal is heated to a high temperature in the absence of air (Table 10.5).



Benzene occupies a pivotal place in the history and practice of chemistry. Michael Faraday discovered this compound in 1825 as a by-product of illuminating gas, a fuel produced by heating coal. Today, benzene is an important industrial chemical, usually ranking among the top 25 chemicals in production annually in the United States. It is used as a solvent and is also the starting point for making thousands of different compounds by replacing the H atoms of the ring.

Toluene was originally obtained from tolu balsam, the pleasant-smelling gum of a South American tree, *Toluifera balsamum*. This balsam has been used in cough syrups and perfumes. Naphthalene is an ingredient in "moth balls," although 1,4dichlorobenzene is now more commonly used. Aspartame and another artificial sweetener, saccharin, are also benzene derivatives.

Common Name	Formula	Boiling Point (°C)	Melting Point (°C)
benzene	C <sub>6</sub> H <sub>6</sub>	80	+6
toluene	$C_6H_5CH_3$	111	-95
<i>o</i> -xylene	$1,2-C_6H_4(CH_3)_2$	144	-25
<i>m</i> -xylene	1,3-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	139	-48
<i>p</i> -xylene	$1,4-C_6H_4(CH_3)_2$	138	+13
naphthalene	$C_{10}H_8$	218	+80

### TABLE 10.5 Some Aromatic Compounds from Coal Tar



Saccharin  $(C_7H_5NO_3S)$ . This compound, an artificial sweetener, contains an aromatic ring.

#### The Structure of Benzene

The formula of benzene suggested to 19th-century chemists that this compound should be unsaturated, but, if viewed this way, its chemistry was perplexing. Whereas alkenes readily add Br<sub>2</sub>, for example, benzene does not do so under similar conditions. The structural question was finally solved by August Kekulé (1829–1896). We now recognize that benzene's different reactivity relates to its structure and bonding, both of which are quite different from the structure and bonding in alkenes. Benzene has equivalent carbon–carbon bonds, 139 pm in length, intermediate between a C—C single bond (154 pm) and a C=C double bond (134 pm). The  $\pi$  bonds are formed by the continuous overlap of the p orbitals on the six carbon atoms (page 421). Using valence bond terminology, the structure is represented by a hybrid of two resonance structures.





Some products containing compounds based on benzene. Examples include sodium benzoate in soft drinks, ibuprofen in Advil, and benzoyl peroxide in Oxy-10.

#### **Benzene Derivatives**

Toluene, chlorobenzene, benzoic acid, aniline, styrene, and phenol are common examples of benzene derivatives.



If more than one H atom of benzene is replaced, isomers can arise. Thus, the systematic nomenclature for benzene derivatives involves naming substituent groups and identifying their positions on the ring by numbering the six carbon atoms ( $\triangleright$  Appendix E). Some common names, which are based on an older naming scheme, are also used. This scheme identified isomers of disubstituted benzenes with the prefixes *ortho* (*o*-, substituent groups on adjacent carbons in the benzene ring), *meta* (*m*-, substituents separated by one carbon atom), and *para* (*p*-, substituent groups on carbons on opposite sides of the ring).





Aspirin, a commonly used analgesic. It is based on benzoic acid with an acetate group,  $-0_2$ CCH<sub>3</sub>, in the *ortho* position.

#### **EXAMPLE 10.5** Isomers of Substituted Benzenes

Problem Draw and name the isomers of C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub>.

**Strategy** Begin by drawing the structure of  $C_6H_5Cl$ . Place a second Cl atom on the ring in the *ortho*, *meta*, and *para* positions. Add the third Cl in one of the remaining positions.

**Solution** The three isomers of  $C_6H_3Cl_3$  are shown here. They are named as derivatives of benzene by specifying the number of substituent groups with the prefix "tri-," the name of the substituent, and the positions of the three groups around the six-member ring.



#### **EXERCISE 10.5** Isomers of Substituted Benzenes

Aniline,  $C_6H_5NH_2$ , is the common name for aminobenzene. Draw a structure for *p*-diaminobenzene, a compound used in dye manufacture. What is the systematic name for *p*-diaminobenzene?

#### **Properties of Aromatic Compounds**

Benzene is a colorless liquid, and simple substituted benzenes are liquids or solids under normal conditions. The properties of aromatic hydrocarbons are typical of hydrocarbons in general: They are insoluble in water, soluble in nonpolar solvents, and oxidized by  $O_2$  to form  $CO_2$  and  $H_2O$ .

One of the most important properties of benzene and other aromatic compounds is an unusual stability that is associated with the unique  $\pi$  bonding in this molecule. Because the  $\pi$  bonding in benzene is typically described using resonance structures, the extra stability is termed **resonance stabilization**. The extent of resonance stabilization in benzene is evaluated by comparing the energy evolved in the hydrogenation of benzene to form cyclohexane

$$C_6H_6(\ell) + 3 H_2(g) \xrightarrow{\text{catalyst}} C_6H_{12}(\ell) \qquad \Delta_r H^\circ = -206.7 \text{ kJ/mol-rxr}$$

with the energy evolved in hydrogenation of three isolated double bonds.

$$3 H_2C = CH_2(g) + 3 H_2(g) \rightarrow 3 C_2H_6(g)$$
  $\Delta_r H^\circ = -410.8 \text{ kJ/mol-rxn}$ 

The hydrogenation of benzene is about 200 kJ less exothermic than the hydrogenation of three moles of ethylene. The difference is attributable to the added stability associated with  $\pi$  bonding in benzene.

### A Closer Look

Much of the world's current technology relies on petroleum. Burning fuels derived from petroleum provides by far the largest amount of energy in the industrial world (see *The Chemistry of Fuels and Energy Sources*, pages 254–267). Petroleum and natural gas are also the chemical raw materials used in the manufacture of plastics, rubber, pharmaceuticals, and a vast array of other compounds.

The petroleum that is pumped out of the ground is a complex mixture whose composition varies greatly, depending on its source. The primary components of petroleum are always alkanes, but, to varying degrees, nitrogen- and sulfur-containing compounds are also present. Aromatic compounds are present as well, but alkenes and alkynes are not.

An early step in the petroleum refining process is distillation, in which the crude mix-



A modern petrochemical plant.

#### **Petroleum Chemistry**

ture is separated into a series of fractions based on boiling point: first a gaseous fraction (mostly alkanes with one to four carbon atoms; this fraction is often burned off), and then gasoline, kerosene, and fuel oils. After distillation, considerable material, in the form of a semi-solid, tar-like residue, remains.

The petrochemical industry seeks to maximize the amounts of the higher-valued fractions of petroleum produced and to make specific compounds for which a particular need exists. This means carrying out chemical reactions involving the raw materials on a huge scale. One process to which petroleum is subjected is known as cracking. At very high temperatures, bond breaking or "cracking" can occur, and longer-chain hydrocarbons will fragment into smaller molecular units. These reactions are carried out in the presence of a wide array of catalysts, materials that speed up reactions and direct them toward specific products. Among the important products of cracking are ethylene and other alkenes, which serve as the raw materials for the formation of materials such as polyethylene. Cracking also produces gaseous hydrogen, a widely used raw material in the chemical industry.

Other important reactions involving petroleum are run at elevated temperatures and in the presence of specific catalysts. Such reactions include *isomerization* reactions, in which the carbon skeleton of an alkane rearranges to form a new isomeric species, and *reformation* processes, in which smaller molecules combine to form new molecules. Each process is directed toward achieving a specific goal, such as increasing the proportion of branched-chain hydrocarbons in gasoline to obtain higher octane ratings. A great amount of chemical research has gone into developing and understanding these highly specialized processes.



**Producing gasoline.** Branched hydrocarbons have a higher octane rating in gasoline. Therefore, an important process in producing gasoline is the isomerization of octane to a branched hydrocarbon such as isooctane, 2,2,4-trimethylpentane.

Although aromatic compounds are unsaturated hydrocarbons, they do not undergo the addition reactions typical of alkenes and alkynes. Instead, *substitution reactions* occur, in which one or more hydrogen atoms are replaced by other groups. Such reactions require a strong Brønsted acid such as H<sub>2</sub>SO<sub>4</sub> or a Lewis acid such as AlCl<sub>3</sub> or FeBr<sub>3</sub>.

$$\begin{array}{lll} \textit{Nitration:} & C_{6}H_{6}(\ell) \ + \ HNO_{3}(\ell) & \xrightarrow{H_{2}SO_{4}} & C_{6}H_{5}NO_{2}(\ell) \ + \ H_{2}O(\ell) \\ \textit{Alkylation:} & C_{6}H_{6}(\ell) \ + \ CH_{3}Cl(\ell) & \xrightarrow{AlCl_{3}} & C_{6}H_{5}CH_{3}(\ell) \ + \ HCl(g) \\ \textit{Halogenation:} & C_{6}H_{6}(\ell) \ + \ Br_{2}(\ell) & \xrightarrow{FeBr_{3}} & C_{6}H_{5}Br(\ell) \ + \ HBr(g) \end{array}$$

### 10.3 Alcohols, Ethers, and Amines

Other types of organic compounds arise as elements other than carbon and hydrogen are included in the compound. Two elements in particular, oxygen and nitrogen, add a rich dimension to carbon chemistry.

Functional Group*	General Formula*	Class of Compound	Examples
F, Cl, Br, I	RF, RCl, RBr, RI	haloalkane	CH <sub>3</sub> CH <sub>2</sub> Cl, chloroethane
OH	ROH	alcohol	CH <sub>3</sub> CH <sub>2</sub> OH, ethanol
OR'	ROR'	ether	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> 0, diethyl ether
NH <sub>2</sub> †	RNH <sub>2</sub>	(primary) amine	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> , ethylamine
0    CH	RCHO	aldehyde	CH3CHO, ethanal (acetaldehyde)
0    	RCOR'	ketone	CH <sub>3</sub> COCH <sub>3</sub> , propanone (acetone)
0 —С—ОН	RCO <sub>2</sub> H	carboxylic acid	CH <sub>3</sub> CO <sub>2</sub> H, ethanoic acid (acetic acid)
0    	RCO <sub>2</sub> R'	ester	CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub> , methyl acetate
0    	RCONH <sub>2</sub>	amide	CH <sub>3</sub> CONH <sub>2</sub> , acetamide

#### **TABLE 10.6** Common Functional Groups and Derivatives of Alkanes

\* R and R' can be the same or different hydrocarbon groups.

<sup>†</sup> Secondary amines (R<sub>2</sub>NH) and tertiary amines (R<sub>3</sub>N) are also possible, see discussion in the text.

Organic chemistry organizes compounds containing elements other than carbon and hydrogen as derivatives of hydrocarbons. Formulas (and structures) are represented by substituting one or more hydrogens in a hydrocarbon molecule by a **functional group.** A functional group is an atom or group of atoms attached to a carbon atom in the hydrocarbon. Formulas of hydrocarbon derivatives are then written as R—X, in which R is a hydrocarbon lacking a hydrogen atom, and X is the functional group that has replaced the hydrogen. The chemical and physical properties of the hydrocarbon derivatives are a blend of the properties associated with hydrocarbons and the group that has been substituted for hydrogen.

Table 10.6 identifies some common functional groups and the families of organic compounds resulting from their attachment to a hydrocarbon.

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### **Alcohols and Ethers**

If one of the hydrogen atoms of an alkane is replaced by a hydroxyl (-OH) group, the result is an **alcohol**, ROH. Methanol, CH<sub>3</sub>OH, and ethanol, CH<sub>3</sub>CH<sub>2</sub>OH, are the most important alcohols, but others are also commercially important (Table 10.7). Notice that several have more than one OH functional group.

More than  $5 \times 10^8$  kg of methanol is produced in the United States annually. Most of this production is used to make formaldehyde (CH<sub>2</sub>O) and acetic acid



David Young/Tom Stack & Associates



<b>TABLE 10.7</b>	Some	Important	Alcohols
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Condensed Formula	BP (°C)	Systematic Name	Common Name	Use
CH₃OH	65.0	methanol	methyl alcohol	fuel, gasoline additive, making formaldehyde
CH <sub>3</sub> CH <sub>2</sub> OH	78.5	ethanol	ethyl alcohol	beverages, gasoline additive, solvent
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	97.4	1-propanol	propyl alcohol	industrial solvent
CH <sub>3</sub> CH(OH)CH <sub>3</sub>	82.4	2-propanol	isopropyl alcohol	rubbing alcohol
HOCH <sub>2</sub> CH <sub>2</sub> OH	198	1,2-ethanediol	ethylene glycol	antifreeze
HOCH <sub>2</sub> CH(OH)CH <sub>2</sub> OH	290	1,2,3-propanetriol	glycerol (glycerin)	moisturizer in consumer products



Methanol, CH<sub>3</sub>OH, is the simplest alcohol. Methanol is often called "wood alcohol" because it was originally produced by heating wood in the absence of air.

 $(CH_3CO_2H)$ , both important chemicals in their own right. Methanol is also used as a solvent, as a de-icer in gasoline, and as a fuel in high-powered racing cars. It is found in low concentration in new wine, where it contributes to the odor, or "bouquet." Like ethanol, methanol causes intoxication, but methanol differs in being more poisonous, largely because the human body converts it to formic acid  $(HCO_2H)$  and formaldehyde  $(CH_2O)$ . These compounds attack the cells of the retina in the eye, leading to permanent blindness.

Ethanol is the "alcohol" of alcoholic beverages, in which it is formed by the anaerobic (without air) fermentation of sugar. For many years, industrial alcohol, which is used as a solvent and as a starting material for the synthesis of other compounds, was made by fermentation. In the last several decades, however, it has become cheaper to make ethanol from petroleum by-products—specifically, by the addition of water to ethylene.



■ Aerobic Fermentation Aerobic fermentation (in the presence of O<sub>2</sub>) of sugar leads to the formation of acetic acid. This is how wine vinegar is made.

Beginning with three-carbon alcohols, structural isomers are possible. For example, 1-propanol and 2-propanol (common name, isopropyl alcohol) are different compounds (Table 10.7).

Ethylene glycol and glycerol are common alcohols having two and three —OH groups, respectively. Ethylene glycol is used as antifreeze in automobiles. Glycerol's most common use is as a softener in soaps and lotions. It is also a raw material for the preparation of nitroglycerin (Figure 10.8).



Systematic name: 1,2-ethanediol Common name: ethylene glycol





**Rubbing alcohol.** Common rubbing alcohol is 2-propanol, also called isopropyl alcohol.



**FIGURE 10.8** Nitroglycerin. (a) Concentrated nitric acid and glycerin react to form an oily, highly unstable compound called nitroglycerin,  $C_3H_5(ONO_2)_3$ . (b) Nitroglycerin is more stable if absorbed onto an inert solid, a combination called dynamite. (c) The fortune of Alfred Nobel (1833–1896), built on the manufacture of dynamite, now funds the Nobel Prizes.

#### **EXAMPLE 10.6 Structural Isomers of Alcohols**

**Problem** How many different alcohols are derivatives of pentane? Draw structures, and name each alcohol.

**Strategy** Pentane,  $C_5H_{12}$ , has a five-carbon chain. An —OH group can replace a hydrogen atom on one of the carbon atoms. Alcohols are named as derivatives of the alkane (pentane) by replacing the "-e" at the end with "-ol" and indicating the position of the —OH group by a numerical prefix (Appendix E).

**Solution** Three different alcohols are possible, depending on whether the —OH group is placed on the first, second, or third carbon atom in the chain. (The fourth and fifth positions are identical to the second and first positions in the chain, respectively.)



**Comment** Additional structural isomers with the formula  $C_5H_{11}OH$  are possible in which the longest carbon chain has three C atoms (one isomer) or four C atoms (four isomers).

#### **EXERCISE 10.6** Structures of Alcohols

Draw the structure of 1-butanol and alcohols that are structural isomers of the compound.

### **Properties of Alcohols and Ethers**

Methane, CH<sub>4</sub>, is a gas (boiling point, -161 °C) with low solubility in water. Methanol, CH<sub>3</sub>OH, by contrast, is a liquid that is *miscible* with water in all proportions. The boiling point of methanol, 65 °C, is 226 °C higher than the boiling point of methane. What a difference the addition of a single atom into the structure can make in the properties of simple molecules!

Alcohols are related to water, with one of the H atoms of  $H_2O$  being replaced by an organic group. If a methyl group is substituted for one of the hydrogens of water, methanol results. Ethanol has a  $-C_2H_5$  (ethyl) group, and propanol has a  $-C_3H_7$  (propyl) group in place of one of the hydrogens of water. Viewing alcohols as related to water also helps in understanding the properties of alcohols.

The two parts of methanol, the  $-CH_3$  group and the -OH group, contribute to its properties. For example, methanol will burn, a property associated with hydrocarbons. On the other hand, its boiling point is more like that of water. The temperature at which a substance boils is related to the forces of attraction between molecules, called *intermolecular forces*: The stronger the attractive, intermolecular forces in a sample, the higher the boiling point ( $\triangleright$  Section 12.4). These forces are particularly strong in water, a result of the polarity of the -OH group in this molecule ( $\triangleleft$  Section 8.8). Methanol is also a polar molecule, and it is the polar -OHgroup that leads to a high boiling point. In contrast, methane is nonpolar and its low boiling point is the result of weak intermolecular forces.

It is also possible to explain the differences in the solubility of methane and methanol in water. The solubility of methanol is conferred by the polar —OH portion of the molecule. Methane, which is nonpolar, has low water-solubility.



As the size of the alkyl group in an alcohol increases, the alcohol boiling point rises, a general trend seen in families of similar compounds and related to molar mass (see Table 10.7). The solubility in water in this series decreases. Methanol and ethanol are completely miscible in water, whereas 1-propanol is moderately water-soluble; 1-butanol is less soluble than 1-propanol. With an increase in the size of the hydrocarbon group, the organic group (the nonpolar part of the molecule) has become a larger fraction of the molecule, and properties associated with nonpolarity begin to dominate. Space-filling models show that in methanol, the polar and nonpolar parts of the molecule are approximately similar in size, but in 1-butanol the —OH group is less than 20% of the molecule. The molecule is less like water and more "organic."

Attaching an additional—OH group to a hydrocarbon framework has an effect on water solubility (Figure 10.9). Two —OH groups on a three-carbon framework, as found in propylene glycol, convey complete miscibility with water, in contrast to the limited solubility of 1-propanol and 2-propanol.

**Ethers** have the general formula ROR'. The best-known ether is diethyl ether,  $CH_3CH_2OCH_2CH_3$ . Lacking an -OH group, the properties of ethers are in sharp contrast to those of alcohols. Diethyl ether, for example, has a lower boiling point (34.5 °C) than ethanol,  $CH_3CH_2OH$  (78.3 °C), and is only slightly soluble in water.

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■ Hydrogen Bonding The intermolecular forces of attraction of compounds with hydrogen attached to a highly electro-negative atom, like 0, N, or F, are so exceptional that they are accorded a special name: hydrogen bonding. We will discuss hydrogen bonding in Section 12.2.



les D. Winter

Safe antifreeze—propylene glycol, CH<sub>3</sub>CHOHCH<sub>2</sub>OH. Most antifreeze sold today consists of about 95% ethylene glycol. Cats and dogs are attracted by the smell and taste of the compound, but it is toxic. In fact, only a few milliliters can prove fatal to a small dog or cat. In the first stage of poisoning, an animal may appear drunk, but within 12–36 hours the kidneys stop functioning, and the animal slips into a coma. To avoid accidental poisoning of domestic and wild animals, you can use propylene glycol antifreeze. This compound affords the same antifreeze protection but is much less toxic.



Methanol is often added to automobile gasoline tanks in the winter to prevent fuel lines from freezing. It is soluble in water and lowers the water's freezing point.





Ethylene glycol is used in automobile radiators. It is soluble in water, and lowers the freezing point and raises the boiling point of the water in the cooling system. (See Section 14.4.) Ethylene glycol, a major component of automobile antifreeze, is completely miscible with water.

FIGURE 10.9 Properties and uses of methanol and ethylene glycol.

### Amines

It is often convenient to think about water and ammonia as being similar molecules: They are the simplest hydrogen compounds of adjacent second-period elements. Both are polar and exhibit some similar chemistry, such as protonation (to give  $H_3O^+$  and  $NH_4^+$ ) and deprotonation (to give  $OH^-$  and  $NH_2^-$ ).

This comparison of water and ammonia can be extended to alcohols and amines. Alcohols have formulas related to water in which one hydrogen in  $H_2O$  is replaced with an organic group (R—OH). In organic **amines**, one or more hydrogen atoms of  $NH_3$  are replaced with an organic group. Amine structures are similar to ammonia's structure; that is, the geometry about the N atom is trigonal pyramidal.

Amines are categorized based on the number of organic substituents as primary (one organic group), secondary (two organic groups), or tertiary (three organic groups). As examples, consider the three amines with methyl groups:  $CH_3NH_2$ ,  $(CH_3)_2NH$ , and  $(CH_3)_3N$ .



CH<sub>3</sub>NH<sub>2</sub> Primary amine Methylamine



(CH<sub>3</sub>)<sub>2</sub>NH Secondary amine Dimethylamine



(CH<sub>3</sub>)<sub>3</sub>N Tertiary amine Trimethylamine

#### **Properties of Amines**

Amines usually have offensive odors. You know what the odor is if you have ever smelled decaying fish. Two appropriately named amines, putrescine and cadaverine, add to the odor of urine, rotten meat, and bad breath.

H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>
putrescine	cadaverine
1,4-butanediamine	1,5-pentanediamine

The smallest amines are water-soluble, but most amines are not. All amines are bases, however, and they react with acids to give salts, many of which are water-soluble. As with ammonia, the reactions involve adding  $H^+$  to the lone pair of electrons on the N atom. This is illustrated by the reaction of aniline (aminobenzene) with  $H_2SO_4$  to give anilinium sulfate, a compound of some historical interest (see "Historical Perspectives: Mauvine").



### Historical Perspectives

Among the roots of modern organic chemistry was the synthesis, in 1856, of the compound mauveine (or mauve) by William Henry Perkin (1838–1907). This discovery led to a flourishing dye industry, one of the first chemical industries.

The discovery of mauve is an interesting tale. At the age of 13, Perkin enrolled at the City of London School. His father paid an



### Mauveine

extra fee for him to attend a lunchtime chemistry course and set up a lab at home for him to do experiments. He began attending the public lectures that Michael Faraday gave on Saturdays at the Royal Institution. At 15, Perkin enrolled in the Royal College of Science in London to study chemistry under the school's Director, August Wilhelm von Hofmann. After he completed his studies at age 17, he took a position at the college as Hofmann's assistant, rather a great honor.

Perkin's first project was to synthesize guinine, an antimalarial drug. The route he proposed involved oxidizing anilinium sulfate. From the reaction, he obtained a black solid that dissolved in a water-ethanol mixture to give a purple solution that stained cloth a beautiful purple color. The color didn't wash out, an essential feature for a dve. Later, it was learned that the anilinium sulfate Perkin used had been impure and that the impurity was essential in the synthesis. Had Perkins used a pure sample or his starting reagent, the discovery of mauve would not have happened. A study in 1994 on samples of mauve preserved in museums determined that Perkin's mauve was actually a mixture of two very similar compounds, along with traces of several others.

At the age of 18, Perkin quit his assistantship and, with financial help from his family, CH<sub>3</sub> set up a dye factory outside of London. By the age of 36, he was a very wealthy man. He then retired from the dye business and devoted the rest of his life to chemical research on various topics, including the synthesis of fragrances and a study of optical activity. During his lifetime, he received numerous honors for his research, but one honor came many years after his death. In 1972, when The Chemical Society (in England) renamed its journals after famous society members, it chose Perkin's name for the organic chemistry journals. (See *Mauve*, a book on Perkin's life, by S. Garfield, W. W. Norton Publishers, New York.)



A silk dress dyed with Perkin's original sample of mauve in 1862, at the dawning of the synthetic dye industry. From *Mauve*.



**Nicotine.** Two nitrogen atoms in the nicotine molecule can be protonated, which is the form in which nicotine is normally found. The protons can be removed, however, by treating it with a base. This "freebase" form is much more poisonous and addictive. See J. F. Pankow: *Environmental Science & Technology*, Vol 31, p. 2428, August 1997.

The facts that an amine can be protonated and that the proton can be removed again by treating the compound with a base have practical and physiological importance. Nicotine in cigarettes is normally found in the protonated form. (This water-soluble form is often used in insecticides.) Adding a base such as ammonia removes the H<sup>+</sup> ion to leave nicotine in its "free-base" form.

$$\text{NicH}_2^{2+}(aq) + 2 \text{ NH}_3(aq) \rightarrow \text{Nic}(aq) + 2 \text{ NH}_4^+(aq)$$

In this form, nicotine is much more readily absorbed by the skin and mucous membranes, so the compound is a much more potent poison.

### **10.4** Compounds with a Carbonyl Group

Formaldehyde, acetic acid, and acetone are among the organic compounds referred to in previous examples. These compounds have a common structural feature: Each contains a trigonal-planar carbon atom doubly bonded to an oxygen. The C==O group is called the **carbonyl group**, and all of these compounds are members of a large class of compounds called **carbonyl compounds**.



In this section, we will examine five groups of carbonyl compounds (Table 10.6, page 462):

- *Aldehydes* (RCHO) have an organic group (—R) and an H atom attached to a carbonyl group.
- *Ketones* (RCOR') have two —R groups attached to the carbonyl carbon; they may be the same groups, as in acetone, or different groups.
- *Carboxylic acids* (RCO<sub>2</sub>H) have an —R group and an —OH group attached to the carbonyl carbon.
- *Esters*  $(\text{RCO}_2\text{R}')$  have -R and -OR' groups attached to the carbonyl carbon.
- Amides (RCONR<sub>2</sub>', RCONHR', and RCONH<sub>2</sub>) have an -R group and an amino group (-NH<sub>2</sub>, -NHR, -NR<sub>2</sub>) bonded to the carbonyl carbon.

Aldehydes, ketones, and carboxylic acids are oxidation products of alcohols and, indeed, are commonly made by this route. The product obtained through oxidation of an alcohol depends on the alcohol's structure, which is classified according to the number of carbon atoms bonded to the C atom bearing the —OH group. *Primary alcohols* have one carbon and two hydrogen atoms attached, whereas *secondary alcohols* have two carbon atoms and one hydrogen atom attached. *Tertiary alcohols* have three carbon atoms attached to the C atom bearing the —OH group.

A *primary alcohol* is oxidized in two steps. It is first oxidized to an aldehyde and then in a second step to a carboxylic acid:



Primary alcohol: ethanol



Secondary alcohol: 2-propanol







For example, the air oxidation of ethanol in wine produces wine (with excess oxygen) vinegar, the most important ingredient of which is acetic acid.



Acids have a sour taste. The word "vinegar" (from the French *vin aigre*) means sour wine. A device to test one's breath for alcohol relies on a similar oxidation of ethanol (Figures 3.21 and 10.10).

In contrast to primary alcohols, oxidation of a *secondary alcohol* produces a ketone:



(-R and -R' are organic groups. They may be the same or different.)

Common oxidizing agents used for these reactions are reagents such as  $KMnO_4$  and  $K_2Cr_2O_7$  (Table 3.4).

Finally, tertiary alcohols do not react with the usual oxidizing agents.

$$(CH_3)_3COH \xrightarrow{\text{oxidizing agent}}$$
 no reaction

#### Aldehydes and Ketones

Aldehydes and ketones have pleasant odors and are often used in fragrances. Benzaldehyde is responsible for the odor of almonds and cherries; cinnamaldehyde is found in the bark of the cinnamon tree; and the ketone 4-(*p*-hydroxyphenyl) 2-butanone is responsible for the odor of ripe raspberries (a favorite of the authors of this book). Table 10.8 lists several simple aldehydes and ketones.



Aldehydes and ketones are the oxidation products of primary and secondary alcohols, respectively. The reverse reactions—reduction of aldehydes to primary alcohols and reduction of ketones to secondary alcohols—are also known.



**FIGURE 10.10** Alcohol tester. This device for testing a person's breath for the presence of ethanol relies on the oxidation of the alcohol. If present, ethanol is oxidized by potassium dichromate,  $K_2Cr_2O_7$ , to acetaldehyde, and then to acetic acid. The yellow-orange dichromate ion is reduced to green  $Cr^{3+}(aq)$ , the color change indicating that ethanol was present.



Aldehydes and odors. The odors of almonds and cinnamon are due to aldehydes, but the odor of fresh raspberries comes from a ketone.

<b>TABLE 10.8</b>	Simple Aldehydes and Ketones	5	
Structure	Common Name	Systematic Name	BP (°C)
0			
НСН	formaldehyde	methanal	-19
0    CH <sub>3</sub> CH	acetaldehyde	ethanal	20
0 ∥ CH₃CCH₃	acetone	propanone	56
0 ∥ CH₃CCH₂CH₃	methyl ethyl ketone	butanone	80
0    CH <sub>3</sub> CH <sub>2</sub> CCH <sub>2</sub> CH	3 diethyl ketone	3-pentanone	102

Commonly used reagents for such reductions are  $\rm NaBH_4$  and  $\rm LiAlH_4$  , although  $\rm H_2$  is used on an industrial scale.



#### **EXERCISE 10.7** Aldehydes and Ketones

(a) Draw the structural formula for 2-pentanone. Draw structures for a ketone and two aldehydes that are isomers of 2-pentanone, and name each of these compounds.

(b) What is the product of the reduction of 2-pentanone with NaBH<sub>4</sub>?

#### **EXERCISE 10.8** Aldehydes and Ketones

Draw the structures, and name the aldehyde or ketone formed upon oxidation of the following alcohols: (a) 1-butanol, (b) 2-butanol, (c) 2-methyl-1-propanol. Are these three alcohols structural isomers? Are the oxidation products structural isomers?

### **Carboxylic Acids**

Acetic acid is the most common and most important **carboxylic acid**. For many years, acetic acid was made by oxidizing ethanol produced by fermentation. Now, however, acetic acid is generally made by combining carbon monoxide and methanol in the presence of a catalyst:

$$CH_3OH(\ell) + CO(g) \xrightarrow{catalyst} CH_3CO_2H(\ell)$$
  
methanol acetic acid

About 1 billion kilograms of acetic acid are produced annually in the United States for use in plastics, synthetic fibers, and fungicides.

Many organic acids are found naturally (Table 10.9). Acids are recognizable by their sour taste (Figure 10.11) and are found in common foods: Citric acid in fruits, acetic acid in vinegar, and tartaric acid in grapes are just three examples.

Some carboxylic acids have common names derived from the source of the acid (Table 10.9). Because formic acid is found in ants, its name comes from the Latin word for ant (*formica*). Butyric acid gives rancid butter its unpleasant odor, and the name is related to the Latin word for butter (*butyrum*). The systematic names of acids (Table 10.10) are formed by dropping the "-e" on the name of the corresponding alkane and adding "-oic" (and the word "acid").

Because of the substantial electronegativity of oxygen, the two O atoms of the carboxylic acid group are slightly negatively charged, and the H atom of the —OH group is positively charged. This charge distribution has several important implications:

• The polar acetic acid molecule dissolves readily in water, which you already know because vinegar is an aqueous solution of acetic acid. (Acids with larger organic groups are less soluble, however.)



**FIGURE 10.11** Acetic acid in bread. Acetic acid is produced in bread when leavened with the yeast *Saccharomyces exigus*. Another group of bacteria, *Lactobacillus sanfrancisco*, contributes to the flavor of sourdough bread. These bacteria metabolize the sugar maltose, excreting acetic acid and lactic acid, CH<sub>3</sub>CH(0H)CO<sub>2</sub>H, thereby giving the bread its unique sour taste.

Name	Structure	Natural Source
benzoic acid		berries
citric acid	$HO_{2}C - CH_{2} - CH_{2} - CH_{2} - CO_{2}H$	citrus fruits
lactic acid	H₃C — CH — CO₂H I OH	sour milk
malic acid	HO <sub>2</sub> CCH <sub>2</sub> CHCO <sub>2</sub> H       	apples
oleic acid	$CH_3(CH_2)_7 - CH = CH - (CH_2)_7 - CO_2H$	vegetable oils
oxalic acid	$HO_2C-CO_2H$	rhubarb, spinach, cabbage, tomatoes
stearic acid	$CH_{3}(CH_{2})_{16}$ - $CO_{2}H$	animal fats
tartaric acid	HO <sub>2</sub> C — CH — CH — CO <sub>2</sub> H     OH OH	grape juice, wine

TABLE 10.9 Some Naturally Occurring Carboxylic Acids



Formic acid, HCO<sub>2</sub>H. This acid puts the sting in ant bites.





TABLE 10.10	Some Simple Carboxylic Acids		
Structure	Common Name	Systematic Name	BP (°C)
0			
НСОН	formic acid	methanoic acid	101
0 ∥ CH₃COH	acetic acid	ethanoic acid	118
0 ∥ CH₃CH₂COH	propionic acid	propanoic acid	141
0    CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COH	butyric acid	butanoic acid	163
0    CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COH	valeric acid	pentanoic acid	187

• The hydrogen of the —OH group is the acidic hydrogen. As noted in Chapter 3, acetic acid is a weak acid in water, as are most other organic acids.

Carboxylic acids undergo a number of reactions. Among these is the reduction of the acid (with reagents such as LiAlH<sub>4</sub> or NaBH<sub>4</sub>) first to an aldehyde and then to an alcohol. For example, acetic acid is reduced first to acetaldehyde and then to ethanol.

$$\begin{array}{c} \mathsf{CH}_3\mathsf{CO}_2\mathsf{H} \xrightarrow{\mathsf{LiAlH}_4} \mathsf{CH}_3\mathsf{CHO} \xrightarrow{\mathsf{LiAlH}_4} \mathsf{CH}_3\mathsf{CH}_2\mathsf{OH} \\ \text{acetic acid} & \text{acetaldehyde} & \text{ethanol} \end{array}$$

Yet another important aspect of carboxylic acid chemistry is these acids' reaction with bases to give carboxylate anions. For example, acetic acid reacts with sodium hydroxide to give sodium acetate (sodium ethanoate).

$$CH_3CO_2H(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(\ell)$$

### **Esters**

Carboxylic acids  $(RCO_2H)$  react with alcohols (R'OH) to form esters  $(RCO_2R')$  in an **esterification** reaction. (These reactions are generally run in the presence of strong acids because acids accelerate the reaction.)





Carboxylate group: \_\_\_\_\_\_\_\_\_\_ portion from Portion from ethanol acetic acid

Ethyl acetate, an ester CH<sub>3</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

### A Closer Look

#### **Glucose and Sugars**



As their name implies, formulas of carbohydrates can be written as though they are a combination of carbon and water,  $C_x(H_2O)_y$ . Thus, the formula of glucose,  $C_6H_{12}O_6$ , is equivalent to  $C_6(H_2O)_6$ . This compound is a sugar, or, more accurately, a **monosaccharide**.

Carbohydrates are polyhydroxy aldehydes or ketones. Glucose is an interesting molecule that exists in three different isomeric forms. Two of the isomers contain six-member rings; the third isomer features a chain structure. In solution, the three forms rapidly interconvert.

Notice that glucose is a chiral molecule. In the chain structure, four of the carbon atoms are bonded to four different groups.



Home test for glucose.



In nature, glucose occurs in just one of its enantiomeric forms; thus, a solution of glucose rotates polarized light.

Knowing glucose's structure allows one to predict some of its properties. With five polar —OH groups in the molecule, glucose is, not surprisingly, soluble in water.

The aldehyde group is susceptible to chemical oxidation to form a carboxylic acid. Detection of glucose (in urine or blood) takes advantage of this fact; diagnostic tests for glucose involve oxidation with subsequent detection of the products.

Glucose is in a class of sugar molecules called hexoses, molecules having six carbon atoms. 2-Deoxyribose, the sugar in the backbone of the DNA molecule, is a pentose, a molecule with five carbon atoms.



part of the DNA backbone

Glucose and other monosaccharides serve as the building blocks for larger carbohydrates. Sucrose, a disaccharide, is formed from a molecule of glucose and a molecule of fructose, another monosaccharide. Starch is a polymer composed of many monosaccharide units.



The structure of sucrose. Sucrose is formed from  $\alpha$ -D-glucose and fructose. An ether linkage is formed by loss of H<sub>2</sub>O from two —OH groups.

When a carboxylic acid and an alcohol react to form an ester, the OR group of the alcohol ends up as part of the ester (as shown above). This fact is known because of isotope labeling experiments. If the reaction is run using an alcohol in which the alcohol oxygen is <sup>18</sup>O, all of the <sup>18</sup>O ends up in the ester molecule.

Table 10.11 lists a few common esters and the acid and alcohol from which they are formed. The two-part name of an ester is given by (1) the name of the hydrocarbon group from the alcohol and (2) the name of the carboxylate group derived from the acid name by replacing "-ic" with "-ate." For example, ethanol (commonly called ethyl alcohol) and acetic acid combine to give the ester ethyl acetate.

An important reaction of esters is their **hydrolysis** (literally, reaction with water), a reaction that is the reverse of the formation of the ester. The reaction, generally



**Esters.** Many fruits such as bananas and strawberries as well as consumer products (here, perfume and oil of wintergreen) contain esters.

TABLE 10.11 Some Acids, Alcohols, and Their Esters			
Acid	Alcohol	Ester	Odor of Ester
CH₃CO₂H	CH3 CH3CHCH2CH2OH	0 CH <sub>3</sub>      CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CHCH <sub>3</sub>	banana
acetic acid	3-methyl-1-butanol	3-methylbutyl acetate	
$CH_3CH_2CH_2CO_2H$ butanoic acid	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH 1-butanol	0    CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> butyl butanoate	pineapple
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H butanoic acid	benzyl alcohol	$\begin{array}{c} 0\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	rose

■ Saponification Fats and oils are esters of glycerol and long-chain acids. When reacted with a strong base (NaOH or KOH), they produce glycerol and a salt of the long-chain acid. Because this product is used as soap, the reaction is called *saponification*. See A Closer Look: Fats and Oils, page 476. done in the presence of a base such as NaOH, produces the alcohol and a sodium salt of the carboxylic acid:



The carboxylic acid can be recovered if the sodium salt is treated with a strong acid such as HCl:

 $\begin{array}{c} 0 & 0 \\ \parallel \\ CH_3CO^-Na^+(aq) \ + \ HCl(aq) \ \longrightarrow \ CH_3COH(aq) \ + \ NaCl(aq) \\ sodium \ acetate \ acetic \ acid \end{array}$ 

Unlike the acids from which they are derived, esters often have pleasant odors (see Table 10.11). Typical examples are methyl salicylate, or "oil of wintergreen," and benzyl acetate. Methyl salicylate is derived from salicylic acid, the parent compound of aspirin.



Benzyl acetate, the active component of "oil of jasmine," is formed from benzyl alcohol ( $C_6H_5CH_2OH$ ) and acetic acid. The chemicals are inexpensive, so synthetic jasmine is a common fragrance in less-expensive perfumes and toiletries.



oil of jasmine

#### **EXERCISE 10.9** Esters

Draw the structure, and name the ester formed from each of the following reactions:

- (a) propanoic acid and methanol
- (b) butanoic acid and 1-butanol
- (c) hexanoic acid and ethanol

#### **EXERCISE 10.10** Esters

Draw the structure, and name the acid and alcohol from which the following esters are derived:

(a) propyl acetate

- (b) 3-methyl-1-pentyl benzoate
- (c) ethyl salicylate

#### **Amides**

An acid and an alcohol react by loss of water to form an ester. In a similar manner, another class of organic compounds—amides—form when an acid reacts with an amine, again with loss of water.



Amides have an organic group and an amino group  $(-NH_2, -NHR', \text{ or } -NR'R)$  attached to the carbonyl group.

The C atom involved in the amide bond has three bonded groups and no lone pairs around it. We would predict it should be  $sp^2$  hybridized with trigonal-planar geometry and bond angles of approximately  $120^\circ$ —and this is what is found. However, the structure of the amide group offers a surprise. The N atom is also observed to have trigonal-planar geometry with bonds to three attached atoms at  $120^\circ$ . Because the amide nitrogen is surrounded by four pairs of electrons, we would have predicted the N atom would have  $sp^3$  hybridization and bond angles of about  $109^\circ$ .



This portion from methylamine

**An amide,** *N***-methylacetamide.** The *N*-methyl portion of the name derives from the amine portion of the molecule, where the *N* indicates that the methyl group is attached to the nitrogen atom. The "-acet" portion of the name indicates the acid on which the amide is based.

### A Closer Look

Fats and oils are among the many compounds found in plants and animal tissues. In the body, these substances serve several functions, a primary one being the storage of energy.

Fats (solids) and oils (liquids) are triesters formed from glycerol (1,2,3-propanetriol) and three carboxylic acids that can be the same or different.



The carboxylic acids in fats and oils, known as *fatty acids*, have a lengthy carbon chain, usually containing between 12 and 18 carbon atoms. The hydrocarbon chains can be saturated or may include one or more double bonds. The latter are referred to as monounsaturated or polyunsaturated, depending on the number of double bonds. Saturated compounds are more common in animal products, while unsaturated fats and oils are more common in plants.



About 94% of the fatty acids in olive oil are monounsaturated. The major fatty acid is oleic acid.

### **Fats and Oils**

#### **Common Fatty Acids**

common racty relas				
Name	Number of C Atoms	Formula		
Saturated Acids				
lauric	C <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> H		
myristic	C <sub>14</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CO <sub>2</sub> H		
palmitic	C <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CO <sub>2</sub> H		
stearic	C <sub>18</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CO <sub>2</sub> H		
Unsaturated Acid				
oleic	C <sub>18</sub>	$CH_3(CH_2)_7CH = CH(CH_2)_7CO_2H$		

In general, fats containing saturated fatty acids are solids, and those containing unsaturated fatty acids are liquids at room temperature. The difference in melting point relates to the molecular structure. With only single bonds linking carbon atoms in saturated fatty acids, the hydrocarbon group is flexible, allowing the molecules to pack more closely together. The double bonds in unsaturated fats introduce kinks that make the hydrocarbon group less flexible; consequently, the molecules pack less tightly together.

Food companies often hydrogenate vegetable oils to reduce unsaturation. The chemical rationale is that double bonds are reactive and unsaturated compounds are more susceptible to oxidation, which results in unpleasant odors. There are also aesthetic reasons for this practice. Food processors often want solid fats to improve the quality and appearance of the food. If liquid vegetable oil is used in a cake icing, for example, the icing may slide off the cake.



**Polar bear fat.** Polar bears feed primarily on seal blubber and build up a huge fat reserve during winter. During summer, they maintain normal activity but eat nothing, relying entirely on body fat for sustenance. A polar bear will burn about 1 to 1.5 kg of fat per day.

The conditions under which hydrogenation occurs can also lead to the isomerization of an unsaturated fat to the *trans* configuration. Such "trans-fats" in the diet have been linked to coronary heart disease.

Like other esters, fats and oils can undergo hydrolysis. This process is catalyzed by enzymes in the body. In industry, hydrolysis is carried out using aqueous NaOH or KOH to produce a mixture of glycerol and the sodium salts of the fatty acids. This reaction is called *saponification*, a term meaning "soap making."



Simple soaps are sodium salts of fatty acids. The anion in these compounds has an ionic end (the carboxylate group) and a nonpolar end (the large hydrocarbon tail). The ionic end allows these molecules to interact with water, and the nonpolar end enables them to mix with oily and greasy substances to form an emulsion that can be washed away with water. Based on the observed geometry of the amide N atom, the atom is assigned  $sp^2$  hybridization. To explain the observed angle and to rationalize  $sp^2$  hybridization, we can introduce a second resonance form of the amide.



Form B contains a C=N double bond, and the O and N atoms have negative and positive charges, respectively. The N atom can be assigned  $sp^2$  hybridization, and the  $\pi$  bond in B arises from overlap of p orbitals on C and N.

The existence of a second resonance structure for an amide link explains why the carbon-nitrogen bond is relatively short, about 132 pm, a value between that of a C—N single bond (149 pm) and a C=N double bond (127 pm). In addition, restricted rotation occurs around the C=N bond, making it possible for isomeric species to exist if the two groups bonded to N are different.

The amide grouping is particularly important in some synthetic polymers (Section 10.5) and in proteins (pages 496–513), where it is referred to as a *peptide* link. The compound *N*-acetyl-*p*-aminophenol, an analgesic known by the generic name acetaminophen and sold under the brand names Tylenol, Datril, and Momentum, among others, is another amide. Use of this compound as an analgesic was apparently discovered by accident when a common organic compound called acetanilide (like acetaminophen but without the —OH group) was mistakenly put into a prescription for a patient. Acetanilide acts as an analgesic, but it can be toxic. An —OH group *para* to the amide group makes the compound nontoxic, an interesting example of how a seemingly small structural difference affects chemical function.

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Sign in at www.thomsonedu.com/login and go to Chapter 10 Contents to see Screen 10.5 for a description of the types of organic functional groups and for tutorials on their structures, bonding, and chemistry.

#### **EXAMPLE 10.7 Functional Group Chemistry**

#### Problem

(a) Name the product of the reaction between ethylene and HCl.

(b) Draw the structure of the product of the reaction between propanoic acid and 1-propanol. What is the systematic name of the reaction product, and what functional group does it contain?

(c) What is the result of reacting 2-butanol with an oxidizing agent? Give the name, and draw the structure of the reaction product.

**Strategy** Ethylene is an alkene (page 453); propanoic acid is a carboxylic acid (page 471); and 2-butanol is an alcohol (page 462). Consult the discussion regarding their chemistry.

#### Solution

(a) HCl will add to the double bond of ethylene to produce chloroethane.



H = H = H H = C = C = 0  $H_3C = C = H$  H = H H = H H = H H = H H = H H = H H = H

Acetaminophen, *N*-acetyl-*p*-aminophenol. This analgesic is an amide. It is used in over-the-counter painkillers such as Tylenol.

Amides, Peptides, and Proteins When amino acids combine, they form amide or peptide links. Polymers of amino acids are proteins. For more on amino acids and proteins, see *The Chemistry of Life: Biochemistry*, pages 496–513. (b) Carboxylic acids such as propanoic acid react with alcohols to give esters.



(c) 2-Butanol is a secondary alcohol. Such alcohols are oxidized to ketones.



#### **EXERCISE 10.11** Functional Groups

(a) Name each of the following compounds and its functional group.

(b) Name the product from the reaction of compounds 1 and 2.

(c) What is the name and structure of the product from the oxidation of 1?

(d) What compound could result from combining compounds 2 and 3?

(e) What is the result of adding an acid (say HCl) to compound 3?

### **10.5** Polymers

We now turn to the very large molecules known as polymers. These can be either synthetic materials or naturally occurring substances such as proteins or nucleic acids. Although these materials have widely varying compositions, their structures and properties are understandable, based on the principles developed for small molecules.

#### **Classifying Polymers**

The word *polymer* means "many parts" (from the Greek, *poly* and *meros*). **Polymers** are giant molecules made by chemically joining many small molecules called **mono-mers.** Polymer molar masses range from thousands to millions.

Extensive use of synthetic polymers is a fairly recent development. A few synthetic polymers (Bakelite, rayon, and celluloid) were made early in the 20th century, but most of the products with which you are familiar originated in the last 50 years. By 1976, synthetic polymers outstripped steel as the most widely used materials in the United States. The average production of synthetic polymers in the United States is approximately 150 kg per person annually.

The polymer industry classifies polymers in several different ways. One is their response to heating. **Thermoplastics** (such as polyethylene) soften and flow when they are heated and harden when they are cooled. **Thermosetting plastics** (such as Formica) are initially soft but set to a solid when heated and cannot be resoftened. Another classification scheme depends on the end use of the polymer—for example, plastics, fibers, elastomers, coatings, and adhesives.

**Biochemical Polymers** Polymer chemistry extends to biochemistry, where chemists study proteins and other large molecules. See *The Chemistry of Life: Biochemistry*, pages 496–513.

### **Case Study**

Biodiesel, promoted as an alternative to petroleum-based fuels used in diesel engines, is made from plant and animal oils. In the past 7 years, there has been a spectacular increase in its production and use, from under 1 million gallons in 1999 to 75 million gallons in 2005. But what is biodiesel?



Biodiesel, a mixture of long-chain esters of fatty acids.

Chemically, biodiesel is a mixture of esters of long-chain fatty acids. It is prepared from plant and animal fats and oils by *trans-esterification*. This is a reaction between an ester and an alcohol in which the -0R'' on the alcohol exchanges with the 0R' group of the ester:

$$RCO_2R' + R''OH \rightarrow RCO_2R'' + R'OH$$

Recall that fats and oils are esters (page 476), derivatives of glycerol and high-molar-mass organic acids (fatty acids). Their reaction with methanol (in the presence of a catalyst to speed up the reaction) produces a mixture of the methyl esters of long chain fatty acids and glycerol.



Glycerol, a by-product of the reaction, is a valuable commodity for the health care products industry, so it is separated and sold. The mixture of esters that remains can be used directly as a fuel in existing diesel engines, or it can be blended with petroleum products. In the latter case, the fuel mixture is identified by a designation such as B20 (B = biodiesel, 20 refers to 20% by volume.) The fuel has the advantage of being clean burning with fewer environmental problems associated with exhaust gases. In particular, there are no SO<sub>2</sub> emissions, one of the common problems associated with petroleum-based diesel fuels.

Proponents of the use of biodiesel note that biodiesel is produced from renewable resources, in contrast to petroleum. Critics point out, however, that growing crops for this purpose brings two problems. The first is that if crops are grown for biodiesel production, this has a negative effect on food supply. The case for biodiesel would be improved significantly, however, if it were possible to convert agricultural waste (corn stalks, for example) into a biofuel. Scientists are now actively trying to do this.

It is also pointed out that it would be impossible to grow enough crops to supply the raw materials to replace all petroleum-based diesel fuel—there isn't enough land available. Economics is also in the picture: Biodiesel is currently more expensive to produce; it is presently competitive only due to government subsidies.

Trans-esterification might seem like another kind of reaction, but it is actually closely related to chemistry we have already seen, the hydrolysis of an ester.

Ester hydrolysis:

$$\begin{array}{c} 0 \\ R - C - C - R' + H - 0 - H \longrightarrow R - C - 0 - H + R'0H \end{array}$$

Trans-esterification:

$$\begin{array}{c} 0 \\ \parallel \\ R - C - 0 - R' + H - 0 - R'' \longrightarrow R - C - 0 - R'' + R'0H \end{array}$$

In both reactions, the OR' group on the ester combines with hydrogen of second reagent (water or alcohol) as shown. In drawing this analogy, it is useful to recognize that there are other similarities in the chemistry of alcohols and water. For example, both can be protonated with strong acids (giving  $H_3O^+$  and  $ROH_2^+$ ) and deprotonated by strong bases (giving  $OH^-$  and  $OR^-$ ).

#### **Questions:**

- Write a balanced chemical equation for the reaction that occurs when methyl myristate, C<sub>13</sub>H<sub>27</sub>CO<sub>2</sub>CH<sub>3</sub>(ℓ), is burned, forming CO<sub>2</sub>(g) and H<sub>2</sub>O(g).
- 2. Using enthalpy of formation data, calculate the standard enthalpy change per mole in the oxidation of methyl myristate  $(\Delta_f H^\circ = -771.0 \text{ kJ/mol}).$
- **3.** Which compound, methyl myristate  $(C_{15}H_{30}O_2)$  or hexadecane  $(C_{16}H_{34}, \text{ one of many hydrocarbons in petroleum based diesel fuel) is predicted to provide the greater energy per mole? Per liter? <math>(\Delta_f H^\circ \text{ for } C_{16}H_{34} = -456.1 \text{ kJ/mol}) [d(methyl myristate) = 0.86 g/mL, and <math>d(C_{16}H_{34}) = 0.77 g/mL]$

Answers to these questions are in Appendix Q.







FIGURE 10.12 Common polymer-based consumer products. (a) Packaging materials from high-density polyethylene; (b) from polystyrene; and (c) from polyvinyl chloride. Recycling information is provided on most plastics (often molded into the bottom of bottles). High-density polyethylene is designated with a "2" inside a triangular symbol and the letters "HDPE." PVC is designated with a "3" inside a triangular symbol with the letter "V" below.

A more chemically oriented approach to polymer classification is based on the method of synthesis. Addition polymers are made by directly adding monomer units together. Condensation polymers are made by combining monomer units and splitting out a small molecule, often water.

### **Addition Polymers**

Polyethylene, polystyrene, and polyvinyl chloride (PVC) are common addition polymers (Figure 10.12). They are built by "adding together" simple alkenes such as ethylene (CH<sub>2</sub>=CH<sub>2</sub>), styrene (C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>), and vinyl chloride (CH<sub>2</sub>=CHCl). These and other addition polymers (Table 10.12), all derived from alkenes, have widely varying properties and uses.

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Sign in at www.thomsonedu.com/login and go to Chapter 10 Contents to see Screen 10.9 for an animation of addition polymerization.

### **Polyethylene and Other Polyolefins**

Polyethylene is by far the leader in terms of addition polymer production. Ethylene  $(C_{9}H_{4})$ , the monomer from which polyethylene is made, is a product of petroleum refining and one of the top five chemicals produced in the United States. When ethylene is heated to between 100 and 250 °C at a pressure of 1000 to 3000 atm in the presence of a catalyst, polymers with molar masses up to several million are formed. The reaction can be expressed as a balanced chemical equation:

$$n \operatorname{H}_{2} \operatorname{C} = \operatorname{C} \operatorname{H}_{2} \longrightarrow \begin{pmatrix} \operatorname{H} & \operatorname{H} \\ - & - \\ \operatorname{C} & - \\ - & - \\ \operatorname{H} & \operatorname{H} \end{pmatrix}_{n}$$
ethylene polyethylene

	Monomer			U.S. Polymer
Formula	Common	Polymer Name		Production
	Ndille	(Indue Names)	Uses	(Metric tons/year)"
	ethylene	polyethylene (polythene)	squeeze bottles, bags, films, toys and molded objects, electric	7 million
Н			insulation	
H C=C CH <sub>3</sub>	propylene	polypropylene (Vectra, Herculon)	bottles, films, indoor- outdoor carpets	1.2 million
Н				
H C = C	vinyl chloride	polyvinyl chloride (PVC)	floor tile, raincoats, pipe	1.6 million
H C=C H	acrylonitrile	polyacrylonitrile	rugs, fabrics	0.5 million
H CN		(Orlan, Acrilan)		
H H C=C	styrene	polystyrene (Styrofoam, Styron)	food and drink coolers, building material insulation	0.9 million
$H C = C H O - C - CH_3$	vinyl acetate	polyvinyl acetate (PVA)	latex paint, adhesives, textile coatings	200,000
H = C = C = C = C = C = C = C = C = C =	methyl methacrylate	polymethyl methacrylate (Plexiglass, Lucite)	high-quality transparent objects, latex paints, contact lenses	200,000
	tetrafluoroethylene	polytetrafluoroethylene (Teflon)	gaskets, insulation, bearings, pan coatings	6,000
• One metric ton = $1000 \text{ kg}$ .				

#### TABLE 10.12 Ethylene Derivatives That Undergo Addition Polymerization

The abbreviated formula of the reaction product,  $(-CH_2CH_2-)_n$ , shows that polyethylene is a chain of carbon atoms, each bearing two hydrogens. The chain length for polyethylene can be very long. A polymer with a molar mass of 1 million would contain almost 36,000 ethylene molecules linked together.

Polyethylene formed under various pressures and catalytic conditions has different properties, as a result of different molecular structures. For example, when chromium oxide is used as a catalyst, the product is almost exclusively a linear chain (Figure 10.13a). If ethylene is heated to 230 °C at high pressure, however, irregular branching occurs. Still other conditions lead to cross-linked polyethylene, in which different chains are linked together (Figures 10.13b and c).

The high-molar-mass chains of linear polyethylene pack closely together and result in a material with a density of  $0.97 \text{ g/cm}^3$ . This material, referred to as



FIGURE 10.13 Polyethylene. (a) The linear form, high-density polyethylene (HDPE). (b) Branched chains occur in low-density polyethylene (LDPE). (c) Cross-linked polyethylene (CLPE).

high-density polyethylene (HDPE), is hard and tough, which makes it suitable for items such as milk bottles. If the polyethylene chain contains branches, however, the chains cannot pack as closely together, and a lower-density material (0.92 g/ cm<sup>3</sup>) known as low-density polyethylene (LDPE) results. This material is softer and more flexible than HDPE. It is used in plastic wrap and sandwich bags, among other things. Linking up the polymer chains in cross-linked polyethylene (CLPE) causes the material to be even more rigid and inflexible. Plastic bottle caps are often made of CLPE.

Polymers formed from substituted ethylenes (CH<sub>2</sub>=CHX) have a range of properties and uses (see Table 10.12). Sometimes, the properties are predictable based on the molecule's structure. Polymers without polar substituent groups, such as polystyrene, often dissolve in organic solvents, a property useful for some types of fabrication (Figure 10.14).

#### Polymers based on substituted ethylenes, H<sub>2</sub>C=CHX



Polyvinyl alcohol is a polymer with little affinity for nonpolar solvents but an affinity for water, which is not surprising, based on the large number of polar OH groups (Figure 10.15). Vinyl alcohol itself is not a stable compound (it isomerizes to acetaldehyde  $CH_3CHO$ ), so polyvinyl alcohol cannot be made from this compound. Instead, it is made by hydrolyzing the ester groups in polyvinyl acetate.

$$\begin{array}{c} \begin{pmatrix} H & H \\ I & I \\ - & C \\ - & C \\ - & I \\ H \\ 0 \\ - & 0 \\ - & n \\ - & n \\ - & n \\ - & 0 \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - & - \\ - &$$

Solubility in water or organic solvents can be a liability for polymers. The many uses of polytetrafluoroethylene [Teflon,  $(-CF_2CF_2)_n$ ] stem from the fact that it does not interact with water or organic solvents.

Polystyrene, with n = 5700, is a clear, hard, colorless solid that can be molded easily at 250 °C. You are probably more familiar with the very light, foam-like mate-

Christopher Springmann/Corbisstockmarket.com



Polyethylene film. The polymer film is produced by extruding the molten plastic through a ring-like gap and inflating the film like a balloon.



**FIGURE 10.14** Polystyrene. (a) The polymer is a clear, hard, colorless solid, but it may be more familiar as a light, foam-like material called Styrofoam. (b) Styrofoam has no polar groups and thus dissolves well in organic solvents such as acetone. See also Figure 10.12b.

rial known as Styrofoam that is used widely for food and beverage containers and for home insulation (Figure 10.14). Styrofoam is produced by a process called "expansion molding." Polystyrene beads containing 4% to 7% of a low-boiling liquid like pentane are placed in a mold and heated with steam or hot air. Heat causes the solvent to vaporize, creating a foam in the molten polymer that expands to fill the shape of the mold.

#### Natural and Synthetic Rubber

Natural rubber was first introduced in Europe in 1740, but it remained a curiosity until 1823, when Charles Macintosh invented a way of using it to waterproof cotton cloth. The mackintosh, as rain coats are still sometimes called, became popular despite major problems: Natural rubber is notably weak and is soft and tacky when warm but brittle at low temperatures. In 1839, after 5 years of research on natural rubber, the American inventor Charles Goodyear (1800–1860) discovered that heating gum rubber with sulfur produces a material that is elastic, water-repellent, resilient, and no longer sticky.

Rubber is a naturally occurring polymer, the monomers of which are molecules of 2-methyl-1,3-butadiene, commonly called *isoprene*. In natural rubber, isoprene monomers are linked together through carbon atoms 1 and 4—that is, through the end carbon atoms of the  $C_4$  chain (Figure 10.16). This leaves a double bond between carbon atoms 2 and 3. In natural rubber, these double bonds have a *cis* configuration.

In vulcanized rubber, the material that Goodyear discovered, the polymer chains of natural rubber are cross-linked by short chains of sulfur atoms. Cross-linking helps to align the polymer chains, so the material does not undergo a permanent change when stretched and it springs back when the stress is removed. Substances that behave this way are called **elastomers**.

With a knowledge of the composition and structure of natural rubber, chemists began searching for ways to make synthetic rubber. When they first tried to make the polymer by linking isoprene monomers together, however, what they made was sticky and useless. The problem was that synthesis procedures gave a mixture of *cis* and *trans* polyisoprene. In 1955, however, chemists at the Goodyear and Firestone companies discovered special catalysts to prepare the all-*cis* polymer. This synthetic material, which was structurally identical to natural rubber, is now manufactured cheaply. In fact, more than  $8.0 \times 10^8$  kg of synthetic polyisoprene is produced annually in the United States.



**FIGURE 10.15** Slime. When boric acid,  $B(OH)_3$ , is added to an aqueous suspension of polyvinyl alcohol,  $(CH_2CHOH)_n$ , the mixture becomes very viscous because boric acid reacts with the —OH groups on the polymer chain, causing cross-linking to occur. (The model shows an idealized structure of a portion of the polymer.)





**FIGURE 10.16** Natural rubber. The sap that comes from the rubber tree is a natural polymer of isoprene. All the linkages in the carbon chain are *cis*. When natural rubber is heated strongly in the absence of air, it smells of isoprene. This observation provided a clue that rubber is composed of this building block.

Other kinds of polymers have further expanded the repertoire of elastomeric materials now available. Polybutadiene, for example, is currently used in the production of tires, hoses, and belts. Some elastomers, called **copolymers**, are formed by polymerization of two (or more) different monomers. A copolymer of styrene and butadiene, made with a 1:3 ratio of these raw materials, is the most important synthetic rubber now made; more than about 1 billion kg of styrene-butadiene rubber (SBR) is produced each year in the United States for making tires.



And a little is left over each year to make bubble gum. The stretchiness of bubble gum once came from natural rubber, but SBR is now used to help you blow bubbles.

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Sign in at www.thomsonedu.com/login and go to Chapter 10 Contents to see Screen 10.11 for a self-study module on the polymer used in bubble gum.

### **Condensation Polymers**

A chemical reaction in which two molecules react by splitting out, or eliminating, a small molecule is called a **condensation reaction**. The reaction of an alcohol with a carboxylic acid to give an ester is an example of a condensation reaction. One way to form a condensation polymer uses *two* different reactant molecules, each containing *two* functional groups. Another route uses a single molecule with two different functional groups. Commercial polyesters are made using both types of reactions.

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#### Polyesters

Terephthalic acid contains two carboxylic acid groups, and ethylene glycol contains two alcohol groups. When mixed, the acid and alcohol functional groups at both ends of these molecules can react to form ester linkages, splitting out water. The



Copolymer of styrene and butadiene, SBR rubber. The elasticity of bubble gum comes from SBR rubber.

result is a polymer called polyethylene terephthalate (PET). The multiple ester linkages make this substance a **polyester.** 



Polyester textile fibers made from PET are marketed as Dacron and Terylene. The inert, nontoxic, noninflammatory, and non-blood-clotting properties of Dacron polymers make Dacron tubing an excellent substitute for human blood vessels in heart bypass operations, and Dacron sheets are sometimes used as temporary skin for burn victims. A polyester film, Mylar, has unusual strength and can be rolled into sheets one-thirtieth the thickness of a human hair. Magnetically coated Mylar films are used to make audio and video tapes (Figure 10.17).

There is considerable interest in another polyester, polylactic acid (PLA). Lactic acid contains both carboxylic acid and alcohol functional groups, so condensation between molecules of this monomer gives a polymer.

$$n \operatorname{HO} - \underset{\operatorname{CH}_{3}}{\overset{\operatorname{H}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\overset{\operatorname{O}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{\operatorname{CH}_{3}}{\underset{CH}_{3}}{\underset{CH}_{3}}{\underset{CH}_{3}}{\underset{CH}_{3}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{1}}{\underset{CH}_{$$

There is interest in polylactic acid for two reasons. First, the monomer used to make this polymer is obtained by biological fermentation of plant materials. (Most of the chemicals used in the manufacture of other types of polymers are derived from petroleum, and there is increased concern about the availability and cost of raw materials in the future.) Second, this polymer, which is currently being used in packaging material, is biodegradable, which has the potential to alleviate land-fill disposal problems.

#### **Polyamides**

In 1928, the DuPont Company embarked on a basic research program headed by Wallace Carothers (1896–1937). Carothers was interested in high–molar-mass compounds, such as rubbers, proteins, and resins. In 1935, his research yielded



**FIGURE 10.17 Polyesters.** Polyethylene terephthalate is used to make clothing and soda bottles. The two students are wearing jackets made from recycled PET soda bottles. Mylar film, another polyester, is used to make recording tape as well as balloons. Because the film has very tiny pores, Mylar can be used for helium-filled balloons; the atoms of gaseous helium move through the pores in the film very slowly.



Active Figure 10.18 Nylon-

**6,6.** Hexamethylenediamine is dissolved in water (bottom layer), and adipoyl chloride (a derivative of adipic acid) is dissolved in hexane (top layer). The two compounds react at the interface between the layers to form nylon, which is being wound onto a stirring rod.

**Chemistry**, , Now<sup>™</sup> Sign in at www. thomsonedu.com/login and go to the Chapter Contents menu to explore an interactive version of this figure accompanied by an exercise. nylon-6,6 (Figure 10.18), a **polyamide** prepared from adipoyl chloride, a derivative of adipic acid, a diacid, and hexamethylenediamine, a diamine:



Nylon can be extruded easily into fibers that are stronger than natural fibers and chemically more inert. The discovery of nylon jolted the American textile industry at a critical time. Natural fibers were not meeting 20th-century needs. Silk was expensive and not durable; wool was scratchy; linen crushed easily; and cotton did not have a high-fashion image. Perhaps the most identifiable use for the new fiber was in nylon stockings. The first public sale of nylon hosiery took place on October 24, 1939, in Wilmington, Delaware (the site of DuPont's main office). This use of nylon in commercial products ended shortly thereafter, however, with the start of World War II. All nylon was diverted to making parachutes and other military gear. It was not until about 1952 that nylon reappeared in the consumer marketplace.

Figure 10.19 illustrates why nylon makes such a good fiber. To have good tensile strength (the ability to resist tearing), the polymer chains should be able to attract one another, albeit not so strongly that the plastic cannot be initially extended to form fibers. Ordinary covalent bonds between the chains (cross-linking) would be too strong. Instead, cross-linking occurs by a somewhat weaker intermolecular force called *hydrogen bonding* ( $\blacktriangleright$  Section 12.2) between the hydrogens of N—H groups on one chain and the carbonyl oxygens on another chain. The polarities of the N<sup> $\delta-$ </sup>—H<sup> $\delta+</sup></sup> group and the C<sup><math>\delta+$ </sup>=O<sup> $\delta-$ </sup> group lead to attractive forces between the polymer chains of the desired magnitude.</sup>

#### **EXAMPLE 10.8 Condensation Polymers**

**Problem** What is the repeating unit of the condensation polymer obtained by combining  $HO_2CCH_2CH_2CO_2H$  (succinic acid) and  $H_2NCH_2CH_2NH_2$  (1,2-ethylenediamine)?

**Strategy** Recognize that the polymer will link the two monomer units through the amide linkage. The smallest repeating unit of the chain will contain two parts, one from the diacid and the other from the diamine.

Solution The repeating unit of this polyamide is





#### FIGURE 10.19 Hydrogen bonding

**between polyamide chains.** Carbonyl oxygen atoms with a partial negative charge on one chain interact with an amine hydrogen with a partial positive charge on a neighboring chain. (This form of bonding is described in more detail in Section 12.3.)

#### **EXERCISE 10.12** Kevlar, a Condensation Polymer

A polymer that is now well known because of its use to construct sports equipment and bulletproof vests is Kevlar. This polymer has the formula shown below. Is this a condensation polymer or an addition polymer? What chemicals would be used to make this polymer? Write a balanced equation for the formation of Kevlar.



### **Chemical Perspectives**

Disposable diapers are a miracle of modern chemistry: Most of the materials used are synthetic polymers. The outer layer is mostly microporous polyethylene; it keeps the urine in but remains breathable. The inside layer is polypropylene, a material prized by wintercamping enthusiasts. It stays soft and dry while wicking moisture away from the skin. Sandwiched between these layers is powdered sodium polyacrylate combined with cellulose;

$$\begin{pmatrix}
H & H \\
-C & -C \\
H & C & -O^{-}Na^{+} \\
0 \\
\end{bmatrix}$$

.. ..

the latter is the only natural part of the materials used. The package is completed with elasticized hydrophobic polypropylene cuffs around the baby's thighs, and Velcro tabs hold the diaper on the baby.



#### **Super Diapers**

The key ingredient in the diaper is the polyacrylate polymer filling. This substance can absorb up to 800 times its weight in water. When dry, the polymer has a carboxylate group associated with sodium ions. When placed in water, osmotic pressure causes water molecules to enter the polymer (because the ion concentration in the polymer is higher than in water; see Chapter 14). As water enters, the sodium ions dissociate from the polymer, and the polar water molecules are attracted to these positive ions and to the negative carboxylate groups of the polymer. At the same time, the negative carboxylate groups repel one another, forcing them apart and causing the polymer to unwind. Evidence for the unwinding of the polymer is seen as swelling of the diaper. In addition, because it contains so much water, the polymer becomes gel-like.

If the gelled polymer is put into a salt solution, water is attracted to the  $Na^+$  and  $Cl^-$  ions and is drawn from the polymer. Thus, the polymer becomes solid once again. The diminished ability of sodium polyacrylate to absorb water in a salt solution is the reason that disposable diapers do not absorb urine as well as pure water.

These kinds of superabsorbent materials sodium polyacrylate and a related material, polyacrylamide—are useful not only in diapers but also for cleaning up spills in hospitals, for protecting power and optical cables from moisture, for filtering water out of aviation gasoline, and for conditioning garden soil to retain water. You will also find them in the toy store as "gro-creatures."



### **Chapter Goals Revisited**

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- Check your readiness for an exam by taking the Pre-Test and exploring the modules recommended in your Personalized Study plan.
- Access **How Do I Solve It?** tutorials on how to approach problem solving using concepts in this chapter.

Now that you have studied this chapter, you should ask whether you have met the chapter goals. In particular, you should be able to:

### Classify organic compounds based on formula and structure

a. Understand the factors that contribute to the large numbers of organic compounds and the wide array of structures (Section 10.1). Study Question(s) assignable in OWL: 3.

## Recognize and draw structures of structural isomers and stereoisomers for carbon compounds

**a.** Recognize and draw structures of geometric isomers and optical isomers (Section 10.1). Study Question(s) assignable in OWL: 11, 12, 15, 58.

### Name and draw structures of common organic compounds

- **a.** Draw structural formulas, and name simple hydrocarbons, including alkanes, alkenes, alkynes, and aromatic compounds (Section 10.2). Study Question(s) assignable in OWL: 1, 5, 7, 28, 67, 69, 70, 96; Go Chemistry Module 15.
- **b.** Identify possible isomers for a given formula (Section 10.2).
- **c.** Name and draw structures of alcohols and amines (Section 10.3). **Study Question(s)** assignable in OWL: 31, 32, 34.
- d. Name and draw structures of carbonyl compounds—aldehydes, ketones, acids, esters, and amides (Section 10.4). Study Question(s) assignable in OWL: 38, 39, 40, 41, 43, 51.

### Know the common reactions of organic functional groups

This goal applies specifically to the reactions of alkenes, alcohols, amines, aldehydes and ketones, and carboxylic acids. Study Question(s) assignable in OWL: 19, 21, 24, 46, 64, 76, 79, 81, 83–85, 90–92, 97.

### Relate properties to molecular structure

- **a.** Describe the physical and chemical properties of the various classes of hydrocarbon compounds (Section 10.2).
- **b.** Recognize the connection between the structures and the properties of alcohols (Section 10.3).
- **c.** Know the structures and properties of several natural products, including carbohydrates (Section 10.4) and fats and oils (Section 10.4). **Study Question(s)** assignable in OWL: 49, 50.

### Identify common polymers

- **a.** Write equations for the formation of addition polymers and condensation polymers, and describe their structures (Section 10.5).
- **b.** Relate properties of polymers to their structures (Section 10.5). Study Question(s) assignable in OWL: 95.

### **STUDY QUESTIONS**

Online homework for this chapter may be assigned in OWL.

- ▲ denotes challenging questions.
- denotes questions assignable in OWL.

Blue-numbered questions have answers in Appendix 0 and fully-worked solutions in the *Student Solutions Manual*.

### **Practicing Skills**

#### Alkanes and Cycloalkanes

(See Examples 10.1 and 10.2 and ChemistryNow Screen 10.3.)

- 1. What is the name of the straight (unbranched) chain alkane with the formula C<sub>7</sub>H<sub>16</sub>?
- **2.** What is the molecular formula for an alkane with 12 carbon atoms?

3. ■ Which of the following is an alkane? Which could be a cycloalkane?

(a) $C_2H_4$	(c) $C_{14}H_{30}$
(b) C <sub>5</sub> H <sub>10</sub>	(d) C <sub>7</sub> H <sub>8</sub>

- 4. Isooctane, 2,2,4-trimethylpentane, is one of the possible structural isomers with the formula C<sub>8</sub>H<sub>18</sub>. Draw the structure of this isomer, and draw and name structures of two other isomers of C<sub>8</sub>H<sub>18</sub> in which the longest carbon chain is five atoms.
- **5.** Give the systematic name for the following alkane:



6. Give the systematic name for the following alkane. Draw a structural isomer of the compound, and give its name.



- 7. Draw the structure of each of the following compounds:
  - (a) 2,3-dimethylhexane
  - (b) 2,3-dimethyloctane
  - (c) 3-ethylheptane
  - (d) 3-ethyl-2-methylhexane
- 8. Draw structures for 3-ethylpentane and 2,3-dimethylpentane.
- 9. Draw Lewis structures, and name all possible compounds that have a seven-carbon chain with one methyl substituent group. Which of these isomers has a chiral carbon center?
- 10. Draw a structure for cycloheptane. Is the seven-member ring planar? Explain your answer.
- **11.** There are two ethylheptanes (compounds with a seven-carbon chain and one ethyl substituent). Draw the structures, and name these compounds. Is either isomer chiral?
- 12. Among the 18 structural isomers with the formula  $C_8H_{18}$  are two with a five-carbon chain having one ethyl and one methyl substituent group. Draw their structures, and name these two isomers.
- 13. List several typical physical properties of C<sub>4</sub>H<sub>10</sub>. Predict the following physical properties of dodecane,  $C_{12}H_{26}$ : color, state (s,  $\ell$ , g), solubility in water, solubility in a nonpolar solvent.

- 14. Write balanced equations for the following reactions of alkanes.
  - (a) The reaction of methane with excess chlorine.
  - (b) Complete combustion of cyclohexane, C<sub>6</sub>H<sub>12</sub>, with excess oxygen.

#### Alkenes and Alkynes

(See Examples 10.3 and 10.4 and ChemistryNow Screens 10.3 and 10.4.)

- 15. Draw structures for the *cis* and *trans* isomers of 4-methyl-2-hexene.
- **16.** What structural requirement is necessary for an alkene to have cis and trans isomers? Can cis and trans isomers exist for an alkane? For an alkyne?
- 17. A hydrocarbon with the formula  $C_5H_{10}$  can be either an alkene or a cycloalkane.
  - (a) Draw a structure for each of the isomers possible for C<sub>5</sub>H<sub>10</sub>, assuming it is an alkene. Six isomers are possible. Give the systematic name of each isomer vou have drawn.
  - (b) Draw a structure for a cycloalkane having the formula C<sub>5</sub>H<sub>10</sub>.
- 18. Five alkenes have the formula  $C_7H_{14}$  and a sevencarbon chain. Draw their structures, and name them.
- **19.** Draw the structure, and give the systematic name for the products of the following reactions:
  - (a)  $CH_3CH = CH_2 + Br_2 \rightarrow$

(

- (b)  $CH_3CH_2CH = CHCH_3 + H_2 \rightarrow$
- **20.** Draw the structure, and give the systematic name for the products of the following reactions:

$$\begin{array}{c} H_{3}C \\ C = C \\ H_{3}C \\ H_{3}C$$

- 21. The compound 2-bromobutane is a product of addition of HBr to an alkene. Identify the alkene and give its name.
- 22. The compound 2,3-dibromo-2-methylhexane is formed by addition of  $Br_2$  to an alkene. Identify the alkene, and write an equation for this reaction.
- 23. Draw structures for alkenes that have the formula C<sub>3</sub>H<sub>5</sub>Cl, and name each compound. (These are derivatives of propene in which a chlorine atom replaces one hydrogen atom.)
- **24.** Elemental analysis of a colorless liquid has given its formula as  $C_5H_{10}$ . You recognize that this could be either a cycloalkane or an alkene. A chemical test to determine the class to which this compound belongs involves adding bromine. Explain how this would allow you to distinguish between the two classes.

#### **Aromatic Compounds**

(See Example 10.5, Exercise 10.5, and ChemistryNow Screen 10.3.)

- 25. Draw structural formulas for the following compounds:
  - (a) 1,3-dichlorobenzene (alternatively called *m*-dichlorobenzene)
  - (b) 1-bromo-4-methylbenzene (alternatively called *p*-bromotoluene)
- **26.** Give the systematic name for each of the following compounds:



- **27.** Write an equation for the preparation of ethylbenzene from benzene and an appropriate compound containing an ethyl group.
- **28.** Write an equation for the preparation of hexylbenzene from benzene and other appropriate reagents.
- **29.** A single compound is formed by alkylation of 1,4-dimethylbenzene. Write the equation for the reaction of this compound with CH<sub>3</sub>Cl and AlCl<sub>3</sub>. What is the structure and name of the product?
- **30.** Nitration of toluene gives a mixture of two products, one with the nitro group (-NO<sub>2</sub>) in the *ortho* position and one with the nitro group in the *para* position. Draw structures of the two products.

#### Alcohols, Ethers, and Amines

(See Example 10.6 and ChemistryNow Screen 10.5.)

- 31. Give the systematic name for each of the following alcohols, and tell if each is a primary, secondary, or tertiary alcohol:
  - (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH
  - (b)  $CH_3CH_2CH_2CH_2OH$ (c)  $CH_3$  (d)  $CH_3$   $H_3C-C-OH$   $H_3C-C-CH_2CH_3$  $CH_3$  OH
- **32.** Draw structural formulas for the following alcohols, and tell if each is primary, secondary, or tertiary:
  - (a) 1-butanol
  - (b) 2-butanol
  - (c) 3,3-dimethyl-2-butanol
  - (d) 3,3-dimethyl-1-butanol
- **33.** Write the formula, and draw the structure for each of the following amines:
  - (a) ethylamine
  - (b) dipropylamine
  - (c) butyldimethylamine
  - (d) triethylamine

- 34. Name the following amines:
   (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>
   (b) (CH<sub>3</sub>)<sub>3</sub>N
   (c) (CH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)NH
  - (d)  $C_6H_{13}NH_2$
- 35. Draw structural formulas for all the alcohols with the formula  $C_4H_{10}O$ . Give the systematic name of each.
- **36.** Draw structural formulas for all primary amines with the formula  $C_4H_9NH_2$ .
- 37. Complete and balance the following equations:
  (a) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>(ℓ) + HCl(aq) →
  (b) (CH<sub>3</sub>)<sub>3</sub>N(aq) + H<sub>2</sub>SO<sub>4</sub>(aq) →
- 38. Aldehydes and carboxylic acids are formed by oxidation of primary alcohols, and ketones are formed when secondary alcohols are oxidized. Give the name and formula for the alcohol that, when oxidized, gives the following products:
  (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO
  - (b) 2-hexanone

#### Compounds with a Carbonyl Group

(See Exercises 10.7–10.10 and ChemistryNow Screen 10.5.)

- 39. Draw structural formulas for (a) 2-pentanone,(b) hexanal, and (c) pentanoic acid.
- 40. Identify the class of each of the following compounds, and give the systematic name for each:
  (a) O

$$CH_{3}CCH_{3}$$
(b) O
$$CH_{3}CH_{2}CH_{2}CH$$
(c) O
$$CH_{3}CCH_{2}CH_{2}CH_{3}CH_{2}CH_{3}CH_{3}CH_{2}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}CH_{3}$$

- **41.** Identify the class of each of the following compounds, and give the systematic name for each:
  - (a)  $CH_3$

CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>CO<sub>2</sub>H

(b) O $\parallel$  $CH_3CH_2COCH_3$ 

$$\begin{array}{ccc} (C) & O \\ & & \\ & \\ & CH_3COCH_2CH_2CH_2CH_2CH_3 \\ (d) & & O \\ \end{array}$$

- **42.** Draw structural formulas for the following acids and esters:
  - (a) 2-methylhexanoic acid
  - (b) pentyl butanoate (which has the odor of apricots)
  - (c) octyl acetate (which has the odor of oranges)

- **43.** Give the structural formula and systematic name for the product, if any, from each of the following reactions:
  - (a) pentanal and KMnO<sub>4</sub>
  - (b) pentanal and LiAlH<sub>4</sub> (c) 2-octanone and  $LiAlH_4$
  - (d) 2-octanone and KMnO<sub>4</sub>
- 44. Describe how to prepare 2-pentanol beginning with the appropriate ketone.
- **45.** Describe how to prepare propyl propanoate beginning with 1-propanol as the only carbon-containing reagent.
- **46.** Give the name and structure of the product of the reaction of benzoic acid and 2-propanol.
- **47.** Draw structural formulas, and give the names for the products of the following reaction:

$$O \\ \parallel \\ CH_3COCH_2CH_2CH_2CH_3 + NaOH \\$$

48. Draw structural formulas, and give the names for the products of the following reaction:

$$\underbrace{\bigcirc}_{\substack{\parallel\\ C \leftarrow O \leftarrow CH_{3}}}^{O} \underbrace{\bigcirc}_{\substack{\parallel\\ CH_{3}}}^{CH_{3}} + \text{NaOH} \longrightarrow ?$$

- **49.** The Lewis structure of phenylalanine, one of the 20 amino acids that make up proteins, is drawn below (without lone pairs of electrons). The carbon atoms are numbered for the purpose of this question.
  - (a) What is the geometry of  $C_3$ ?
  - (b) What is the O—C—O bond angle?
  - (c) Is this molecule chiral? If so, which carbon atom is chiral?
  - (d) Which hydrogen atom in this compound is acidic?



50. The Lewis structure of vitamin C, whose chemical name is ascorbic acid, is drawn below (without lone pairs of electrons).



(a) What is the approximate value for the O-C-O bond angle?

- (b) There are four OH groups in this structure. Estimate the C—O—H bond angles for these groups. Will they be the same value (more or less), or should there be significant differences in these bond angles?
- (c) Is the molecule chiral? How many chiral carbon atoms can be identified in this structure?
- (d) Identify the shortest bond in this molecule.
- (e) What are the functional groups of the molecule?

### **Functional Groups**

(See Example 10.7 and ChemistryNow Screen 10.5.)

**51.** ■ Identify the functional groups in the following molecules. (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH (b) Ο H<sub>3</sub>CCNHCH<sub>3</sub> (c) 0 CH<sub>2</sub>CH<sub>2</sub>COH (d) CH<sub>3</sub>CH<sub>9</sub>COCH<sub>3</sub>

52. Consider the following molecules:

1. O  

$$H_3CH_2CCH_3$$
  
2. O  
 $H_3CH_2COH$   
3.  $H_2C=CHCH_2OH$ 

- 4. OH CH<sub>3</sub>CH<sub>9</sub>CHCH<sub>3</sub>
- (a) What is the result of treating compound 1 with NaBH<sub>4</sub>? What is the functional group in the product? Name the product.
- (b) Draw the structure of the reaction product from compounds 2 and 4. What is the functional group in the product?
- (c) What compound results from adding H<sub>2</sub> to compound 3? Name the reaction product.
- (d) What compound results from adding NaOH to compound 2?

#### Polymers

(See Example 10.8, Exercise 10.10, and ChemistryNow Screens 10.9 and 10.10.)

- 53. Polyvinyl acetate is the binder in water-based paints. (a) Write an equation for its formation from vinyl acetate.
  - (b) Show a portion of this polymer with three monomer units.
  - (c) Describe how to make polyvinyl alcohol from polyvinyl acetate.

- 54. Neoprene (polychloroprene, a kind of rubber) is a polymer formed from the chlorinated butadiene H<sub>2</sub>C=CHCCl=CH<sub>2</sub>.
  - (a) Write an equation showing the formation of polychloroprene from the monomer.
  - (b) Show a portion of this polymer with three monomer units.
- **55.** Saran is a copolymer of 1,1-dichloroethene and chloroethene (vinyl chloride). Draw a possible structure for this polymer.
- 56. The structure of methyl methacrylate is given in Table 10.12. Draw the structure of a polymethyl methacrylate (PMMA) polymer that has four monomer units. (PMMA has excellent optical properties and is used to make hard contact lenses.)

### General Questions on Organic Chemistry

These questions are not designated as to type or location in the chapter. They may combine several concepts.

- 57. Three different compounds with the formula  $C_2H_2Cl_2$  are known.
  - (a) Two of these compounds are geometric isomers. Draw their structures.
  - (b) The third compound is a structural isomer of the other two. Draw its structure.
- 58. Draw the structure of 2-butanol. Identify the chiral carbon atom in this compound. Draw the mirror image of the structure you first drew. Are the two molecules superimposable?
- **59.** Draw Lewis structures, and name three structural isomers with the formula  $C_6H_{12}$ . Are any of these isomers chiral?
- **60.** Draw structures, and name the four alkenes that have the formula  $C_4H_8$ .
- **61.** Write equations for the reactions of *cis*-2-butene with the following reagents, representing the reactants and products using structural formulas.
  - (a) H<sub>2</sub>O
  - (b) HBr
  - (c)  $Cl_2$
- **62.** Draw the structure, and name the product formed if the following alcohols are oxidized. Assume an excess of the oxidizing agent is used. If the alcohol is not expected to react with a chemical oxidizing agent, write NR (no reaction).
  - (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
  - (b) 2-butanol
  - (c) 2-methyl-2-propanol
  - (d) 2-methyl-1-propanol
- **63.** Write equations for the following reactions, representing the reactants and products using structural formulas.
  - (a) The reaction of acetic acid and sodium hydroxide
  - (b) The reaction of methylamine with HCl

- **64.** Write equations for the following reactions, representing the reactants and products using structural formulas.
  - (a) The formation of ethyl acetate from acetic acid and ethanol
  - (b) The hydrolysis of glyceryl tristearate (the triester of glycerol with stearic acid, a fatty acid)
- **65.** Write an equation for the formation of the following polymers.
  - (a) Polystyrene, from styrene (C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>)
  - (b) PET (polyethylene terephthalate), from ethylene glycol and terephthalic acid
- **66.** Write equations for the following reactions, representing the reactants and products using structural formulas.
  - (a) The hydrolysis of the amide C<sub>6</sub>H<sub>5</sub>CONHCH<sub>3</sub> to form benzoic acid and methylamine
  - (b) The hydrolysis  $(-CO(CH_2)_4CONH(CH_2)_6NH \rightarrow_n,$  (nylon-6, 6, a polyamide) to give a carboxylic acid and an amine
- **67.** Draw the structure of each of the following compounds:
  - (a) 2,2-dimethylpentane
  - (b) 3,3-diethylpentane
  - (c) 3-ethyl-2-methylpentane
  - (d) 3-ethylhexane
- **68. ▲** Structural isomers.
  - (a) Draw all of the isomers possible for  $C_3H_8O$ . Give the systematic name of each, and tell into which class of compound it fits.
  - (b) Draw the structural formulas for an aldehyde and a ketone with the molecular formula  $C_4H_8O$ . Give the systematic name of each.
- 69. ▲ Draw structural formulas for possible isomers of the dichlorinated propane, C<sub>3</sub>H<sub>6</sub>Cl<sub>2</sub>. Name each compound.
- **70.** Draw structural formulas for possible isomers with the formula  $C_3H_6ClBr$ , and name each isomer.
- Give structural formulas and systematic names for the three structural isomers of trimethylbenzene, C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>.
- **72.** Give structural formulas and systematic names for possible isomers of dichlorobenzene, C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>.
- **73.** Voodoo lilies depend on carrion beetles for pollination. Carrion beetles are attracted to dead animals, and because dead and putrefying animals give off the horriblesmelling amine cadaverine, the lily likewise releases cadaverine (and the closely related compound putrescine) (page 466). A biological catalyst, an enzyme, converts the naturally occurring amino acid lysine to cadaverine.



lysine

What group of atoms must be replaced in lysine to make cadaverine? (Lysine is essential to human nutrition but is not synthesized in the human body.)

- 74. Benzoic acid occurs in many berries. When humans eat berries, benzoic acid is converted to hippuric acid in the body by reaction with the amino acid glycine H<sub>2</sub>NCH<sub>2</sub>CO<sub>2</sub>H. Draw the structure of hippuric acid, knowing it is an amide formed by reaction of the carboxylic acid group of benzoic acid and the amino group of glycine. Why is hippuric acid referred to as an acid?
- **75.** Consider the reaction of *cis*-2-butene with  $H_2$  (in the presence of a catalyst).
  - (a) Draw the structure, and give the name of the reaction product. Is this reaction product chiral?
  - (b) Draw an isomer of the reaction product.
- **76.** Give the name of each compound below, and name the functional group involved.

(a) 
$$H_{3}C - C - CH_{2}CH_{2}CH_{3}$$
$$H$$
$$(b) H_{3}C - CCH_{2}CH_{2}CH_{3}$$
$$H$$
$$(c) H_{3}C - CCH_{2}CH_{2}CH_{3}$$
$$H O$$
$$H_{3}C - C - C - H$$
$$CH_{3}$$
$$(d) H_{3}CCH_{2}CH_{3} - C - OH$$

- **77.** Draw the structure of glyceryl trilaurate. When this triester is saponified, what are the products? (See page 476.)
- 78. ▲ A well-known company selling outdoor clothing has recently introduced jackets made of recycled polyethylene terephthalate (PET), the principal material in many soft drink bottles. Another company makes PET fibers by treating recycled bottles with methanol to give the diester dimethylterephthalate and ethylene glycol and then repolymerizes these compounds to give new PET. Write a chemical equation to show how the reaction of PET with methanol can give dimethylterephthalate and ethylene phthalate and ethylene glycol.
- **79.** Identify the reaction products, and write an equation for the following reactions of CH<sub>2</sub>==CHCH<sub>2</sub>OH.
  - (a)  $H_2$  (hydrogenation, in the presence of a catalyst)
  - (b) Oxidation (excess oxidizing agent)
  - (c) Addition polymerization
  - (d) Ester formation, using acetic acid

- **80.** Write a chemical equation describing the reaction between glycerol and stearic acid to give glyceryl tristearate.
- 81. The product of an addition reaction of an alkene is often predicted by Markovnikov's rule.
  - (a) Draw the structure of the product of adding HBr to propene, and give the name of the product.
  - (b) Draw the structure, and give the name of the compound that results from adding  $H_2O$  to 2-methyl-1-butene.
  - (c) If you add H<sub>2</sub>O to 2-methyl-2-butene, is the product the same or different than the product from the reaction in part (b)?
- **82.** An unknown colorless liquid has the formula  $C_4H_{10}O$ . Draw the structures for the four alcohol compounds that have this formula.

### In the Laboratory

83. ■ Which of the following compounds produces acetic acid when treated with an oxidizing agent such as KMnO<sub>4</sub>?

(a) 
$$H_3C-CH_3$$
 (c)  $H_3C-C-H_1$   
(b)  $H_3C-C-H$  (d)  $H_3C-C-CH_3$ 

**84.** Consider the reactions of  $C_3H_7OH$ .

$$\begin{array}{c} H & H & H \\ H_{3}CCH_{2} - \stackrel{I}{C} - O - H \xrightarrow{Rxn A}{H_{2}SO_{4}} H_{3}C - \stackrel{I}{C} = \stackrel{I}{\stackrel{O}{C}} + H_{2}O \\ H & H \\ Rxn B \downarrow + CH_{3}CO_{2}H \\ H & H \\ H_{3}CCH_{2} - \stackrel{I}{C} - O - \stackrel{I}{C}CH_{3} \\ H \end{array}$$

- (a) Name the reactant C<sub>3</sub>H<sub>7</sub>OH.
- (b) Draw a structural isomer of the reactant, and give its name.
- (c) Name the product of reaction A.
- (d) Name the product of reaction B.
- **85.** You have a liquid that is either cyclohexene or benzene. When the liquid is exposed to dark-red bromine vapor, the vapor is immediately decolorized. What is the identity of the liquid? Write an equation for the chemical reaction that has occurred.

- 86. ▲ Hydrolysis of an unknown ester of butanoic acid, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>R, produces an alcohol A and butanoic acid. Oxidation of this alcohol forms an acid B that is a structural isomer of butanoic acid. Give the names and structures for alcohol A and acid B.
- 87. A You are asked to identify an unknown colorless, liquid carbonyl compound. Analysis has determined that the formula for this unknown is  $C_3H_6O$ . Only two compounds match this formula.
  - (a) Draw structures for the two possible compounds.
  - (b) To decide which of the two structures is correct, you react the compound with an oxidizing agent and isolate from that reaction a compound that is found to give an acidic solution in water. Use this result to identify the structure of the unknown.
  - (c) Name the acid formed by oxidation of the unknown.
- **88.** Describe a simple chemical test to tell the difference between CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> and its isomer cyclopentane.
- **89.** Describe a simple chemical test to tell the difference between 2-propanol and its isomer methyl ethyl ether.
- **90.** An unknown ester has the formula  $C_4H_8O_2$ . Hydrolysis gives methanol as one product. Identify the ester, and write an equation for the hydrolysis reaction.
- 91. ▲ Addition of water to alkene X gives an alcohol Y. Oxidation of Y produces 3,3-dimethyl-2-pentanone. Identify X and Y, and write equations for the two reactions.
- 92. 2-Iodobenzoic acid, a tan, crystalline solid, can be prepared from 2-aminobenzoic acid. Other required reagents are NaNO<sub>2</sub> and KI (as well as HCl).



- (a) If you use 4.0 g of 2-aminobenzoic acid, 2.2 g of NaNO<sub>2</sub>, and 5.3 g of KI, what is the theoretical vield of 2-iodobenzoic acid?
- (b) Are other isomers of 2-iodobenzoic acid possible?
- (c) To verify that you have isolated 2-iodobenzoic acid, you titrate it in water/ethanol. If you use 15.62 mL of 0.101 M NaOH to titrate 0.399 g of the product, what is its molar mass? Is it in reasonable agreement with the theoretical molar mass?

### Summary and Conceptual Questions

The following questions may use concepts from this and previous chapters.

- **93.** Carbon atoms appear in organic compounds in several different ways with single, double, and triple bonds combining to give an octet configuration. Describe the various ways that carbon can bond to reach an octet, and give the name, and draw the structure of a compound that illustrates that mode of bonding.
- **94.** There is a high barrier to rotation around a carboncarbon double bond, whereas the barrier to rotation around a carbon–carbon single bond is considerably smaller. Use the orbital overlap model of bonding (Chapter 9) to explain why there is restricted rotation around a double bond.
- **95.** What important properties do the following characteristics impart on an polymer?
  - (a) Cross linking in polyethylene
  - (b) The OH groups in polyvinyl alcohol
  - (c) Hydrogen bonding in a polyamide like nylon
- **96.** One of the resonance structures for pyridine is illustrated here. Draw another resonance structure for the molecule. Comment on the similarity between this compound and benzene.



- **97.** Write balanced equations for the combustion of ethane gas and liquid ethanol (to give gaseous products).
  - (a) Calculate the enthalpy of combustion of each compound. Which has the more negative enthalpy change for combustion per gram?
  - (b) If ethanol is assumed to be partially oxidized ethane, what effect does this have on the heat of combustion?
- **98.** Plastics make up about 20% of the volume of landfills. There is, therefore, considerable interest in reusing or recycling these materials. To identify common plastics, a set of universal symbols is now used, five of which are illustrated here. They symbolize low- and high-density polyethylene, polyvinyl chloride, polypropylene, and polyethylene terephthalate.



- (a) Tell which symbol belongs to which type of plastic.
- (b) Find an item in the grocery or drug store made from each of these plastics.
- (c) Properties of several plastics are listed in the table.Based on this information, describe how to separate samples of these plastics from one another.

	Density	Melting
Plastic	$(g/cm^3)$	Point (°C)
Polypropylene	0.92	170
High-density polyethylene	0.97	135
Polyethylene terephthalate	1.34 - 1.39	245

- **99.** ▲ Maleic acid is prepared by the catalytic oxidation of benzene. It is a dicarboxylic acid; that is, it has two carboxylic acid groups.
  - (a) Combustion of 0.125 g of the acid gives 0.190 g of  $CO_2$  and 0.0388 g of  $H_2O$ . Calculate the empirical formula of the acid.
  - (b) A 0.261-g sample of the acid requires 34.60 mL of 0.130 M NaOH for complete titration (so that the H ions from both carboxylic acid groups are used). What is the molecular formula of the acid?
  - (c) Draw a Lewis structure for the acid.
  - (d) Describe the hybridization used by the C atoms.
  - (e) What are the bond angles around each C atom?

#### Appendix N | Answers to Exercises

- **9.7**  $\operatorname{Li}_2^{-}$  is predicted to have an electron configuration  $(\sigma_1 s)^2 (\sigma_1^* s)^2 (\sigma_2 s)^2 (\sigma_2^* s)^1$  and a bond order of  $\frac{1}{2}$ , the positive value implying that the ion might exist.
- **9.8**  $O_2^+$ : [core electrons]  $(\sigma_2 s)^2 (\sigma_2^* s)^2 (\pi_2 p)^4 (\sigma_2 p)^2 (\pi_2 p)^1$ . The bond order is 2.5. The ion is paramagnetic with one unpaired electron.

### Chapter 10

10.1 (a) Isomers of  $C_7H_{16}$ 

CH<sub>3</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>3</sub>CH<sub>3</sub> heptane  $CH_3$ CH<sub>3</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>9</sub>CHCH<sub>3</sub> 2-methylhexane  $CH_3$ CH<sub>3</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> 3-methylhexane  $CH_3$ CH<sub>3</sub>CH<sub>2</sub>CHCHCH<sub>3</sub> 2,3-dimethylpentane ĊH<sub>3</sub>  $CH_3$ CH<sub>3</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>9</sub>CH<sub>3</sub> 2,2-dimethylpentane ĊH<sub>3</sub> CH<sub>3</sub> 3,3-dimethylpentane ĊH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub>CHCH<sub>2</sub>CHCH<sub>3</sub> 2,4-dimethylpentane ĊH<sub>3</sub>

2-Ethylpentane is pictured on page 450.

$$\begin{array}{ccc} H_3C & CH_3 \\ | & | \\ CH_3C - CHCH_3 & 2,2,3 \text{-trimethylbutane} \\ | & \\ CH_3 \end{array}$$

- (b) Two isomers, 3-methylhexane, and 2,3-dimethylpentane, are chiral.
- **10.2** The names accompany the structures in the answer to Exercise 10.1.

**10.3** Isomers of  $C_6H_{12}$  in which the longest chain has six C atoms:



**10.6**  $CH_{3}CH_{2}CH_{2}CH_{2}OH$  1-butanol OH CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub> 2-butanol CH<sub>3</sub>CHCH<sub>2</sub>OH 2-methyl-1-propanol CH<sub>3</sub> OH CH<sub>3</sub>CCH<sub>3</sub> 2-methyl-2-propanol

NH<sub>9</sub>

ĊH<sub>3</sub>



**10.8** (a) 
$$O$$
  
||  
1-butanol gives butanal  $CH_3CH_2CH_2CH$ 

(b)

2-butanol gives butanone  $CH_3CH_9CCH_3$ 

(c) 2-methyl-1-propanol gives 2-methylpropanal

$$\begin{array}{c} H & O \\ | & \parallel \\ CH_3C - CH \\ | \\ CH_3 \end{array}$$

The oxidation products from these three reactions are structural isomers.

10.9 (a) 
$$O$$
  
 $H_2COCH_3$  methyl propanoate  
(b)  $O$ 

$$CH_{3}CH_{2}CH_{2}COCH_{2}CH_{2}CH_{2}CH_{3}$$
  
butyl butanoate

(c) 
$$O$$
  
 $\parallel$   
 $CH_3CH_2CH_2CH_2CH_2CCH_2CH_3$   
ethyl hexanoate

**10.10** (a) Propyl acetate is formed from acetic acid and propanol:

$$\begin{array}{c} O\\ \parallel\\ CH_{3}COH + CH_{3}CH_{2}CH_{2}OH \end{array}$$

(b) 3-Methylpentyl benzoate is formed from benzoic acid and 3-methylpentanol:

(c) Ethyl salicylate is formed from salicylic acid and ethanol:

**10.11** (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH: 1-propanol, has an alcohol (—OH) group

 $CH_3CO_2H$ : ethanoic acid (acetic acid), has a carboxylic acid (-CO<sub>2</sub>H) group

CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>: ethylamine, has an amino (-NH<sub>2</sub>) group

- (b) 1-propyl ethanoate (propyl acetate)
- (c) Oxidation of this primary alcohol first gives propanal, CH<sub>3</sub>CH<sub>2</sub>CHO. Further oxidation gives propanoic acid, CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H.
- (d) N-ethylacetamide, CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>3</sub>
- (e) The amine is protonated by hydrochloric acid, forming ethylammonium chloride, [CH<sub>3</sub>CH<sub>2</sub>NH<sub>3</sub>]Cl.
- **10.12** Kevlar is a polyamide polymer, prepared by the reaction of terephthalic acid and 1,4-diaminobenzene.

 $n \operatorname{H_2NC_6H_4NH_2} + n \operatorname{HO_2CC_6H_4CO_2H} \longrightarrow$ -(-HNC<sub>6</sub>H<sub>4</sub>NHCOC<sub>6</sub>H<sub>4</sub>CO-)<sub>n</sub>- + 2n H<sub>2</sub>O

### Chapter 11

- **11.1** 0.83 bar (0.82 atm) > 75 kPa (0.74 atm) > 0.63 atm > 250 mm Hg (0.33 atm)
- **11.2**  $P_1 = 55 \text{ mm Hg and } V_1 = 125 \text{ mL}; P_2 = 78 \text{ mm Hg}$ and  $V_2 = ?$  $V_2 = V_1(P_1/P_2) = (125 \text{ mL})(55 \text{ mm Hg}/78 \text{ mm Hg})$ = 88 mL
- **11.3**  $V_1 = 45$  L and  $T_1 = 298$  K;  $V_2 = ?$  and  $T_2 = 263$  K  $V_2 = V_1(T_2/T_1) = (45 \text{ L})(263 \text{ K}/298 \text{ K}) = 40$ . L
- **11.4**  $V_2 = V_1(P_1/P_2) (T_2/T_1)$ = (22 L) (150 atm/0.993 atm) (295 K/304 K) = 3200 L

At 5.0 L per balloon, there is sufficient He to fill 640 balloons.

**11.6** 
$$PV = nRT$$
  
(750/760 atm) (V) =  
(1300 mol) (0.08206 L · atm/mol · K) (296 K)  
 $V = 3.2 \times 10^4$  L

#### **9.53** (a) C, $sp^2$ ; N, $sp^3$

(b) The amide or peptide link has two resonance structures (shown here with formal charges on the O and N atoms). Structure B is less favorable, owing to the separation of charge.



(c) The fact that the amide link is planar indicates that structure B has some importance.

The principal sites of positive charge are the nitrogen in the amide linkage, and the hydrogen of the -O-H group. The principal regions of negative charge are oxygen atoms and the nitrogen of the free  $-NH_2$  group.

- **9.55** MO theory is better to use when explaining or understanding the effect of adding energy to molecules. A molecule can absorb energy and an electron can thus be promoted to a higher level. Using MO theory, one can see how this can occur. Additionally, MO theory is a better model to use to predict whether a molecule is paramagnetic.
- **9.57** Lowest Energy = Orbital C < Orbital B < Orbital A = Highest Energy
- **9.59** (a) The attractive forces must be greater than the repulsive forces if a covalent bond is to form.
  - (b) As the atoms approach each other, the energy drops as the electron clouds overlap and electron density increases between the two nuclei. If the atoms approach still more closely, electrostatic repulsion of the nuclei for each other and of the electrons for each other increases dramatically.
  - (c) In neon, all of the orbitals in the 2s and 2p sublevels are filled with paired electrons; there is no orbital available that can overlap with another orbital on another atom. In the case of fluorine, there is an orbital on each atom that is not completely filled that can overlap with another orbital to form a bond.
- **9.61** (a) The molecule with the double bond requires a great deal more energy because the  $\pi$  bond must be broken in order for the ends of the molecules to rotate relative to each other.
  - (b) No. The carbon–carbon double bonds in the molecule prevent the CH<sub>2</sub> fragments from rotating.

### **CHAPTER 10**

- 10.1 Heptane
- **10.3**  $C_{14}H_{30}$  is an alkane and  $C_5H_{10}$  could be a cycloalkane.
- 10.5 2,3-dimethylbutane
- 10.7 (a) 2,3-Dimethylhexane

$$CH_3 \\ H_3 - CH - CH - CH_2 - CH_2 - CH_3 \\ H_3 - CH - CH_3 - C$$

(b) 2,3-Dimethyloctane

$$\begin{array}{c} \operatorname{CH}_3\\ |\\ \operatorname{CH}_3-\operatorname{CH}-\operatorname{CH}-\operatorname{CH}_2-\operatorname{CH}_2-\operatorname{CH}_2-\operatorname{CH}_2-\operatorname{CH}_2\\ |\\ \operatorname{CH}_3\end{array}$$

(c) 3-Ethylheptane

10.

$$CH_2CH_3$$
  
 $\downarrow$   
 $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ 

(d) 3-Ethyl-2-methylhexane

ĊH<sub>3</sub>

$$CH_2CH_3$$
  
 $CH_3$ - $CH$ - $CH$ - $CH$ - $CH_2$ - $CH_2$ - $CH_3$   
 $CH_3$ 

....

9 H  

$$H_{3}C-C-CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$$
 2-methylheptane  
 $CH_{3}$   
H  
 $CH_{3}CH_{2}CH_{2}-C-CH_{2}CH_{2}CH_{3}$  4-methylheptane  
 $CH_{3}$   
H  
 $CH_{3}CH_{2}CH_{2}-C-CH_{2}CH_{2}CH_{3}$  4-methylheptane  
 $CH_{3}$   
H  
 $CH_{2}CH_{2}-C-CH_{2}CH_{2}CH_{3}$  4-methylheptane  
 $CH_{3}$  4-methylheptane  
 $CH$ 

10.11 H  

$$CH_3CH_2CH_2$$
  $-C$   $-CH_2CH_2CH_3$   $4$ -ethylheptane. The compound is not chiral. CH\_2CH\_3 H

$$CH_3CH_2 - C - CH_2CH_2CH_2CH_3$$
 3-ethylheptane. Not chiral.

chiral.

**10.13**  $C_4H_{10}$ , butane: a low-molecular–weight fuel gas at room temperature and pressure. Slightly soluble in water.

 $C_{12}H_{26}$ , dodecane: a colorless liquid at room temperature. Expected to be insoluble in water but quite soluble in nonpolar solvents.



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3-chloro-1-propene

CH<sub>3</sub>

Br

o-bromotoluene

C

10.25

trans-1-chloropropene

Cl

*m*-dichlorobenzene

Cl



(c) 2-methyl-1-propanol

$$\begin{array}{c} \mathsf{H}\\ \mathsf{C}\mathsf{H}_{3} - \begin{array}{c} \mathsf{C} - \mathsf{C}\mathsf{H}_{2}\mathsf{O}\mathsf{H}\\ \mathsf{H}\\ \mathsf{C}\mathsf{H}_{3}\end{array}$$

CH<sub>2</sub>CH<sub>3</sub>

ethylbenzene

1,2,4-trimethylbenzene

CH<sub>3</sub>

CH<sub>3</sub>CH<sub>2</sub>Cl/AlCl<sub>3</sub>

 $CH_3$ 

ĊH<sub>3</sub>

 $CH_3CH_2CH_2-N-CH_2CH_2CH_3\\ |\\H$ 

 $\begin{array}{c} \mathrm{CH_3CH_2CH_2CH_2-}\mathbf{N-}\mathbf{CH_3}\\ \downarrow\\ \mathrm{CH_3}\end{array}$ 

 $\begin{array}{c} CH_3CH_2 {-} \underbrace{N {-} CH_2CH_3}_{| \\ CH_2CH_3} \end{array}$ 

CH<sub>3</sub>

 $CH_3$ 

(b) 1-Butanol, primary

CH<sub>3</sub>Cl/AlCl<sub>3</sub>

(c) 2-Methyl-2-propanol, tertiary

(d) 2-Methyl-2-butanol, tertiary

(d) 2-methyl-2-propanol

$$CH_3 - C - CH_3 CH_3$$

10.37 (a)  $C_6H_5NH_2(aq) + HCl(aq) \rightarrow (C_6H_5NH_3)Cl(aq)$ (b)  $(CH_3)_3N(aq) + H_2SO_4(aq) \rightarrow$ [(CH<sub>3</sub>)<sub>3</sub>NH]HSO<sub>4</sub>(aq)

$$CH_{3} - C - CH_{2}CH_{2}CH_{3}$$

$$O$$

$$H - C - CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$$

 $\mathbf{O}$ 

- 10.41 (a) Acid, 3-methylpentanoic acid
  - (b) Ester, methyl propanoate
  - (c) Ester, butyl acetate (or butyl ethanoate)
  - (d) Acid, p-bromobenzoic acid
- 10.43 (a) Pentanoic acid (see Question 39c)
  (b) 1-Pentanol, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
  OH

(c) 
$$H_3C \stackrel{|}{-}C - CH_2CH_2CH_2CH_2CH_2CH_3$$
  
|  
H

(d) No reaction. A ketone is not oxidized by KMnO<sub>4</sub>.

10.45 Step 1: Oxidize 1-propanol to propanoic acid.



Step 2: Combine propanoic acid and 1-propanol.

$$CH_{3}CH_{2} \xrightarrow{O} C \xrightarrow{H} CH_{3}CH_{2} \xrightarrow{-C} OH \xrightarrow{-H_{2}O} OH \xrightarrow{-H_{2}O} H$$

- **10.47** Sodium acetate, NaCH<sub>3</sub>CO<sub>2</sub>, and 1-butanol, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
- 10.49 (a) Trigonal planar
  - (b) 120°
  - (c) The molecule is chiral. There are four different groups around the carbon atom marked 2.
  - (d) The acidic H atom is the H attached to the  $CO_2H$  (carboxyl) group.

**10.51** (a) Alcohol (c) Acid

10.53 (a) Prepare polyvinyl acetate (PVA) from vinylacetate.



(b) The three units of PVA:



- (c) Hydrolysis of polyvinyl alcohol
- **10.55** Illustrated here is a segment of a copolymer composed of two units of 1,1–dichloroethylene and two units of chloroethylene.



with a branched chain.

cyclohexane methylcyclopentane



$$\begin{array}{c} O \\ H_{3}C - C - OH + NaOH \longrightarrow \begin{bmatrix} H_{3}C - C - O^{-} \end{bmatrix} Na^{+} + H_{2}O$$

(b) 
$$\begin{array}{c} H\\ I\\ H_{3}C-N-H+HCl \longrightarrow CH_{3}NH_{3}^{+}+Cl^{-}\end{array}$$

10.65





10.67 (a) 2, 3-Dimethylpentane

 $\begin{array}{c} CH_3\\ |\\H_3C-C-C-CH_2CH_2CH_3\\ |\\CH_3\end{array}$ 

(b) 3, 3-Dimethylpentane

$$CH_{2}CH_{2}CH_{3}$$

$$CH_{3}CH_{2}-C-CH_{2}CH_{3}$$

$$|$$

$$CH_{2}CH_{3}$$

(c) 3-Ethyl-2-methylpentane

$$\begin{array}{c} H \quad CH_2CH_3 \\ | \quad | \\ CH_3 - C - C - C - CH_2CH_3 \\ | \quad | \\ CH_3 \quad H \end{array}$$

(d) 3-Ethylhexane

$$\begin{array}{c} CH_2CH_3\\ |\\ CH_3CH_2 - C - CH_2CH_2CH_3\\ |\\ H\\ H\end{array}$$

10.69







1,2,3-trimethylbenzene

10.75

**10.73** Replace the carboxylic acid group with an H atom.



1,2,4-trimethylbenzene



1,3,5-trimethylbenzene









- **10.83** Compound (b), acetaldehyde, and (c), ethanol, produce acetic acid when oxidized.
- **10.85** Cyclohexene, a cyclic alkene, will add  $Br_2$  readily (to give  $C_6H_{12}Br_2$ ). Benzene, however, needs much more stringent conditions to react with bromine; then  $Br_2$  will substitute for H atoms on benzene and not add to the ring.
- **10.87** (a) The compound is either propanone, a ketone, or propanal, an aldehyde.



- (b) The ketone will not undergo oxidation, but the aldehyde will be oxidized to the acid, CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H. Thus, the unknown is likely propanal.
- (c) Propanoic acid

**10.89** 2-Propanol will react with an oxidizing agent such as  $KMnO_4$  (to give the ketone), whereas methyl ethyl ether ( $CH_3OC_2H_5$ ) will not react. In addition, the alcohol should be more soluble in water than the ether.



- **10.95** (a) Cross-linking makes the material very rigid and inflexible.
  - (b) The OH groups give the polymer a high affinity for water.

triple bond

- (c) Hydrogen bonding allows the chains to form coils and sheets with high tensile strength.
- **10.97** (a) Ethane heat of combustion = -47.51 kJ/gEthanol heat of combustion = -26.82 kJ/g
  - (b) The heat obtained from the combustion of ethanol is less negative than for ethane, so partially oxidizing ethane to form ethanol decreases the amount of energy per mole available from the combustion of the substance.
- 10.99 (a) Empirical formula, CHO
  - (b) Molecular formula,  $C_4H_4O_4$

$$\begin{array}{c} c) & O & O \\ \parallel & \parallel & \parallel \\ HO - C - C = C - C - OH \\ H & H \end{array}$$

- (d) All four C atoms are  $sp^2$  hybridized.
- (e) 120°

(

#### Appendix Q Answers to Chapter Opening Puzzler and Case Study Questions

 The compound has sp<sup>3</sup> hybridized B and N atoms and is polar. The B atom has a −1 formal charge and N has a +1 form charge. All bond angles are about 109°.



**3.**  $(54.3 \times 10^{-3} \text{ g AgBF}_4) (1 \text{ mol}/194.7 \text{ g}) = 2.79 \times 10^{-4} \text{ mol}$ 

The amount of  $Ag(C_2H_4)_xBF_4$  that must have decomposed is  $2.79 \times 10^{-4}$  mol.

Molar mass of unknown =  $(62.1 \times 10^{-3} \text{ g})/(2.79 \times 10^{-4} \text{ mol}) = 223 \text{ g/mol}$ 

The compound  $Ag(C_2H_4)BF_4$  where x = 1 has a molar mass of 223 g/mol.

### **CHAPTER 10**

### **Puzzler:**

- (a) Trigonal planar, sp<sup>2</sup> hybridized. The other carbon atoms in this molecule have tetrahedral geometry and sp<sup>3</sup> hybridization.
  - (b) The non-planarity allows all of the atoms in the molecule to assume an unstrained geometry.
  - (c) Actually, there are two chiral centers, labeled with an asterisk (\*) in the drawing below.



2. Camphor is a ketone.

### Case Study: Biodiesel, a Fuel for the Future

- **1.**  $C_{12}H_{25}CO_2CH_3(\ell) + 20 O_2(g) \rightarrow 14 CO_2(g) + 14 H_2O(g)$
- 2.  $\Delta_{\rm r} H^{\circ} = (14 \text{ mol } {\rm CO}_2/\text{mol-rxn}) [\Delta_f H^{\circ}({\rm CO}_2)] + (14 \text{ mol } {\rm H}_2{\rm O}/\text{mol-rxn}) [\Delta_f H^{\circ}({\rm H}_2{\rm O})] (1 \text{ mol } {\rm C}_{12}{\rm H}_{25}{\rm CO}_2{\rm CH}_3/\text{mol-rxn}) [\Delta_f H^{\circ}({\rm C}_{12}{\rm H}_{25}{\rm CO}_2{\rm CH}_3)]$

 $\begin{array}{l} \Delta_r H^\circ = (14 \mbox{ mol} CO_2/mol\mbox{-}rxn) [-393.5 \mbox{ kJ/mol} \\ CO_2] + (14 \mbox{ mol} H_2O/mol\mbox{-}rxn) [-241.8 \mbox{ kJ/} \\ mol \mbox{ H}_2O] - (1 \mbox{ mol} C_{12}H_{25}CO_2CH_3/mol\mbox{-}rxn) \\ [-771.0 \mbox{ kJ/mol} C_{12}H_{25}CO_2CH_3)] = \\ -8123.2 \mbox{ kJ/mol\mbox{-}rxn} \end{array}$ 

1 mol methyl myristate per mol-rxn, so q per mol = -8123.2 kJ/mol

**3.** Burning hexadecane:  $C_{16}H_{34}(\ell) + 24.5 O_2(g) \rightarrow 16 CO_2(g) + 17 H_2O(g)$ 

 $\begin{array}{l} \Delta_{\rm r} H^{\circ} = (16 \ {\rm mol} \ {\rm CO}_2/{\rm mol}{\rm -rxn}) \left[ \Delta_f H^{\circ}({\rm CO}_2) \right] + \\ (17 \ {\rm mol} \ {\rm H}_2 {\rm O}/{\rm mol}{\rm -rxn}) \left[ \Delta_f H^{\circ}({\rm H}_2 {\rm O}) \right] - (1 \ {\rm mol} \ {\rm C}_{16} {\rm H}_{34}/{\rm mol}{\rm -rxn}) \left[ \Delta_f H^{\circ}({\rm C}_{16} {\rm H}_{34}) \right] \end{array}$ 

 $\begin{array}{l} \Delta_r H^\circ = (16 \mbox{ mol} CO_2/mol\mbox{-}rxn) [-393.5 \mbox{ kJ/mol}\\ CO_2] + (17 \mbox{ mol} H_2O/mol\mbox{-}rxn) [-241.8 \mbox{ kJ/}\\ mol\mbox{ H}_2O] - (1 \mbox{ mol} C_{16}H_{34}/mol\mbox{-}rxn)\\ [-456.1 \mbox{ kJ/mol} C_{16}H_{34})] = -9950.5 \mbox{ kJ/}\\ mol\mbox{-}rxn \end{array}$ 

1 mole hexadecane per mol-rxn, so q per mol: -9950.5 kJ/mol

For methyl myristate, q per liter = (-8123.2 kJ/mol)(1 mol/228.4 g)(0.86 g/L) = -30.6 kJ/L

For hexadecane, q per liter = (-9950.5 kJ/mol)(1 mol/226.43 g)(0.77 g/1 L) = -33.8 kJ/L

### CHAPTER 11

### **Puzzler:**

- P(O<sub>2</sub>) at 3000 m is 70% of 0.21 atm, the value P(O<sub>2</sub>) at sea level, thus P(O<sub>2</sub>) at 3000 m = 0.21 atm × 0.70 = 0.15 atm (110 mm Hg). At the top of Everest, P(O<sub>2</sub>) = 0.21 atm × 0.29 = 0.061 atm (46 mm Hg).
- **2.** Blood saturation levels (estimated from table): at 3000 m, >95%; at top of Everest, 75%.