CHEM 1152: SURVEY OF CHEMISTRY II



Tanesha Osborne
Georgia Southern University

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Licensing

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CHAPTER OVERVIEW

1: CHEM 1151 Organic Review

We begin our study of organic chemistry with the alkanes, compounds containing only two elements, carbon and hydrogen, and having only single bonds. There are several other kinds of hydrocarbons, distinguished by the types of bonding between carbon atoms and by the properties that result from that bonding. We will first examine hydrocarbons with double bonds, with triple bonds, and with a special kind of bonding called aromaticity. Then we will study some compounds considered to be derived from hydrocarbons by replacing one or more hydrogen atoms with an oxygen-containing group. Finally, we focuse on organic acids and bases, after which we will be ready to look at the chemistry of life itself—biochemistry—in the remaining five chapters.

1.1: Organic Chemistry
1.2: Structures of Organic Compounds
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1.1: Organic Chemistry

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them **organic** because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled **inorganic**. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{1.1.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today organic chemistry is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table **1.1.1**.

Table **1.1.1**: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane		Inorganic	NaCl
low melting points	−95°C		high melting points	801°C
low boiling points	69°C		high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline		greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable		nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive		aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds		exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table **1.1.1** also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table **1.1.1**.

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1.2: Structures of Organic Compounds

Learning Objectives

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A ***molecular formula*** shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it does not distinguish between butane and isobutane. While a molecular formula indicates the number and types of atoms present, it does not indicate how the atoms are bonded to one another. In contrast to molecular formulas, structural formulas do illustrate how the atoms are joined together. There are different types of structural formulas and they each show different levels of detail and types of information.

A **structural formula (or Lewis Structure)** shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms. This is the most time consuming of the structural formulas, but it gives the most information as to the bonding arrangement of the atoms.

Condensed structural formulas are often used to alleviate the difficulty that comes with typing/writing the structural form. A condensed structure does not illustrate all of the bonds in a molecule, but it does give information regarding the bonding in the molecule. This structural representation shows hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for propane (Figure **1.2.1**).

Skeletal Structures (or line-angle structures) provide a simpler way to represent large organic molecules. These represent the ultimate condensed formula where carbon atoms are implied at the corners and ends of lines. Skeletal structures involve bonds between carbon atoms always being shown, but hydrogen atoms attached to carbons are implied and not shown. Each carbon atom is understood to be attached to enough hydrogen atoms to give the carbon four bonds.

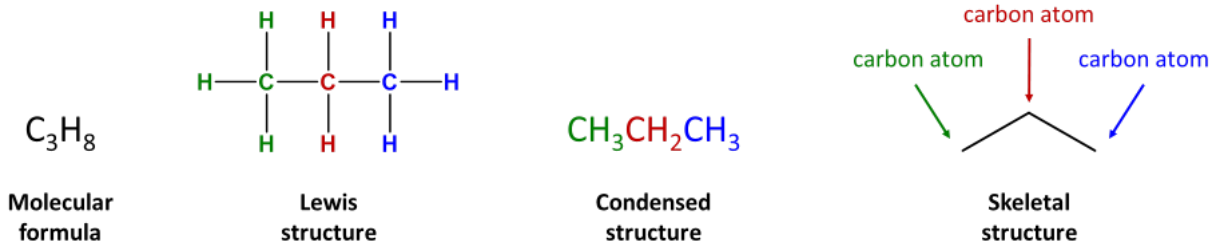


Figure **1.2.1**: Molecular and structural representations of propane. DrTOsborne, CC BY 4.0, via Wikimedia Commons

As you will see in the next section, some molecules will have an atom or groups of atoms branching from a chain of carbon atoms. These molecules can also be represented using the structural formulas described above. These condensed structural formulas would use parentheses to indicate the group that is attached to the adjacent carbon atom (Figure **1.2.2**).

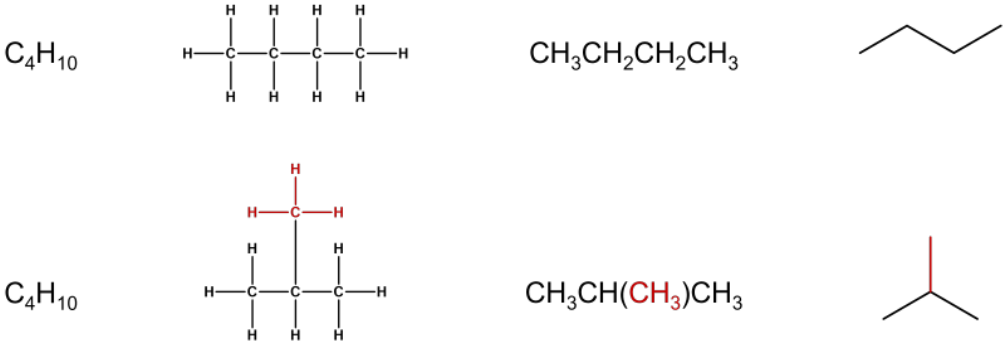


Figure **1.2.2**: Structural representations of butane (top) and isobutane (bottom).

Key Takeaways

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

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1.3: Branched Alkanes

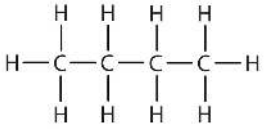
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

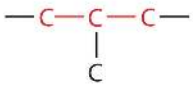
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

$$–C–C–C–C–$$

and then adding enough hydrogen atoms to give each carbon atom four bonds:



The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds.

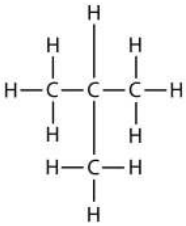


Figure 1.3.1: Structure of 2-methylpropane (also known as isobutane).

Structural isomers have identical molecular formulas but a different connectivity of atoms and are named differently. For example, butane and 2-methylpropane (isobutane) are structural isomers (Figure 1.3.2). They both have the same molecular formula, but the atoms are arranged differently, and they have different names.

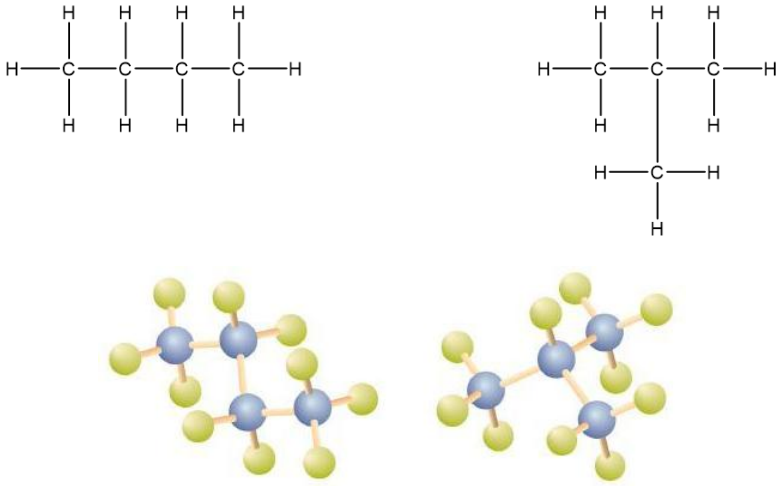
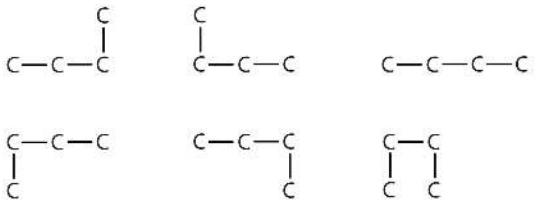


Figure 1.3.2: Butane (left) and Isobutane (right). The Lewis structure (top) and ball-and-stick models (bottom) of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}.

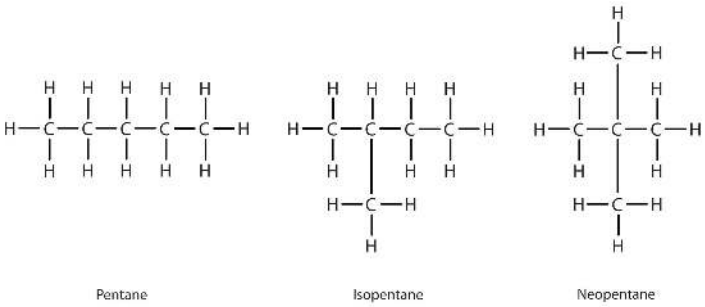
Notice that C_4H_{10} is depicted with a bent chain in Figure **1.3.2**. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure **1.3.2**.

Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C.



A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

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1.4: Alkane IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

The number of structural isomers increases rapidly as the number of carbon atoms increases. There are 3 structural isomers of pentane, 5 of hexane, 9 of heptane, and 18 of octane. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.)

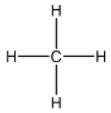
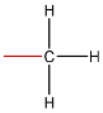
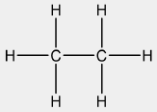
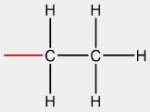
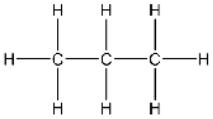
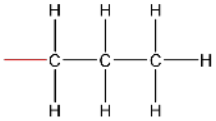
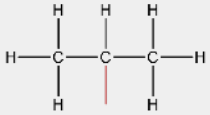
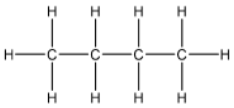
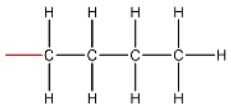
A parent name (Table **1.4.1**) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to the LCC are called ***substituents***. Alkyl substituents are those containing carbon and hydrogen atoms. These substituents are named, using the same prefixes used to determine the parent name, to represent the number of carbon atoms present.

Table **1.4.1**: Prefixes That Indicate the Number of Carbon Atoms in Organic Molecules

Prefix	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the $-CH_3$ group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table **1.4.2**. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

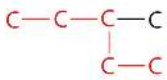
Table **1.4.2**: Common Alkyl Groups

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		—CH_3
ethane		ethyl		—CH_2CH_3
propane		propyl		—$CH_2CH_2CH_3$
		isopropyl		—$CH(CH_3)_2$
butane		butyl*		—$CH_2CH_2CH_2CH_3$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 1.4.1).

1. **Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.
2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

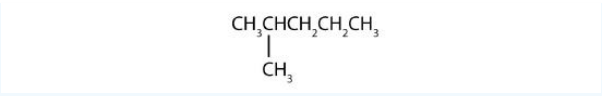
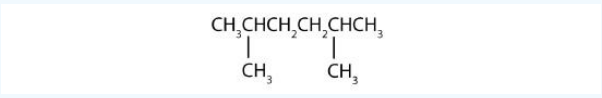
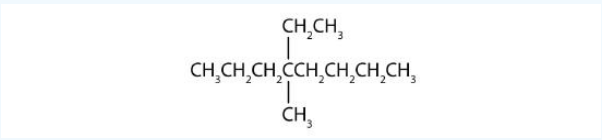


3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 1.4.1

Name each compound.

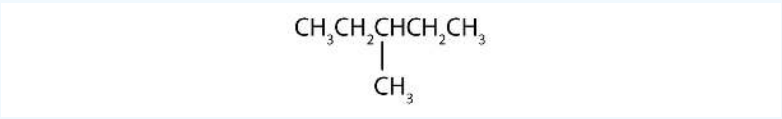
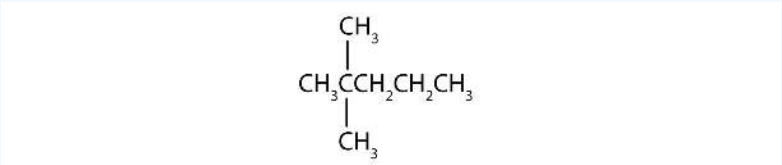
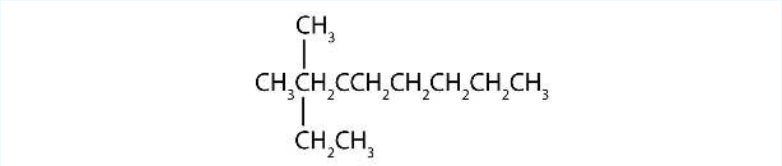
1. 
2. 
3. 

Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexane (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

Exercise 1.4.1

Name each compound.

1. 
2. 
3. 

Example 1.4.2

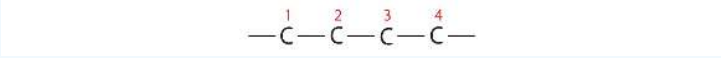
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

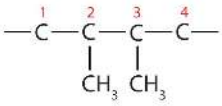
Solution

In drawing structures, always start with the parent chain.

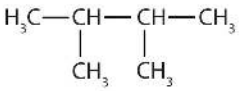
a. The parent chain is butane, indicating four carbon atoms in the LCC.



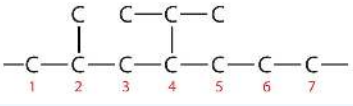
Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.



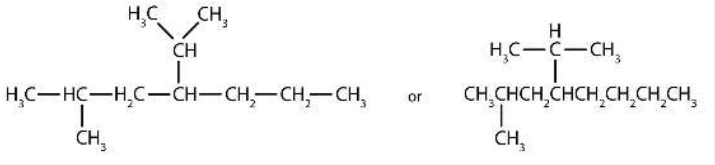
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.



b. Adding the groups at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas:



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

? Exercise 1.4.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

Key Takeaway

- In general, an IUPAC name will have three essential features: Substituents + Parent Name + Suffix

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1.5: Halogenated Alkanes

Learning Objectives

- To name halogenated hydrocarbons given formulas and write formulas for these compounds given names.

Many organic compounds are closely related to the alkanes. There are different types of substituents and not all will be alkyl substituents. Some molecules will have one or more hydrogen atoms replaced with a halogen (Figure **1.5.1**).

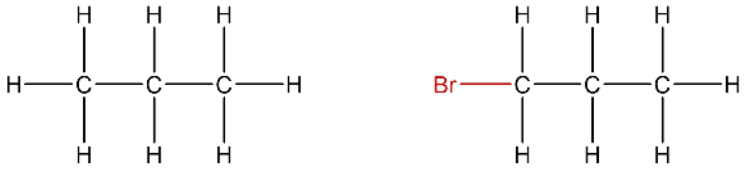


Figure **1.5.1**: Structures of alkane (left) and haloalkane (right) that was formed by bromine replacing a hydrogen.

The replacement of only one hydrogen atom gives an ***alkyl halide***, also referred to as a *haloalkane*. The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*. For example, the alkyl halide shown in Figure **1.5.1** would have a common name of *propyl bromide*. The propyl indicates the alkyl group that the bromine is attached to.

The IUPAC nomenclature of haloalkanes utilize the same steps as naming alkanes. This system uses the identity and location of the halogen substituents followed bby the name of the parent alkane. The difference is that the halogen substituents are named by replacing the *–ine* (or *-ide*) ending with *–o* to become fluoro, chloro, bromo, or iodo. Thus, the IUPAC name of the haloalkane shown in Figure **1.5.1** is 1-bromopropane.

Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

Example 1.5.1

Give the common and IUPAC names for each compound.

a. $CH_3CH_2CH_2CH_2Br$
b. $(CH_3)_2CHCl$

Solution

a. The alkyl group ($CH_3CH_2CH_2CH_2$–) is a butyl group, and the halogen is bromine (Br). The common name is therefore buhyl bromide. For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a four-carbon chain (butane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromobutane.
b. The alkyl group [$(CH_3)_2CH$–] has three carbon atoms, with a chlorine (Cl) atom attached to the middle carbon atom. The alkyl group is therefore isopropyl, and the common name of the compound is isopropyl chloride. For the IUPAC name, the Cl atom (prefix *chloro-*) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

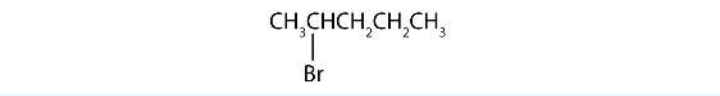
Exercise 1.5.1

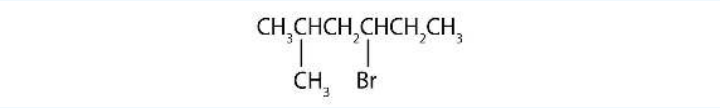
Give common and IUPAC names for each compound.

a. CH_3CH_2I
b. $CH_3CH_2CH_2CH_2F$

Example 1.5.2

Give the IUPAC name for each compound.

1. 

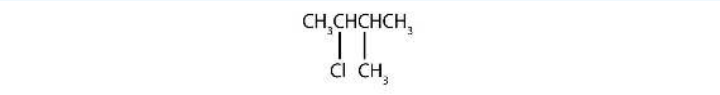
2. 

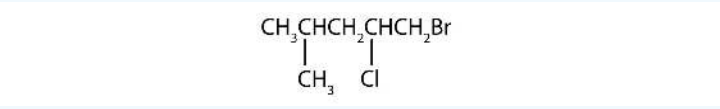
Solution

1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl ($CH_{3)}$ and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

Exercise 1.5.2

Give the IUPAC name for each compound.

a. 

b. 

Some Halogenated Hydrocarbons

A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table **1.5.1**, along with some of their uses.

Table **1.5.1**: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

To Your Health: Halogenated Hydrocarbons

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

To Your Health: Chlorofluorocarbons and the Ozone Layer

Alkanes substituted with both fluorine (F) and chlorine (Cl) atoms have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. Two of the best known of these chlorofluorocarbons (CFCs) are listed in Table **1.5.1**.

Chlorofluorocarbons contribute to the greenhouse effect in the lower atmosphere. They also diffuse into the stratosphere, where they are broken down by ultraviolet (UV) radiation to release Cl atoms. These in turn break down the ozone (O_3) molecules that protect Earth from harmful UV radiation. Worldwide action has reduced the use of CFCs and related compounds. The CFCs and other Cl- or bromine (Br)-containing ozone-destroying compounds are being replaced with more benign substances. Hydrofluorocarbons (HFCs), such as CH_2FCF_3, which have no Cl or Br to form radicals, are one alternative. Another is

hydrochlorofluorocarbons (HCFCs), such as $CHCl_2CF_3$. HCFC molecules break down more readily in the troposphere, and fewer ozone-destroying molecules reach the stratosphere.

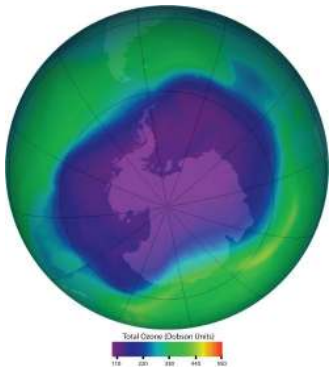


Figure **1.5.2**: Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly over Antarctica from late August through early October and fill in about mid-November. Ozone depletion has also been noted over the Arctic regions. The largest ozone hole ever observed occurred on 24 September 2006. Source: Image courtesy of NASA, http://ozonewatch.gsfc.nasa.gov/daily.php?date=2006-09-24.

Key Takeaway

- The replacement of a hydrogen atom on an alkane by a halogen atom—F, Cl, Br, or I—forms a halogenated compound. Alkyl halides with simple alkyl groups are often called by common names, while those with a larger number of carbon atoms are usually given IUPAC names.

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1.6: Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form ***cycloalkanes***. Cycloalkanes are ring or cyclic structures containing carbon-carbon single bonds. They have the general formula C_nH_{2n} and the simplest of these cyclic hydrocarbons has the formula C_3H_6. Each carbon atom has two hydrogen atoms attached (Figure **1.6.1**) and is called cyclopropane.

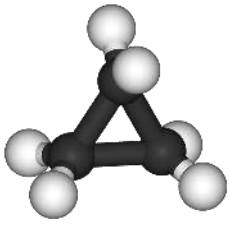
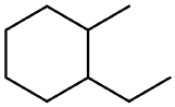


Figure **1.6.1**: Ball-and-Stick Model of Cyclopropane.

Naming Cycloalkanes

Cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring. These compounds are named in a similar manner as alkanes. The principal difference in the rules and procedures occurs in the numbering system. Since a ring has no ends like a chain does, all the carbon atoms of a ring are equivalent.



Applying the rules for naming cycloalkanes to the above molecule:

1. **Determine the parent chain.** Count the number of carbon atoms in the ring and in the largest alkyl substituent.
    a. If the number of carbon atoms in the ring is greater than or equal to the number of carbon atoms present in the largest substituent, the compound is named as an alkyl-substituted cycloalkane. Therefore, the parent chain is named as cyclo____ane, based on the number of carbon atoms in the ring.
    b. If the number of carbon atoms in the ring is less than the number of carbon atoms in the substituent, it is named as a cycloalkyl-substituted alkane. The compound is named based on the rules for naming alkanes.

The longest continuous chain of carbon atoms in this example is the ring which contains six carbon atoms. Therefore, the parent name is cyclohexane.

2. **Identify the substituents** in the same manner as with alkanes.

There are two substituents: one substituent consists of a single carbon atom making it a methyl group (derived from methane) and a substituent that contains two carbon atoms making it an ethyl group (derived from ethane).

3. **Number the carbon atoms in the ring**. If substituents are present, Carbon 1 will always have a substituent.
    a. If there is one substituent, there is no need to show the number 1 for the location of the substituent.
    b. If two or more substituents are present, assign carbon 1 to the site of a substituent. Continue numbering such that the remaining substituents have as low a number as possible. When two or more different substituents could receive the same number, the numbers are assigned in alphabetical order.

Since there are two substituents present that could both receive the same number, the substituent to receive the lower number is determined based on alphabetical order. Therefore, the ethyl group is assigned to carbon 1. The ring should then be numbered to give the methyl group the lowest number possible. which is 2.

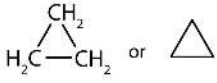
4. Put the name together as in alkanes with the order of: location and identity of substituent(s) followed by the parent name of the compound.

Utilizing these steps indicates that the name of the compound is 1-ethyl-3-methylcyclohexane.

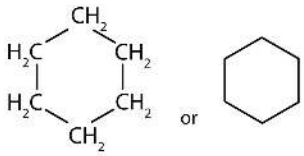
To Your Health: Cyclopropane as an Anesthetic

With its boiling point of −33°C, cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



cyclopropane



cyclohexane

Some cyclic compounds have substituent groups attached. Example **1.6.1** interprets the name of a cycloalkane with a single substituent group.

Properties of Cycloalkanes

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure **1.6.1**.) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

✔ Example 1.6.1

Draw the structure for each compound.

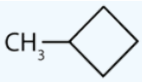
a. cyclopentane
b. methylcyclobutane

Solution

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



b. The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.

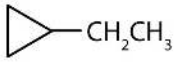


Exercise 1.6.1

1. Draw the structure for each compound.
    a. cycloheptane
    b. ethylcyclohexane

Example 1.6.2

1. What is the molecular formula of cyclooctane?
2. What is the IUPAC name for this compound?

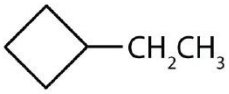


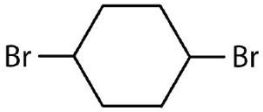
Solution

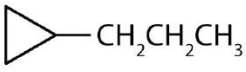
a. The name *cyclooctane* indicates a cyclic (cyclo) alkane with eight (oct-) carbon atoms. It can be represented as an octagon. Since the general formula of cycloalkanes is C_nH_{2n}, the molecular formula for cyclooctane is C_8H_{16}.
b. The parent chain is a ring that contains three carbon atoms, so it represents *cyclopropane*. There is one substituent that has two carbon atoms, so it represents *ethyl*. Since there is only one substituent present, no number is needed. Therefore, the IUPAC name ofo the compound is *ethylcyclopropane*.

Exercise 1.6.2

1. Give the IUPAC name of the following molecules:

a. 

b. 

c. 

Key Takeaway

- Cycloalkanes are cyclic hydrocarbons that are named in a similar manner as alkanes.

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1.E: CHEM 1151 Organic Review (Exercises)

1.1 Organic Chemistry

Concept Review Exercises

1. Classify each compound as organic or inorganic.
   a. C_3H_8O
   b. $CaCl_2$
   c. $Cr(NH_3)_3Cl_3$
   d. $C_{30}H_{48}O_3N$
2. Which compound is likely organic and which is likely inorganic?
   a. a flammable compound that boils at 80°C and is insoluble in water
   b. a compound that does not burn, melts at 630°C, and is soluble in water
3. Which member of each pair has a higher melting point?
   a. CH_3OH and NaOH
   b. CH_3Cl and KCl
   c. $CoCl_2$ and C_2H_6
   d. CH_4 and LiH

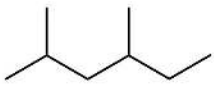
Answers

1. a. organic
   b. inorganic
   c. inorganic
   d. organic
2. a. organic
   b. inorganic
3. a. NaOH
   b. KCl
   c. $CoCl_2$
   d. LiH

1.2 Structures of Organic Compounds

Concept Review Exercises

1. In alkanes, can there be a two-carbon branch off the second carbon atom of a four-carbon chain? Explain.
2. A student is asked to write structural formulas for two different hydrocarbons having the molecular formula C_5H_{12}. She writes one formula with all five carbon atoms in a horizontal line. She then shows another with four carbon atoms in a line and a CH_3 group extending down from the first carbon atom. Do these structural formulas represent different molecular formulas? Explain why or why not.
3. A condensed structural formula for isohexane can be written as $(CH_3)_2CHCH_2CH_2CH_3$. Draw the line-angle formula for isohexane.
4. Give the structural formula for the compound represented by this line-angle formula:

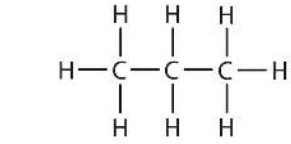


5. Write the condensed structural formula for each molecule.

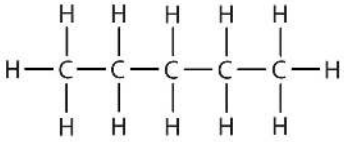


a.

b.



c.



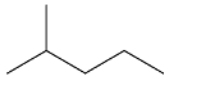
Answers

1. No; the branch would make the longest continuous chain of five carbon atoms.
2. No; both are five-carbon continuous chains.
3. 
4. $CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH_3$
5. a. CH_3CH_3
   b. $CH_3CH_2CH_3$
   c. $CH_3CH_2CH_2CH_2CH_3$

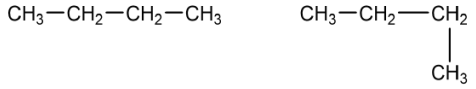
1.3 Branched Alkanes

Concept Review Exercises

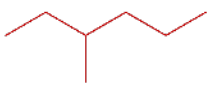
1. Briefly identify the important distinctions between a straight-chain alkane and a branched-chain alkane.
2. How are butane and isobutane related? How do they differ?
3. Draw a line-angle formula for the compound $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$.
4. Indicate whether the structures in each set represent the same compound or isomers.

a. 



b. 

Answers

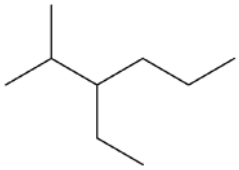
1. Straight-chain alkanes and branched-chain alkanes have different properties as well as different structures. The names will also be different.
2. Butane and isobutane have the same molecular formula, C_4H_{10}. However, the atoms are connected differently, so that have different names.
3. 
4. a. isomers (left: branched alkane and right: straight-chain alkane)
   b. same compound (both are butane)

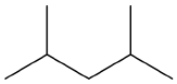
1.4 Alkane IUPAC Nomenclature

Concept Review Exercises

1. What is a CH_3 group called when it is attached to a chain of carbon atoms—a substituent or a functional group?
2. How many carbon atoms are present in each molecule?
   a. 2,3-dimethylbutane
   b. 3-ethyl-2-methylheptane
3. Draw the structures of the following compounds:
   a. 3-methylpentane
   b. 2,2,5-trimethylhexane
   c. 4-ethyl-3-methyloctane
4. Give the IUPAC name of the following compounds:

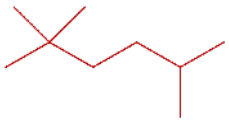
a. 

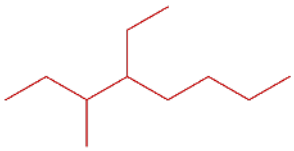
b. 

c. 

Answers

1. substituent
2. a. 6
   b. 10
   c. 11
3. a. 

b. 

c. 

4. a. 2,2-dimethylbutane
   b. 3-ethyl-2-methylhexane
   c. 2,4-dimethylpentane

1.5 Halogenated Alkanes

Concept Review Exercises

1. What is the IUPAC name for the HFC that has the formula CH_2FCF_3? (Hint: you must use a number to indicate the location of each substituent F atom)
2. Write the condensed structural formula for each compound:
   a. ethyl bromide
   b. carbon tetrachloride
3. Write the condensed structural formulas for the two isomers that have the molecular formula C_3H_7Br. Give the common name and the IUPAC name of each.

Answers

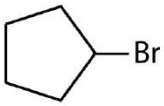
1. 1,1,1,2-tetrafluoroethane
2. a. CH_3CH_2Br
   b. CCl_4
3. $CH_3CH_2CH_3Br$ common name: propyl bromide; IUPAC name: 1-bromopropane

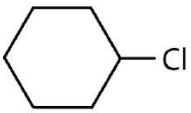
   $CH_3CH(Br)CH_3$ common name: isopropyl bromide; IUPAC name: 2-bromopropane

1.6 Cycloalkanes

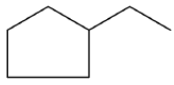
Concept Review Exercises

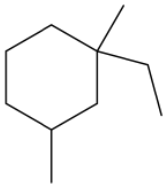
1. Draw the structure for each compound:
   a. methylcyclohexane
   b. butylcyclobutane
2. Cycloalkyl groups can be derived from cycloalkanes in the same way that alkyl groups are derived from alkanes. These groups are named as cyclopropyl, cyclobutyl, and so on. Name each cycloalkyl halide.

   a. 

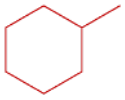
   b. 

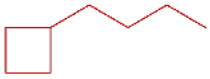
3. Give the IUPAC name of the following molecule:

   a. 

   b. 

Answers

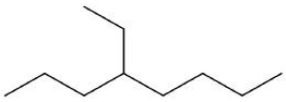
1. a. 

   b. 

2. a. cyclopentyl bromide
   b. cyclohexyl chloride
3. a. ethylcyclopentane
   b. 1-ethyl-1,3-dimethylcyclohexane

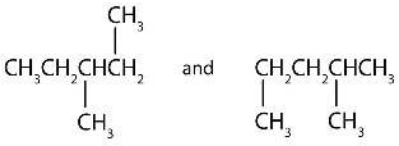
Additional Exercises

1. You find an unlabeled jar containing a solid that melts at 48°C. It ignites readily and burns readily. The substance is insoluble in water and floats on the surface. Is the substance likely to be organic or inorganic?
2. Give the molecular formulas for methylcyclopentane, 2-methylpentane, and cyclohexane. Which are isomers?
3. What is wrong with each name? (Hint: first write the structure *as if* it were correct.) Give the correct name for each compound.
   a. 2-dimethylpropane
   b. 2,3,3-trimethylbutane
   c. 2,4-diethylpentane
   d. 3,4-dimethyl-5-propylhexane
4. The following is the line formula for an alkane. Give the IUPAC name of the compound.



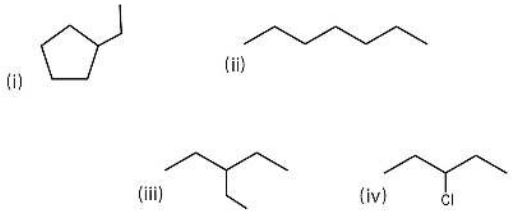
5. Draw the structures for the five isomeric hexanes (C_6H_{14}). Name each by the IUPAC system.
6. Indicate whether the structures in each set represent the same compound or isomers.

   a. 

   b. 

   c. 

7. Consider the line-angle formulas shown here and answer the questions.



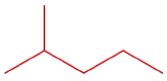
a. Which pair of formulas represents isomers?
b. Which formula represents an alkyl halide? Give the IUPAC name of the compound and write its condensed structural formula.
c. Which formula represents a cycloalkane? Give the IUPAC name of the compound.
d. What is the molecular formula of the compound represented by (i)?

Answers

1. organic

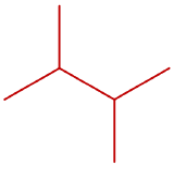
3. a. Two numbers are needed to indicate two substituents; 2,2-dimethylpropane.
   b. The lowest possible numbers were not used; 2,2,3-trimethylbutane.
   c. An ethyl substituent is not possible on the second carbon atom; 3,5-dimethylheptane.
   d. A propyl substituent is not possible on the fifth carbon atom; 3,4,5-trimethyloctane.

5.  hexane

 2-methylpentane

 3-methylpentane

 2,2-dimethylbutane

 2,3-dimethylbutane

7. a. ii and iii
   b. iv; 3-chloropentane; $CH_3CH_2CHClCH_2CH_3$
   c. i; ethylcyclopentane
   d. C_7H_{14}

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1.S: CHEM 1151 Organic Review (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the summary and ask yourself how they relate to the topics in the chapter.

Organic chemistry is the chemistry of carbon compounds, and **inorganic chemistry** is the chemistry of all the other elements. Carbon atoms can form stable covalent bonds with other carbon atoms and with atoms of other elements, and this property allows the formation the tens of millions of organic compounds. **Hydrocarbons** contain only hydrogen and carbon atoms.

Hydrocarbons in which each carbon atom is bonded to four other atoms are called **alkanes** or **saturated hydrocarbons**. They have the general formula C_nH_{2n+2}. Any given alkane differs from the next one in a series by a CH_2 unit. Any family of compounds in which adjacent members differ from each other by a definite factor is called a **homologous series**.

The physical properties of alkanes reflect the fact that alkane molecules are nonpolar. Alkanes are insoluble in water and less dense than water.

arbon atoms in alkanes can form straight chains or branched chains. Two or more compounds having the same molecular formula but different structural formulas are **isomers** of each other. There are no isomeric forms for the three smallest alkanes; beginning with C_4H_{10}, all other alkanes have isomeric forms.

A **structural formula** shows all the carbon and hydrogen atoms and how they are attached to one another. A **condensed structural formula** shows the hydrogen atoms right next to the carbon atoms to which they are attached. A **line-angle formula** is a formula in which carbon atoms are implied at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

The **IUPAC System of Nomenclature** provides rules for naming organic compounds. An **alkyl group** is a unit formed by removing one hydrogen atom from an alkane. When the alkyl group replaces one or more hydrogen from the longest continuous chain, the group is referred to as an **alkyl substituent**. If a halogen replaces one or more hydrogen in the longest continuous chain, a halogenated hydrocarbon known as an **alkyl halide (haloalkane)** forms.

Cycloalkanes are hydrocarbons whose molecules are closed rings rather than straight or branched chains. A **cyclic hydrocarbon** is a hydrocarbon with a ring of carbon atoms

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CHAPTER OVERVIEW

2: Organic Nomenclature - Unsaturated Hydrocarbons

2.1: Alkenes - Structures and Names

2.2: Geometric Isomers

2.3: Alkynes - Structures and Names

2.4: Aromatic Compounds

2.5: Aromatics - Structure and Names

2.E: Unsaturated Hydrocarbons (Exercises)

2.S: Unsaturated Hydrocarbons (Summary)

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2.1: Alkenes - Structures and Names

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

Alkenes are hydrocarbons with carbon-carbon double bonds ($R_2C{=}CR_2$). These compounds are called *unsaturated* hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

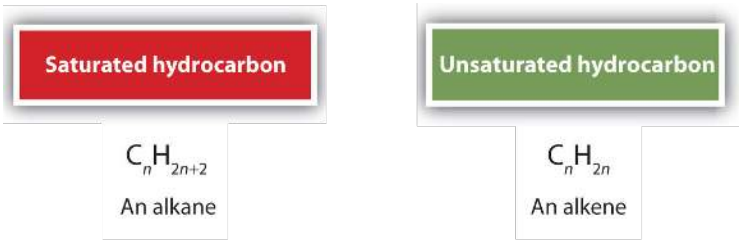


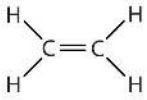
Figure **2.1.1**: General molecular formula of saturated and unsaturated hydrocarbons. " Alkenes- Structures and Names" by LibreTexts is licensed under CC BY-NC-SA (Modified).

The double bond of alkenes is shorter and stronger than the single bond of alkanes. Depending on the number of carbon-carbon double bonds present in a molecule, it can be further classifed. Alkenes containing two carbon-carbon double bonds are called *dienes* and those containing several double bonds are called *polyenes*. Some representative alkenes—their names, structures, and physical properties—are given in Table **2.1.1**.

Table **2.1.1**: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

We used only condensed structural formulas in Table **2.1.1**. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table **2.1.1**, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure **2.1.2**). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

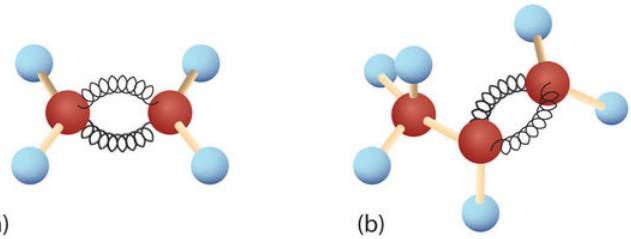


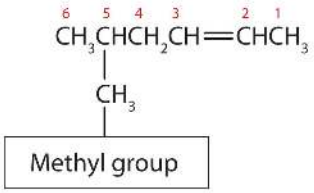
Figure **2.1.2**: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

Naming Alkenes

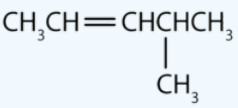
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

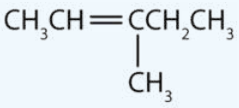
1. The **longest chain of carbon atoms *containing both carbon atoms of the double bond*** is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but the *-ane* suffix is replaced with *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must **indicate the position of the double bond**. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. **Substituents are identified (as with other organic compounds) and their location is indicated by a number**. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



Example 2.1.1

Name each compound.

a. 

b. 

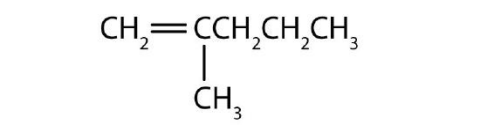
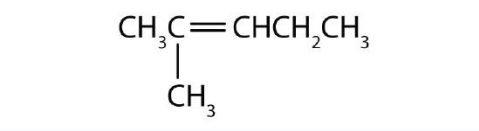
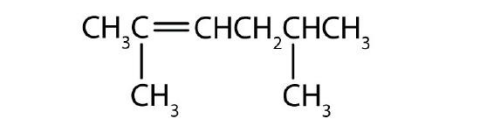
Solution

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the name of the compound is 4-methyl-2-pentene.

b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the name of the compound is 3-methyl-2-pentene.

? Exercise 2.1.1

Name each compound.

1. 
2. 
3. 

Cycloalkenes

Just as there are cycloalkanes, there are **cycloalkenes**. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name. Since the carbon of the double bond always has priority in numbering, carbons 1 and 2 of the cycloalkene represent the carbons of the carbon-carbon double bond.

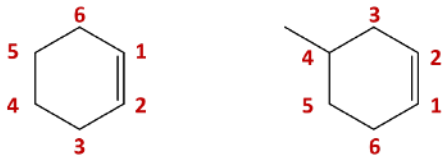


Figure **2.1.3**: Numbering cycloalkenes. The double bond occurs between carbons 1 and 2, even if it causes substituents to have higher numbers.

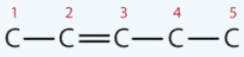
✓ Example 2.1.2

Draw the structure for each compound.

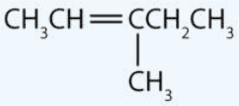
1. 3-methyl-2-pentene
2. cyclohexene

Solution

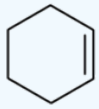
1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:



Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



2. First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



? Exercise 2.1.2

Draw the structure for each compound.

1. 2-ethyl-1-hexene
2. cyclopentene
3. 2-methyl-2-butene

Key Takeaway

- Alkenes are hydrocarbons with one carbon-carbon double bond; dienes contain two carbon-carbon double bonds; and polyenes contain several carbon-carbon double bonds.
- IUPAC nomenclature of alkenes: location and identity of substituents + parent prefix + ene suffix

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2.2: Geometric Isomers

Learning Objectives

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure **2.2.1**.

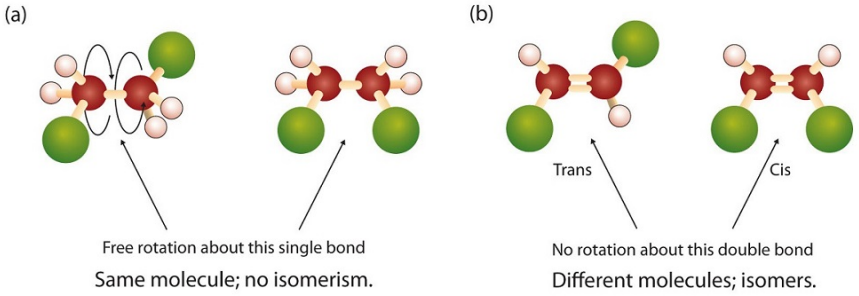


Figure **2.2.1**: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.

In 1,2-dichloroethane (part (a) of Figure **2.2.1**), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:

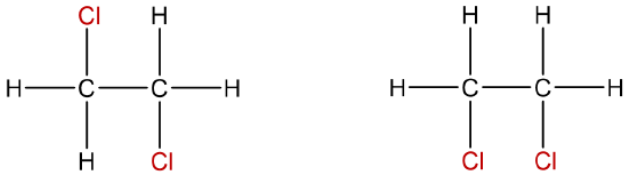


Figure **2.2.2**: Structural formulas of 1,2-dichloroethane.

In 1,2-dichloroethene (Figure **2.2.1***b*), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the **cis isomer** (Latin *cis*, meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the **trans isomer** (Latin *trans*, meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are **cis-trans isomers (or geometric isomers)**, compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure **2.2.3**).

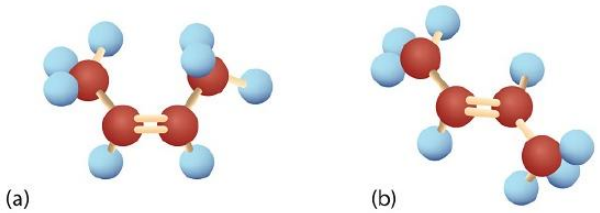


Figure 2.2.3: Models of (a) cis-2-Butene and (b) trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

Cis-2-butene has both methyl groups on the same side of the molecule. Trans-2-butene has the methyl groups on opposite sides of the molecule. Notice that the names of these molecules are identical except for the prefix cis or trans. Their structural formulas are as follows:



Figure 2.2.4: Structures of cis-2-Butene (left) and trans-2-Butene (right).

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 2.2.5). We can draw two *seemingly* different propenes:



Figure 2.2.5: Different views of the propene molecule (flip vertically). These are not isomers.

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** doubly bonded carbon atom (one hydrogen and another atom/group of atoms).

In the propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached (H and CH_3), but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C{=}CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C{=}CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-carbon double bond.

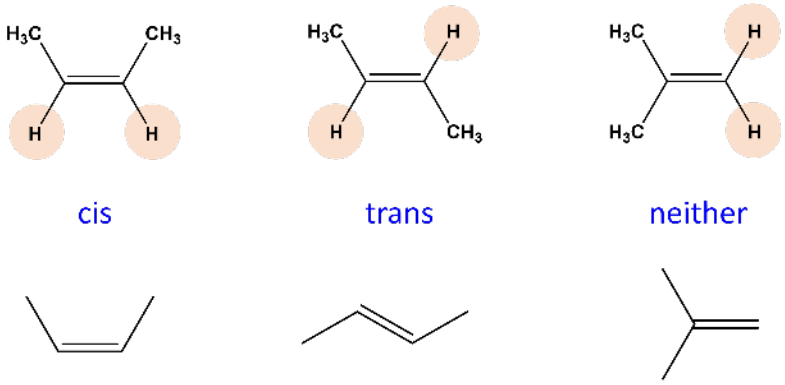


Figure **2.2.6**: Structural formulas (top) and skeletal structures (bottom) of cis-trans isomers. DrTOsborne, CC BY 4.0, via Wikimedia Commons

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the carbon–carbon bonds in the ring. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). The orientation of the substitutents will be designated with either a solid and/or dashed wedge to indicate the 3-dimensional arrangement or as a Haworth projection to indicate positions above and below the plane of the ring plane (Figure **2.2.7**).



Figure **2.2.7**. Indication of the 3-dimensional structure (left) and Haworth projection (right) of cis-1,2-dimethylcyclopropane (left structure of both pair) and trans-1,2-dimethylcyclopropane (right structure of both pair).

Example 2.2.1

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. CHCl=CHBr
2. CH_2=CBrCH_3
3. $(CH_3)_2$C=CHCH_2CH_3
4. CH_3CH=CHCH_2CH_3

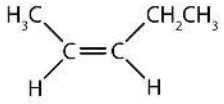
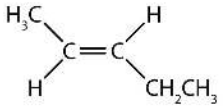
Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:

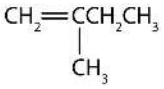
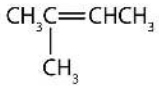


2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:

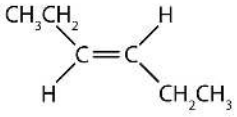
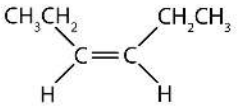
Exercise 2.2.1

Which compounds can exist as cis-trans isomers? Draw them.

a. $CH_2=CHCH_2CH_2CH_3$
b. $CH_3CH=CHCH_2CH_3$
c. $CH_3CH_2CH=CHCH_2CH_3$
d. 
e. 

Example 2.2.2

Classify each compound as a cis isomer, a trans isomer, or neither. Provide the IUPAC name of the molecule.

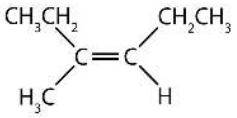
1. 
2. 

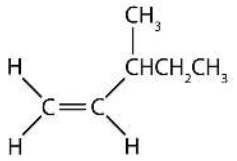
Solution

1. This compound meets rule 1 (restricted rotation due to the double bond) and rule 2 (it has two nonidentical groups on *each* carbon atom: H and CH_2CH_3). Since the H are on opposite sides of the molecule, this is a trans isomer. Using the rules for naming alkenes, the longest continuous chain has six carbon atoms with a double bond between carbons 3 and 4. This means that the parent name is 3-hexene. Putting this together indicates that the IUPAC name of the molecule is trans-3-hexene.
2. This compound meets rule 1 (restricted rotation due to the double bond) and rule 2 (it has two nonidentical groups on *each* carbon atom: H and CH_2CH_3). Since the H are on the same side of the molecule, this is a cis isomer. Using the rules for naming alkenes, the longest continuous chain has six carbon atoms with a double bond between carbons 3 and 4. This means that the parent name is 3-hexene. Putting this together indicates that the IUPAC name of the molecule is cis-3-hexene.

Exercise 2.2.2

1. Classify each compound as a cis isomer, a trans isomer, or neither. Provide the IUPAC name of the molecule.

a. 

b. 

2. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
   a. 2-bromo-2-pentene
   b. 3-hexene
   c. 4-methyl-2-pentene

Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.
- The IUPAC naming is the same as alkene except for the addition of the cis or trans prefix.

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2.3: Alkynes - Structures and Names

Learning Objectives

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

Alkynes are hydrocarbons with carbon-carbon triple bonds (R–C≡C–R). These compounds are also called *unsaturated* hydrocarbons because they have fewer hydrogen atoms than does an alkane or alkene with the same number of carbon atoms, as is indicated in the following general formulas:

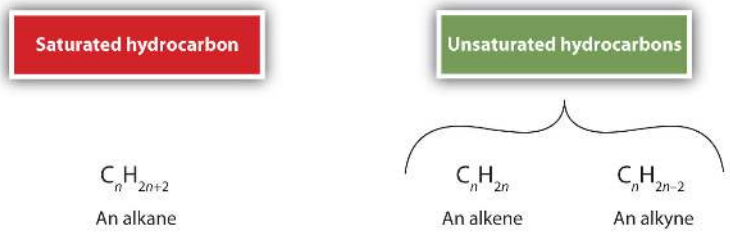


Figure **2.3.1**: General molecular formula of saturated and unsaturated hydrocarbons.

Alkynes are similar to alkenes in both physical and chemical properties. The triple bond of an alkyne is shorter and stronger than the double bond of an alkene. The simplest alkyne has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure **2.3.2**). Its structure is H–C≡C–H.

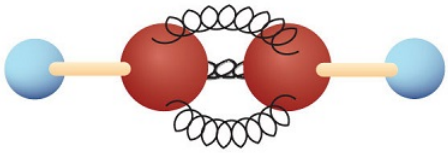


Figure **2.3.2**: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Naming Alkynes

The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. Here are some basic rules for naming alkynes using the IUPAC system:

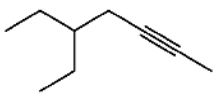


Figure **2.3.3**: Skeletal structure of a molecule that will be named as discussing the steps for naming alkynes.

1. The **longest chain of carbon atoms *containing both carbon atoms of the triple bond*** is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but the *-ane* suffix is replaced with *-yne* to identify it as an alkyne. The skeletal structure of alkynes tend to be shown with the geometry of the carbon atoms of the triple bond represented (linear, 180°). *Thus the parent chain is heptyne.*

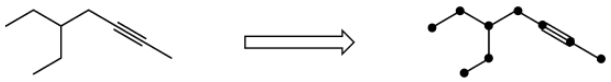
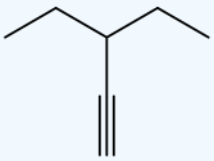
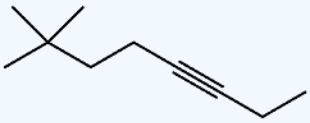


Figure 2.3.3b: Illustration of the carbon atoms present in the alkyne. Each dot represents a carbon.

2. If there are four or more carbon atoms in a chain, we must **indicate the position of the triple bond**. The carbons atoms are numbered so that the first of the two that are triple bonded is given the lower of the two possible numbers. Therefore, this representts 2-heptyne (not 5-heptyne).
3. **Substituents are identified (as with other organic compounds) and their location is indicated by a number**. Thus, the structure shown in Figure 2.3.3 is *5-ethyl-2-heptyne*. Note that the numbering of the parent chain is always done in such a way as to give the triple bond the lowest number, even if that causes a substituent to have a higher number. *The triple bond always has priority in numbering*. Also note that cis-trans isomers do not occur in alkynes.

Example 2.3.1

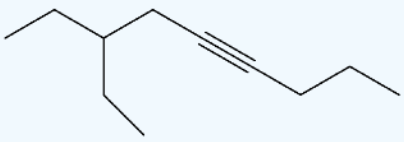
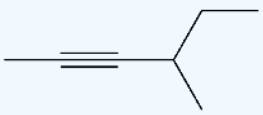
Name each compound.

1. 
2. 

Solution

1. The longest chain containing both carbon of the triple bond has five carbon atoms, so the compound is a *pentyne* (rule 1). To give the first carbon atom of the triple bond the lowest number (rule 2), we number from the bottom of the molecule, so the compound is a 1-pentyne. There is an ethyl group on the third carbon atom (rule 3), so the name of the compound is 3-ethyl-1-pentyne.
2. The longest chain containing both carbon of the triple bond has eight carbon atoms, so the compound is an *octyne* (rule 1). To give the first carbon atom of the triple bond the lowest number (rule 2), we number from right-to-left, so the compound is a 3-octyne. There are two methyl groups and both are attached to the seventh carbon atom (rule 3), so the name of the compound is 7,7-dimethyl-3-octyne.

Exercise 2.3.1

1. Name the following compounds.
   a. 
   b. 

2. Draw the structure for each compound.
    a. 4-methyl-2-hexyne
    b. 3-octyne
    c. 3,4-dimethyl-1-pentyne

Key Takeaway

- Alkynes are hydrocarbons with carbon-carbon triple bonds and properties much like those of alkenes.
- IUPAC nomenclature of alkynes: location and identity of substituents + parent prefix + yne suffix

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2.4: Aromatic Compounds

Learning Objectives

- Describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called **aromatic hydrocarbons**, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

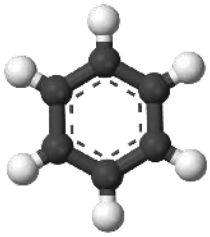


Figure **2.4.1**: Ball-and-Stick module of benzene.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:

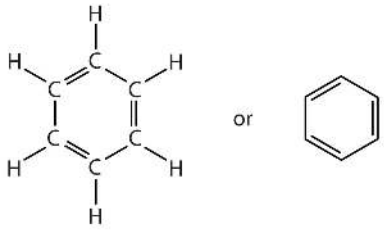


Figure **2.4.2**: Structural (left) and skeletal (right) structures of benzene.

However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



Figure 2.4.3: Skeletal stucture of benzene showing the presence of delocalized electrons.

The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

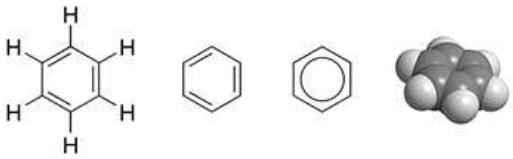


Figure 2.4.4: Structural representations of benzene. Cacycle, Benzene Structure, CC BY-SA 3.0, via Wikimedia Commons

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding that make them more stable and resistant to certain chemical reactions.

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2.5: Aromatics - Structure and Names

Learning Objectives

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

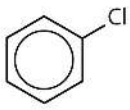
Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table **2.5.1**, where the benzene ring is represented as C_6H_5.

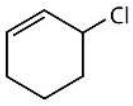
Table **2.5.1**: *Some Representative Aromatic Compounds*

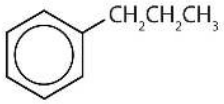
Name	Structure	Typical Uses
aniline	$C_6H_5–NH_2$	starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
benzoic acid	$C_6H_5–COOH$	food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
bromobenzene	$C_6H_5–Br$	starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
nitrobenzene	$C_6H_5–NO_2$	starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
phenol	$C_6H_5–OH$	disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
toluene	$C_6H_5–CH_3$	solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

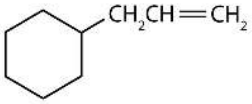
Example 2.5.1

Which compounds are aromatic?

1. 

2. 

3. 

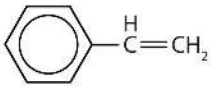
4. 

Solution

1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

? Exercise 2.5.1

Which compounds are aromatic?

1. 

2. 

3. 

Naming Aromatics

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named with the benzene ring serving as the parent chain. The name of these compounds provide details about the identity of the substituent(s) followed by benzene. If one substituent is present, no locator number is added. If two or more substituents are present, locator numbers must be assigned to each substituent.

Figure 2.5.1 shows examples of aromatic compounds containing one substituent. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

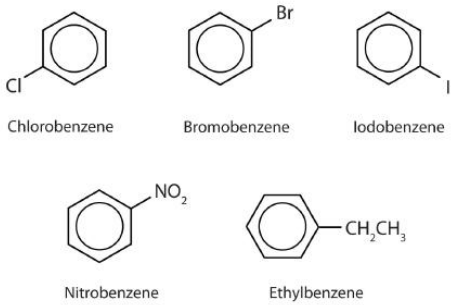


Figure 2.5.1: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO_2 as nitro, and CH_3CH_2 as ethyl.

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table **2.5.1**. Structures of some common aromatics typically referred to by their common names are shown below in Figure **2.5.2**



Figure **2.5.2**: Common aromatics that are frequently referred to by their common name.

When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. When the benzene ring has two substituents, there are three possible disubstituted benzenes that could be present. We use numbers to distinguish them (Figure **2.5.3**). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.

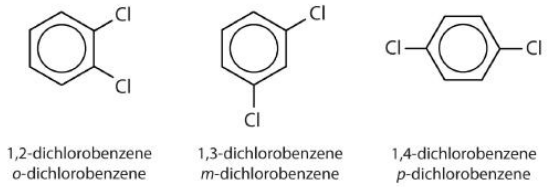


Figure **2.5.3**: Structures of the three isomeric dichlorobenzenes with the IUPAC name (top) and common name (bottom) of each.

In Figure **2.5.3**, common names are also used: the prefix

- *ortho* (*o*-) for 1,2-disubstitution,
- *meta* (*m*-) for 1,3-disubstitution, and
- *para* (*p*-) for 1,4-disubstitution.

The substituent names are listed in alphabetical order and the first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1. For example, when a methyl group is directly attached to a benzene ring, the common name of the molecule is toluene. If additional substituents are present, carbon 1 is assigned to the carbon bearing the methyl group.

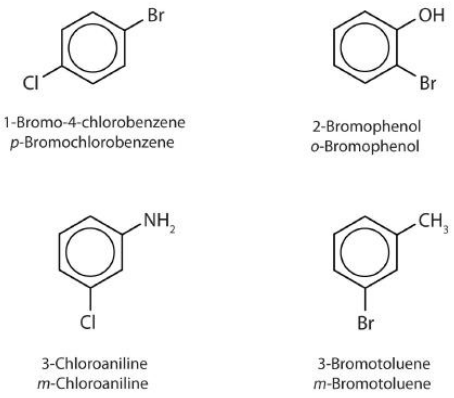
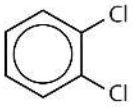
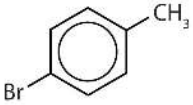


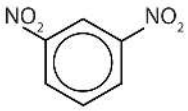
Figure **2.5.4**: Structures of disubstituted aromatics with the IUPAC (top) and common name (bottom) of each.

Example 2.5.2

Name each compound using both the common name and the IUPAC name.

1. 

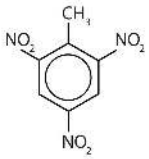
2. 

3. 

Solution

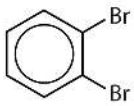
1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl (CH_3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro (NO_2) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.

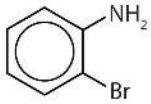
Note: The nitro (NO_2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).

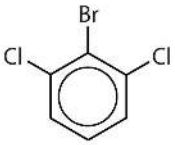


? Exercise 2.5.2

Name each compound using both the common name and the IUPAC name.

1. 

2. 

3. 

Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an **aryl group**. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a **phenyl group**, from *pheno*, an old name for benzene.

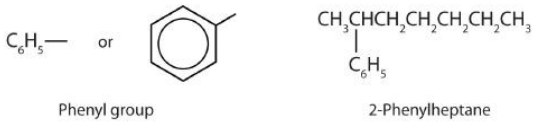


Figure **2.5.5**: Structures of phenyl group (left) and a phenyl-substituted molecule.

Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).

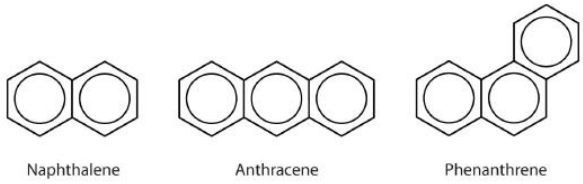


Figure **2.5.1**: Structures of common polycyclic aromatic hydrocarbons.

The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

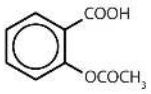
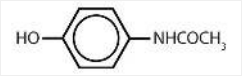
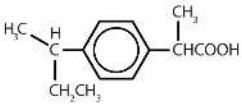
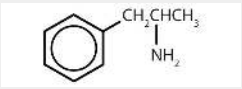
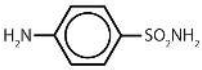
The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, B_2 (riboflavin), and B_9 (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table **2.5.2**, also feature a benzene ring.

> So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table **2.5.2**: Some Drugs That Contain a Benzene Ring

Name	Structure
aspirin	
acetaminophen	
ibuprofen	
amphetamine	
sulfanilamide	

Key Takeaway

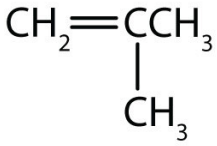
- Aromatic compounds contain a benzene ring or have certain benzene-like properties; for our purposes, you can recognize aromatic compounds by the presence of one or more benzene rings in their structure.
- IUPAC nomenclature of aromatics: location and identity of substituents + benzene

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2.E: Unsaturated Hydrocarbons (Exercises)

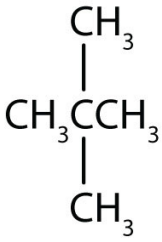
Additional Exercises

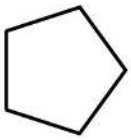
1. Classify each compound as saturated or unsaturated.

a. 

b. $CH_3C{\equiv}CCH_3$

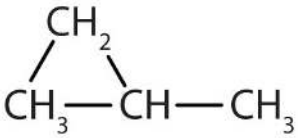
2. Classify each compound as saturated or unsaturated.

a. 

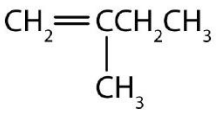
b. 

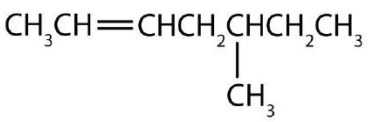
3. Give the molecular formula for each compound.

a. 

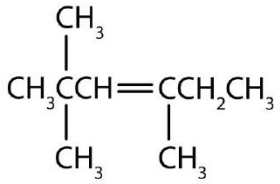
b. 

4. Name each compound according to the IUPAC system.

a. 

b. 

https://chem.libretexts.org/@go/page/338687

c. 

5. Draw and name all the alkene cis-trans isomers corresponding to the molecular formula C_5H_{10}. (Hint: there are only two.)

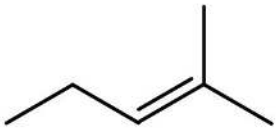
6. What is wrong with each name? Draw the structure and give the correct name for each compound.

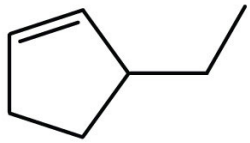
   a. 2-methyl-4-heptene
   b. 2-ethyl-2-hexene
   c. 2,2-dimethyl-3-pentene

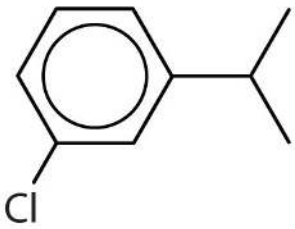
7. What is wrong with each name?

   a. 2-bromobenzene
   b. 3,3-dichlorotoluene
   c. 1,4-dimethylnitrobenzene

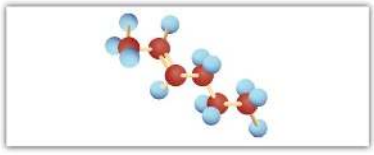
8. Following are line-angle formulas for three compounds. Draw the structure and give the name for each.

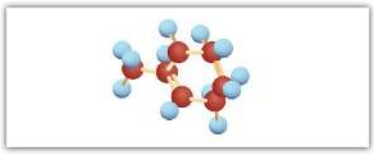
a. 

b. 

c. 

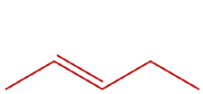
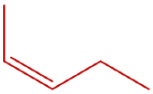
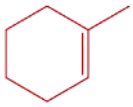
9. Following are ball-and-stick molecular models for three compounds (blue balls represent H atoms; red balls are C atoms). Provide the skeletal structure and give the name for each.

a. 

b. 

c. 

Answers

1. a. unsaturated
   b. unsaturated
3. a. C_6H_{10}
   b. C_4H_8
5.  
7. a. number not needed
   b. can't have two groups on one carbon atom on a benzene ring
   c. can't have a substituent on the same carbon atom as the nitro group
9. a.  ; 2-hexene
   b.  ; 1-methylcyclohexene
   c.  ; 3-methyl-2-pentene

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2.S: Unsaturated Hydrocarbons (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Any hydrocarbon containing either a double or triple bond is an **unsaturated hydrocarbon**. Organic molecules that have a carbon-carbon double bond are called **alkenes**. If the molecule contains two carbon-carbon double bonds, it is called a **diene**. When more than two carbon-carbon double bonds are present, the molecule is called a **polyene**. If the carbon-carbon double is present in a cyclic hydrocarbon, the molecule is called a **cycloalkene**.

The general formula for alkenes with one double bond is C_nH_{2n}. These molecules can be straight-chained, branched-chained, or cyclic. Simple alkenes often have common names, but all alkenes can be named by the system of the International Union of Pure and Applied Chemistry.

Cis-trans isomers (or geometric isomers) are characterized by molecules that differ only in their three-dimensional configuration around a rigid part of the structure, such as a carbon–carbon double bond or a ring. The molecule having two identical (or closely related) atoms or groups on the same side is the **cis isomer**; the one having the two groups on opposite sides is the **trans isomer**. When naming geometric isomers, the cis or trans designation is included as a prefix prior to identifying the substituents.

The physical properties of alkenes are quite similar to those of alkanes. Like other hydrocarbons, alkenes are insoluble in water but soluble in organic solvents.

Alkynes have a carbon-carbon triple bond. The general formula for alkynes is C_nH_{2n-2}. The properties of alkynes are quite similar to those of alkenes. They are named much like alkenes but with the *-yne* ending and no geometric isomers.

The cyclic hydrocarbon *benzene* (C_6H_6) has a ring of carbon atoms. The molecule seems to be unsaturated, but it does not undergo the typical reactions expected of alkenes. The electrons that might be fixed in three double bonds are instead *delocalized* over all six carbon atoms.

A hydrocarbon containing one or more benzene rings (or other similarly stable electron arrangements) is an **aromatic hydrocarbon**, and any related substance is an **aromatic compound**. One or more of the hydrogen atoms on a benzene ring can be replaced by other atoms. When two hydrogen atoms are replaced, the common name is based on the relative position of the replacement atoms (or atom groups). A 1,2-disubstituted benzene is designated as an *ortho* (*o*-) isomer; 1,3-, a *meta* (*m*-) isomer; and 1,4-, a *para* (*p*-) isomer. An aromatic group as a substituent is called an **aryl** group. When benzene is a substituent, it is called a **phenyl** group.

A **polycyclic aromatic hydrocarbon (PAH)** has fused benzene rings sharing a common side.

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CHAPTER OVERVIEW

3: Organic Nomenclature - Functional Groups

3.1: Functional Groups
3.2: Alcohols
3.3: Phenols
3.4: Ethers
3.5: Thiols
3.6: Amines - Structures and Names
3.E: Functional Groups (Exercises)
3.S: Functional Groups (Summary)

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3.1: Functional Groups

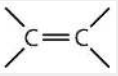
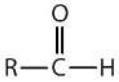
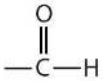
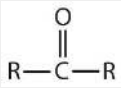
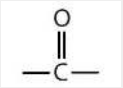
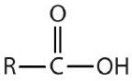
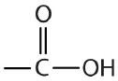
Learning Objectives

- to describe functional groups and explain why they are useful in the study of organic chemistry.

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups. **Functional groups** are specific structural arrangements of atoms or bonds that are used to classify organic compounds. Many functional groups contain oxygen, nitrogen, and sulfur, which are known as **heteroatoms**. These groups influence the physical properties of a compound and are responsible for the reactivity of families of organic compounds. If you understand the behavior of a particular functional group, you will know a great deal about the general properties of that class of compounds. In this chapter, we make a brief yet systematic study of some of the common organic compound families. Additional families will be covered in the next chapter.

Some common organic families and their functional groups are listed in Table **3.1.1**.

Table **3.1.1**: Selected Organic Functional Groups

Name of Family	General Formula	Functional Group	Suffix*
alkane	RH	none	*-ane*
alkene	$R_2C{=}CR_2$		*-ene*
alkyne	RC≡CR	–C≡C–	*-yne*
alcohol	ROH	–OH	*-ol*
thiol	RSH	–SH	*-thiol*
ether	ROR	–O–	ether
aldehyde			*-al*
ketone			*-one*
carboxylic acid			*-oic acid*

*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

Summary

The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.

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3.2: Alcohols

Learning Objectives

- Identify the general structure for an alcohol.
- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.
- Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
- Name alcohols with both common names and IUPAC names.

An **alcohol** is an organic compound with a hydroxyl (—OH) functional group on an aliphatic carbon atom. Because the hydroxyl (not to be confused with hydroxide) is the functional group of all alcohols, we often represent alcohols by the general formula R—OH, where R is an alkyl group. If the molecule contains two hydroxyl groups, the compound is referred to as a **diol**. If the alcohol has three hydroxyl groups, the molecule is called a **triol**. When multiple alcohol functional groups are present, the compound is known as a **polyol**.

Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are the first two members of the homologous series of alcohols.

Properties of Alcohols

Alcohols can be considered derivatives of water (H_2O; also written as HOH).



Figure **3.2.1**: Structural formula of water (left) and an alcohol (right).

Like the H–O–H bond in water, the R–O–H bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with a hydroxyl group allows the molecules to associate through hydrogen bonding (Figure **3.2.2**).

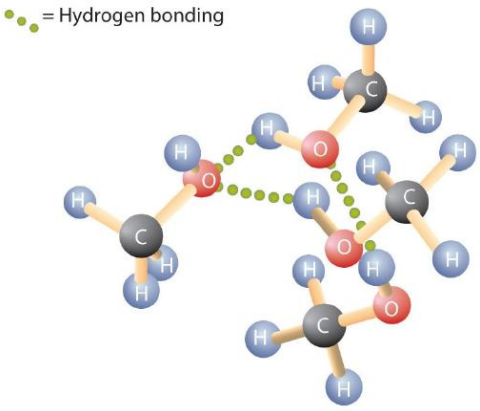


Figure **3.2.2**: Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table **3.2.1** lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table **3.2.1**: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point (°C)
CH_4	methane	16	–164
HOH	water	18	100
C_2H_6	ethane	30	–89
CH_3OH	methanol	32	65
C_3H_8	propane	44	–42
CH_3CH_2OH	ethanol	46	78
C_4H_{10}	butane	58	–1
$CH_3CH_2CH_2OH$	1-propanol	60	97

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules. Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names. The common names of alcohols indicate the identity of the alkyl group followed by the word alcohol (Figure **3.2.3**.

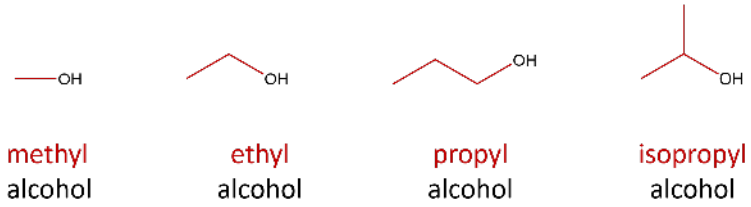


Figure **3.2.3**: Structure and common name of some small alcohols.

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

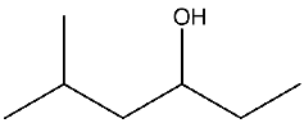


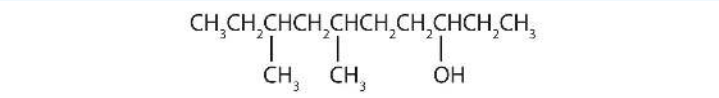
Figure **3.2.4**: Skeletal structure of a molecule that will be named as discussing the steps for naming alcohols.

1. The **longest continuous chain (LCC)** of carbon atoms containing the carbon that the OH group is attached to is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but the *-ane* suffix is replaced with *-ol* to identify it as an alcohol. *Thus the parent chain for the molecule in Figure* **3.2.4** *is a hexanol.*

2. The **parent chain is numbered to indicate the location of the hydroxyl group**. The carbon chain is numbered starting from the end nearest the OH group (even if this causes any substitutents to have a higher number). The number that indicates the position of the functional group is prefixed to the name of the parent hydrocarbon. The locator number may also be shown hyphenated between the stem prefix and -ol suffix. In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name. The number should always be shown in the acyclic molecules. *This parent chain represents 3-hexanol or hexan-3-ol.*
3. **Substituents are named and numbered** as in alkanes. These groups are listed in alphabetical order prior to the parent name. *According to these rules, the IUPAC name for the molecule shown in Figure* **3.2.4** *can be shown as 5-methyl-3-hexanol or 5-methylhexan-3-ol.*

✔ Example 3.2.1

Give the IUPAC name for each compound.

a. 

b. $CH_2CH_2CH_2CH_2CH_2OH$

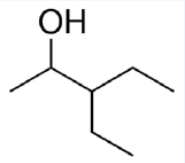
Solution

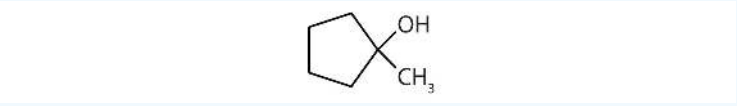
a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2). The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH_3) groups at the sixth and eighth positions (rule 3). The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

b. Five carbon atoms in the LCC make the compound a derivative of pentane. The OH group is on the first carbon and there are no substituents. This gives the name 1-pentanol.

? Exercise 3.2.1

Give the IUPAC name for each compound.

a. 

b. 

✔ Example 3.2.2

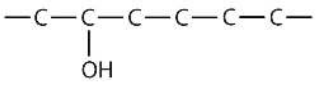
Draw the structure for each compound.

a. 2-hexanol

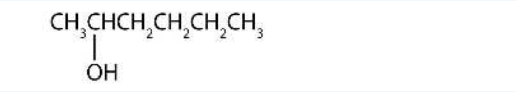
b. 3-methyl-2-pentanol

Solution

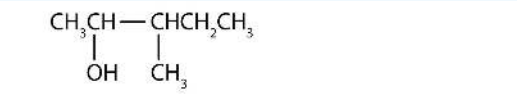
a. The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: –C–C–C–C–C–C–. The 2 indicates that the OH group is attached to the second carbon atom.



Finally, we add enough hydrogen atoms to give each carbon atom four bonds.



b. The ending *-ol* indicates an OH functional group, and the *pent-* stem tells us that there are five carbon atoms in the LCC. We start by drawing a chain of five carbon atoms: –C–C–C–C–C–. The numbers indicate that there is a methyl (CH_3) group on the third carbon atom and an OH group on the second carbon atom.



? Exercise 3.2.2

Draw the structure for each compound.

a. 3-heptanol

b. 2-methyl-3-hexanol

Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A **primary (1°) alcohol** is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is RCH_2OH.
- A **secondary (2°) alcohol** is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is R_2CHOH.
- A **tertiary (3°) alcohol** is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is R_3COH.

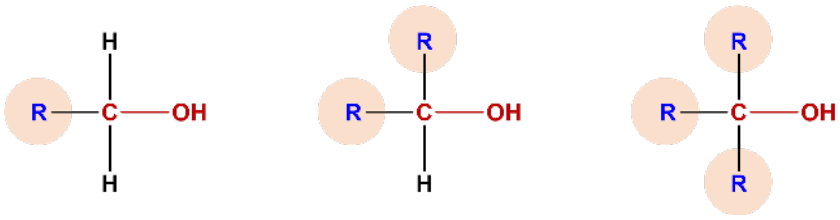


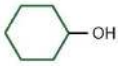
Figure **3.2.5**: Classification of Alcohols. Structures of primary (left), secondary (middle), and tertiary (right) alcohols. *R represents the rest of the molecule and can be an acyclic or cyclic group of carbon atoms.

Table **3.2.2** names and classifications of some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec–*) or tertiary (*tert–*). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group (—$CH_2CH_2CH_2CH_3$) discussed before, and three others:



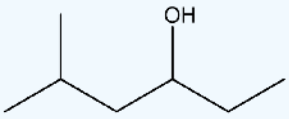
Figure **3.2.6**: Common names of butyl substituents.

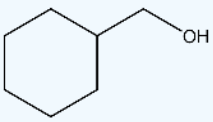
Table **3.2.2**: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH_3OH	—	methyl alcohol	methanol
CH_3CH_2OH	primary	ethyl alcohol	ethanol
$CH_3CH_2CH_2OH$	primary	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	secondary	isopropyl alcohol	2-propanol
$CH_3CH_2CH_2CH_2OH$	primary	butyl alcohol	1-butanol
$CH_3CH_2CHOHCH_3$	secondary	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	primary	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	tertiary	*tert*-butyl alcohol	2-methyl-2-propanol
	secondary	cyclohexyl alcohol	cyclohexanol

Example 3.2.3

Identify both of the the following as a primary, secondary, or tertiary alcohol.

a. 

b. 

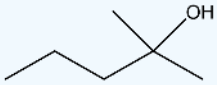
Solution

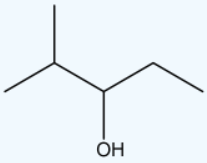
a. Secondary. First locate the functional group and identify the carbon that it is bonded to. Then determine how many carbon atoms are directly bonded to it. In this molecule, the functional group is bonded to C3. Since C3 is bonded to C2 and C4, this represents a secondary alcohol.

b. Primary. After locating the functional group and the carbon that it is bonded to, it appears that only one additional carbon is attached. Therefore, this represents a primary alcohol.

Exercise 3.2.3

Identify both of the the following as a primary, secondary, or tertiary alcohol.

a. 

b. 

Summary

- Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.
- IUPAC nomenclature of alcohols: location and identity of substituents + parent prefix (with location of functional group) + ol suffix
- Common name of alcohols: identity of alkyl group + alcohol

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3.3: Phenols

Learning Objectives

- Describe the structure and uses of some phenols.
- Generate the name of phenolic compounds.

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called **phenols**. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.

$$\mathrm{ArOH\,(aq) + NaOH\,(aq) \rightarrow ArONa\,(aq) + H_2O} \tag{3.3.1}$$

The parent compound, C_6H_5OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive ("hospital smell") odor.

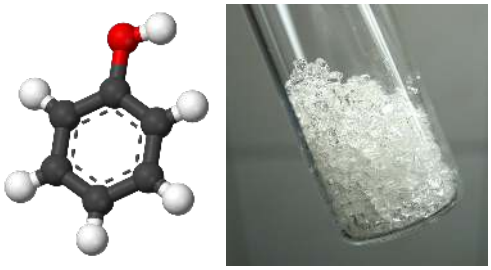


Figure 3.3.1: (Left) Structure of Phenol (right) Approximately two grams of phenol in glass vial. Image used with permisison from Wikipedia

To Your Health: Phenols and Us

Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.



Figure 3.3.2: *An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.*

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring). It is much more powerful than phenol as a germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.

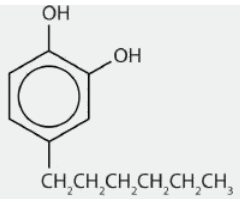


Figure **3.3.3**:*The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.*

Naming Phenols

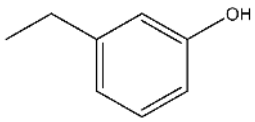
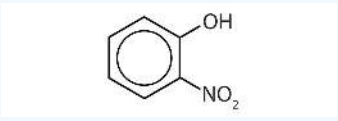


Figure **3.3.4**: Structure of a substitued phenol.

In the International Union of Pure and Applied Chemistry (IUPAC) system, the rules for naming phenols are similar to naming substituted aromatics. When naming phenols, the **parent name is phenol**. This accounts for the benzene ring and the hydroxyl attached to it. The **carbon atom bearing the OH group is designated C1**, but the 1 is not used in the name. The **location of substituents** is then determined using the shortest path. The location of all substituents (even if only one is present) must be shown. The name is then determine by indicating the location and identity of the substituents followed by the word phenol. According to these rules, the name of the molecule shown in Figure **3.3.4** would be *3-ethylphenol*.

✔ Example 3.3.1

Name each compound.

a. 

b. 

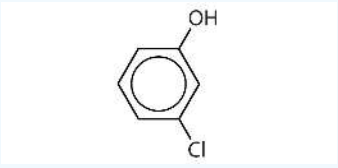
Solution

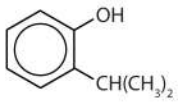
a. The parent chain is phenol and C1 would represent the carbon with the OH attached. There is one substituent present on the adjacent carbon, so the parent chain would be numbered clockwise to represent the shortest path. The substituent, which is identified as a nitro group, is on C2. Therefore, the name of the molecule is 2-nitrophenol (or o-nitrophenol).

b. The parent chain is phenol and C1 would represent the carbon with the OH attached. There is one substituent present on the carbon oppositie C1. In this position, the same number is obtained regardless of the chosen path. Therefore, the bromo substituent, is on C4. This indicates that the name of the molecule is 4-bromophenol (or p-bromophenol)

? Exercise 3.3.1

Name the following compounds.

a. 

b. 

Summary

- Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.
- IUPAC nomenclature of phenols: location and identity of substituents + phenol

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3.4: Ethers

Learning Objectives

- Describe the structural difference between an alcohol and an ether that affects physical characteristics and reactivity of each.
- Name simple ethers.
- Describe the structure and uses of some ethers.

With the general formula R–O–R′, an **ether** may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups. It may also be considered a derivative of an alcohol (R–OH) in which the hydrogen atom of the OH group is been replaced by a second alkyl or aryl group:

$$\mathrm{HOH} \xrightarrow[\text{H atoms}]{\text{replace both}} \mathrm{ROR'} \xleftarrow[\text{of OH group}]{\text{replace H atom}} \mathrm{ROH} \tag{3.4.1}$$

Simple ethers have simple common names, formed from the names of the groups attached to oxygen atom (listed in alphabetical order), followed by the generic name *ether*. For example, CH_3–O–$CH_2CH_2CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di-*, as in dimethyl ether (CH_3–O–CH_3) and diethyl ether (CH_3CH_2–O–CH_2CH_3).

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table **3.4.1**).

Table **3.4.1**: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3–O–CH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
CH_3CH_2–O–CH_2CH_3	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

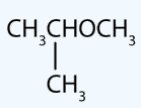
Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

Example 3.4.1

What is the common name for each ether?

a. $CH_3CH_2CH_2$–O–$CH_2CH_2CH_3$

b.



Solution

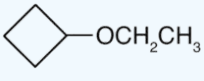
a. The carbon groups on either side of the oxygen atom are propyl ($CH_3CH_2CH_2$) groups, so the compound is dipropyl ether.

b. The three-carbon group is attached by the middle carbon atom, so it is an isopropyl group. The one-carbon group is a methyl group. The compound is isopropyl methyl ether.

? Exercise 3.4.1

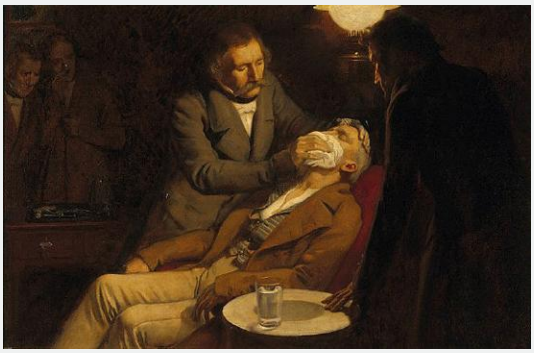
What is the common name for each ether?

a. $CH_3CH_2CH_2CH_2–O–CH_2CH_2CH_2CH_3$

b. 

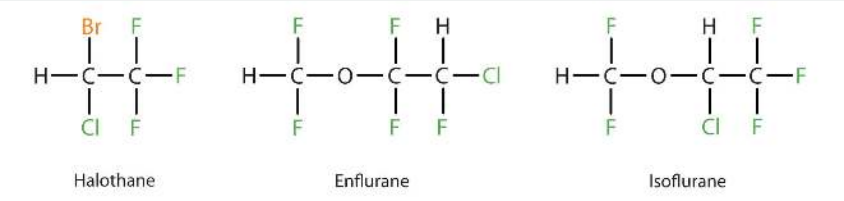
To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.



William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.

Summary

- To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*.
- Ether molecules have no OH group and thus no hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

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3.5: Thiols

Learning Objectives

- Identify thiols by the presence of an SH group.
- Identify thioethers by the presence of an R–S–R′ group

Because sulfur is in the same group (6A) of the periodic table as oxygen, the two elements have some similar properties. We might expect sulfur to form organic compounds related to those of oxygen, and indeed it does. **Thiols** (also called mercaptans) are organic molecules that contain a sulfhydryl (–SH) group. These compounds, which are sulfur analogs of alcohols, have the general formula R–SH. Methanethiol (also called methyl mercaptan), has the formula CH_3SH. Ethanethiol (ethyl mercaptan) is the most common odorant for liquid propane (LP) gas.

The mild oxidation of thiols gives compounds called disulfides.

$$2RSH \xrightarrow{[O]} RSSR \tag{3.5.1}$$

The amino acids cysteine [$HSCH_2CH(NH_2)COOH$] and methionine [$CH_3SCH_2CH_2CH(NH_2)COOH$] (Figure **3.5.1**) contain sulfur atoms, as do all proteins that contain these amino acids. Disulfide linkages (–S–S–) between protein chains are extremely important in protein structure.

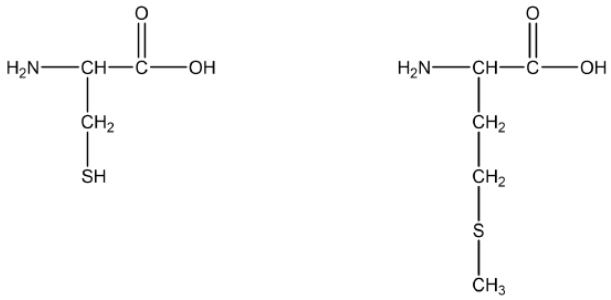


Figure **3.5.1**: Structure of cysteine (left) and methionine (right).

Thioethers, which are sulfur analogs of ethers, have the form general formula R–S–R′. An example is dimethylsulfide (CH_3–S–CH_3), which is responsible for the sometimes unpleasant odor of cooking cabbage and related vegetables. Note that methionine has a thioether functional group.

Career Focus: Paramedic

Paramedics are highly trained experts at providing emergency medical treatment. Their critical duties often include rescue work and emergency medical procedures in a wide variety of settings, sometimes under extremely harsh and difficult conditions. Like other science-based professions, their work requires knowledge, ingenuity, and complex thinking, as well as a great deal of technical skill. The recommended courses for preparation in this field include anatomy, physiology, medical terminology, and—not surprisingly—chemistry. An understanding of basic principles of organic chemistry, for example, is useful when paramedics have to deal with such traumas as burns from fuel (hydrocarbons) or solvent (alcohols, ethers, esters, and so on) fires and alcohol and drug overdoses.

To become a paramedic requires 2–4 y of training and usually includes a stint as an emergency medical technician (EMT). An EMT provides basic care, can administer certain medications and treatments, such as oxygen for respiratory problems and epinephrine (adrenalin) for allergic reactions, and has some knowledge of common medical conditions. A paramedic, in contrast, must have extensive knowledge of common medical problems and be trained to administer a wide variety of emergency drugs.

Paramedics usually work under the direction of a medical doctor with a title such as “medical director.” Some paramedics are employed by fire departments and may work from a fire engine that carries medical equipment as well as fire-fighting gear. Some work from hospital-sponsored ambulances and continue to care for their patients after reaching the hospital emergency

room. Still other paramedics work for a government department responsible for emergency health care in a specific geographical area. Finally, some work for private companies that contract to provide service for a government body.

An experienced paramedic has a broad range of employment options, including training for mountain or ocean rescue, working with police department special weapons and tactics (SWAT) teams, or working in isolated settings such as on oil rigs. With their expertise at treating and stabilizing patients before quickly moving them to a hospital, paramedics often provide the first critical steps in saving an endangered life. The following quotation, inscribed on the Arlington National Cemetery headstone of Army Lieutenant R. Adams Cowley, who is often called the "father" of shock trauma medicine, serves as the motto for many paramedic units: "Next to creating a life the finest thing a man can do is save one." —Abraham Lincoln

Naming Thiols

Rules for naming thiols are similar to rules for naming alcohols. Thiols are named by adding the word **–thiol** as the suffix of the parent name. The longest
carbon chain is then **numbered to give the sulfhydryl group the lowest possible number**.

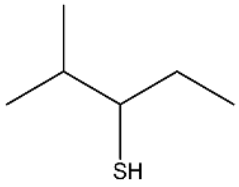
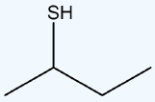


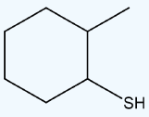
Figure **3.5.2**: Structure of a thiol.

Based on the rules for naming thiols, the molecule shown in Figure **3.5.2** would be named *2-methyl-3-pentanethiol (or 2-methylpentane-3-thiol)*. Since the functional group has priority in numbering, if the sulhydryl group is bonded to a ring, the carbon that it is bonded to is assigned to C1 and the number is omitted from the name.

? Exercise 3.5.1

Name the following compounds.

a. 

b. 

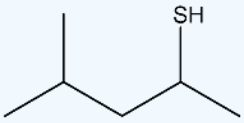
Answer

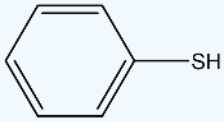
a. The longest continuous chain of carbon has four carbon atoms, so the stem name is butane. The parent name is obtained by adding the word thiol, to give butanethiol. We number from the left to give the sulfhydryl group the lowest number. Since there are no substituents present, the name of the molecule is *2-butanethiol (or butane-2-thiol)*.

b. The longest continuous chain of carbon has six carbon atoms in a ring, so the stem name is cyclohexane. The parent name is obtained by adding the word thiol, to give cyclohexanethiol. The carbon that has the sulfhydryl group is assigned as C1, since any carbon in the ring can be C1. The ring is then number counterclockwise to give the methyl substituent the lowest possible number. Therefore, the the name of the molecule is *2-methylcyclohexanethiol*.

Exercise 3.5.1

Name the following compounds.

a. 

b. 

Summary

- Thiols, thioethers, and disulfides are common in biological compounds that contain carbon.
- Nomenclature of thiols: location and identity of substituents + parent alkane + thiol suffix (with location of functional group)

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3.6: Amines - Structures and Names

Learning Objectives

- Identify the general structure for an amine.
- Determine the structural feature that classifies amines as primary, secondary, or tertiary.
- Generate common names of amines.
- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

An **amine** is an organic derivative of ammonia (NH_3) where one or more of the hydrogen atoms is replaced with a carbon group. Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A **primary (1°) amine** has one alkyl (or aryl) group on the nitrogen atom, a **secondary (2°) amine** has two, and a **tertiary (3°) amine** has three (Figure **3.6.1**).

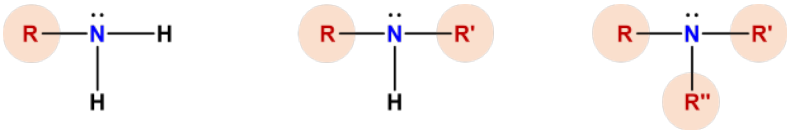


Figure **3.6.1**: Structures of a primary (left), secondary (middle), and tertiary (right) amine.

Note

To classify alcohols, we look at the number of carbon atoms bonded to the *carbon atom* bearing the OH group, not the oxygen atom itself. Thus, although isopropylamine looks similar to isopropyl alcohol, the former is a *primary* amine, while the latter is a *secondary* alcohol.

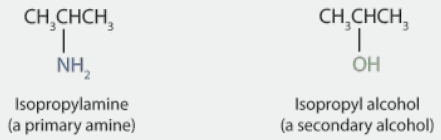


Figure **3.6.2**: Structures of isopropylamine (left) and isopropyl alcohol (right).

Physical Properties of Amines

Primary and secondary amines have hydrogen atoms bonded to an nitrogen atom and are therefore capable of hydrogen bonding (**3.6.3*a***), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine (CH_3NH_2; −6°C) with those of ethane (CH_3CH_3; −89°C) and methanol (CH_3OH; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table **3.6.1**).

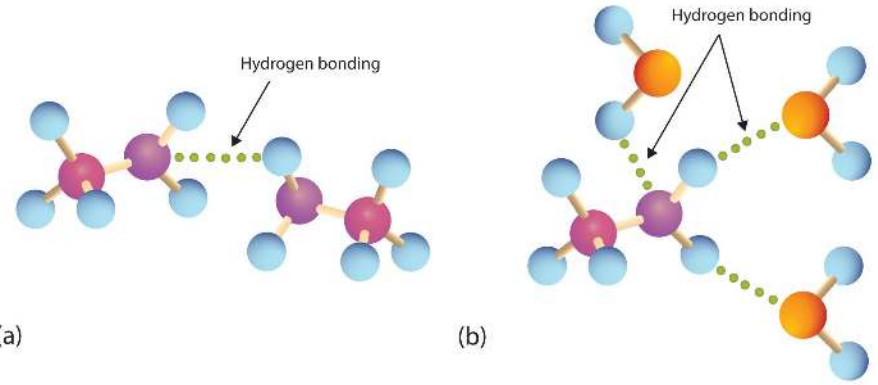


Figure **3.6.3**: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

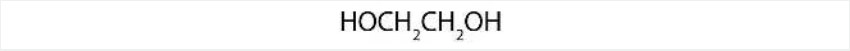
Table **3.6.1**. Comparison of properties of amines and oxygen-containing molecules.

Name	Condensed Structure	Classification	Molar Mass (g/mol)	Boiling Point (°C)	Solubility at 25 °C (g/100 g water)
butylamine	$CH_3CH_2CH_2CH_2NH_2$	1°	73	78	miscible
diethylamine	$(CH_3CH_2)_2NH$	2°	73	55	miscible
butyl alcohol	$CH_3CH_2CH_2CH_2OH$	—	74	118	8
dipropylamine	$(CH_3CH_2CH_2)_2NH$	2°	101	111	4
triethylamine	$(CH_3CH_2)_3N$	3°	101	90	14
dipropyl ether	$(CH_3CH_2CH_2)_2O$	—	102	91	0.25

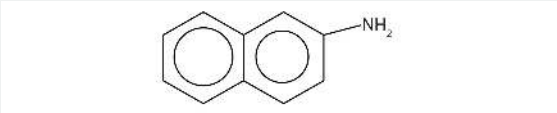
All three classes of amines can engage in hydrogen bonding with water (Figure **3.6.3*b***). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.



Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.



Naming Amines

The common names for simple aliphatic amines consist of an alphabetic list of alkyl groups attached to the nitrogen atom, followed by the suffix ***-amine***. The amino group (NH_2) is named as a substituent in more complicated amines, such as those that incorporate

other functional groups or in which the alkyl groups cannot be simply named.

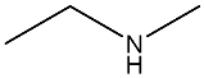


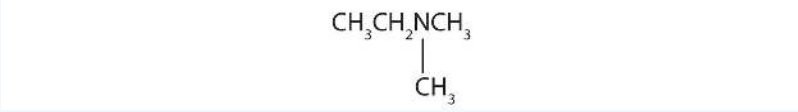
Figure **3.6.4**: Structure of a simple amine.

Determining the classification of an amine can help with identifying the common name. Since the above amine has two carbon groups attached to the nitrogen, it represents a secondary amine. This indicates that two carbon groups should be identified and included in the common name. The group to the left of the nitrogen represents an ethyl group and the group to the right is a methyl group. Therefore, the common name of the amine shown in Figure **3.6.4** is *ethylmethylamine*.

Example 3.6.1

Name and classify each compound.

a. $CH_3CH_2CH_2NH_2$

b. 

c. $CH_3CH_2NHCH_2CH_3$

d. $CH_3CH_2CH_2NHCH_3$

Solution

a. There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is propylamine.

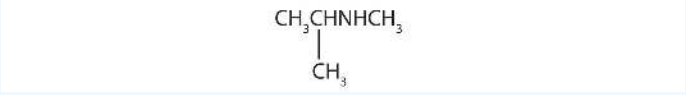
b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is ethyldimethylamine, a tertiary amine.

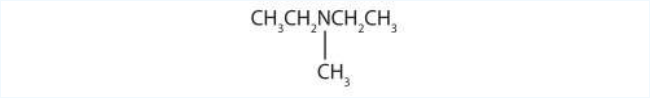
c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is diethylamine.

d. The nitrogen atom has a methyl group and a propyl group, so the compound is methylpropylamine, a secondary amine.

Exercise 3.6.1

Name and classify each compound.

a. 

b. 

c. $CH_3CH_2CH_2CH_2NH_2$

d. $CH_3CH_2CH_2NHCH_2CH_2\ CH_3$

Example 3.6.2

Draw the structure for each compound and classify.

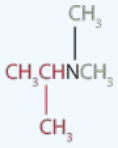
a. isopropyldimethylamine

b. dipropylamine

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Solution

a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.



b. The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) $CH_3CH_2CH_2NHCH_2CH_2CH_3$

Exercise 3.6.2

Draw the structure for each compound and classify.

a. ethylisopropylamine
b. diethylpropylamine

The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—**aniline**. Aryl amines are named as derivatives of aniline.

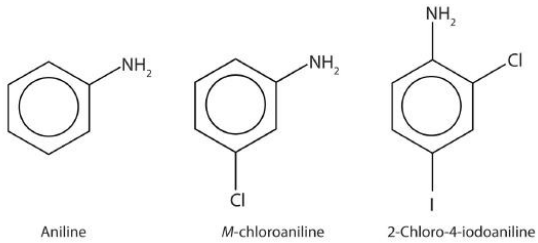
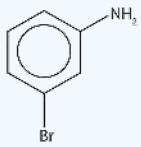


Figure **3.6.5**: Structure of anlinine (left) and its derivatives.

Example 3.6.3

Name this compound.

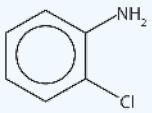


Solution

The benzene ring with an amino (NH_2) group is aniline. The compound is named as a derivative of aniline: 3-bromoaniline or *m*-bromoaniline.

Exercise 3.6.3

Name this compound.

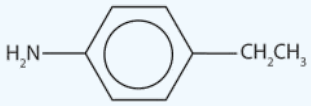


Example 3.6.4

Draw the structure for *p*-ethylaniline and classify.

Solution

The compound is a derivative of aniline. It is a primary amine having an ethyl group located *para* to the amino (NH_2) group.



Exercise 3.6.4

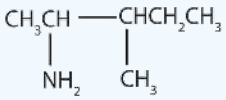
Draw the structure for *p*-isopropylaniline and classify.

Example 3.6.5

Draw the structure for 2-amino-3-methylpentane.

Solution

Always start with the parent compound: draw the pentane chain. Then attach a methyl group at the third carbon atom and an amino group at the second carbon atom.



Exercise 3.6.5

Draw the structure for 2-amino-3-ethyl-1-chloroheptane.

Chemical Behavior of Amines

Amines behave as weak Brønsted-Lowry bases in water. These weak bases gain protons from water to form a **protonated amine** (Figure **3.6.6**).

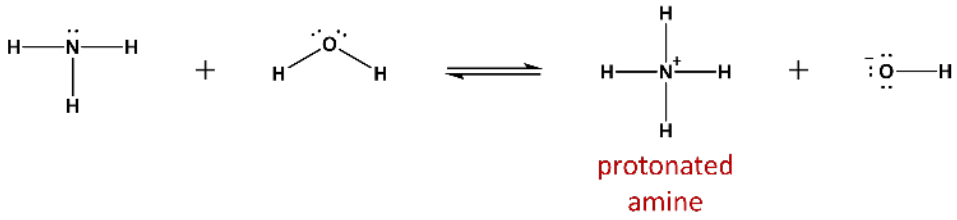


Figure **3.6.6**: Acid-base reaction where the amine gains a proton from water to form a protonated amine.

When an amine is neutralized by an acid, an **amine salt** is produced (Figure **3.6.7**).

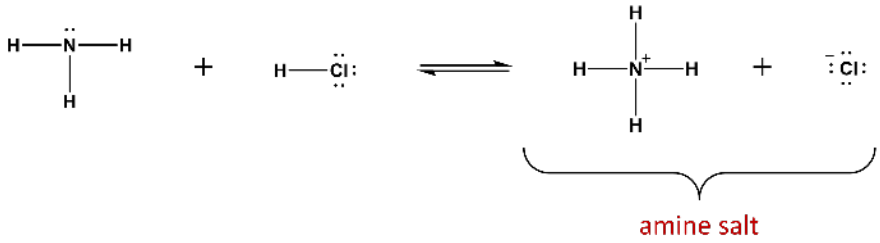


Figure **3.6.7**: Acid-base reaction where the amine gains a proton from a strong acid to form an amine salt.

Ammonium (NH_4^+) ions, in which one or more hydrogen atoms are replaced with alkyl groups, are named in a manner analogous to that used for simple amines. The alkyl groups are named as substituents, and the parent species is regarded as the NH_4^+ ion. For example, $CH_3NH_3^+$ is the methylammonium ion. The ion formed from aniline ($C_6H_5NH_3^+$) is called the anilinium ion.

Example 3.6.6

Name each ion.

a. $CH_3NH_3^+$
b. $(CH_3)_2NH_2^+$
c. $(CH_3)_3NH^+$
d. $(CH_3)_4N^+$

Solution

The ions have one, two, three, and four methyl (CH_3) groups attached to a nitrogen atom. Their names are as follows:

a. methylammonium ion
b. dimethylammonium ion
c. trimethylammonium ion
d. tetramethylammonium ion

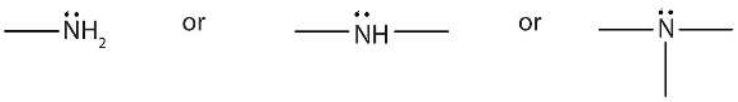
Exercise 3.6.6

Name each ion.

a. $CH_3CH_2NH_3^+$
b. $(CH_3CH_2)_3NH^+$
c. $(CH_3CH_2CH_2)_2NH_2^+$
d. $(CH_3CH_2CH_2CH_2)_4N^+$

Summary

- An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. Amines are classified as primary, secondary, or tertiary based on the number of hydrocarbon groups attached to the nitrogen atom. The amine functional group is as follows:



- Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

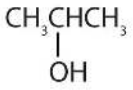
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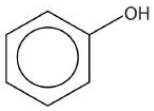
3.E: Functional Groups (Exercises)

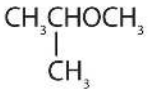
Additional Exercises

1. Identify each compound as an alcohol, a phenol, or an ether. Classify any alcohols as primary (1°), secondary (2°), or tertiary (3°).

   a. $CH_3CH_2CH_2OH$

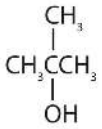
   b. 

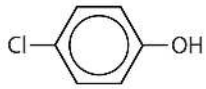
   c. 

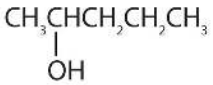
   d. 

2. Identify each compound as an alcohol, a phenol, or an ether. Classify any alcohols as primary, secondary, or tertiary.

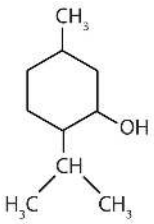
   a. $CH_3CH_2OCH_2CH_3$

   b. 

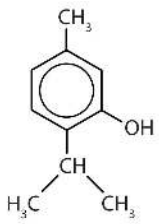
   c. 

   d. 

3. In addition to ethanol, the fermentation of grain produces other organic compounds collectively called fusel oils (FO). The four principal FO components are 1-propanol, isobutyl alcohol, 3-methyl-1-butanol, and 2-methyl-1-butanol. Draw a structure for each. (FO is quite toxic and accounts in part for hangovers.)
4. Draw and name the isomeric ethers that have the formula $C_5H_{12}O$.
5. Menthol is an ingredient in mentholated cough drops and nasal sprays. It produces a cooling, refreshing sensation when rubbed on the skin and so is used in shaving lotions and cosmetics. Thymol, the aromatic equivalent of menthol, is the flavoring constituent of thyme.



Menthol

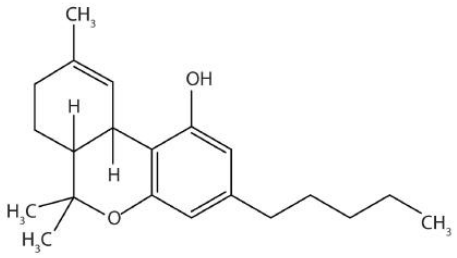


Thymol

a. To what class of compounds does each belong?

b. Give an alternate name for thymol.

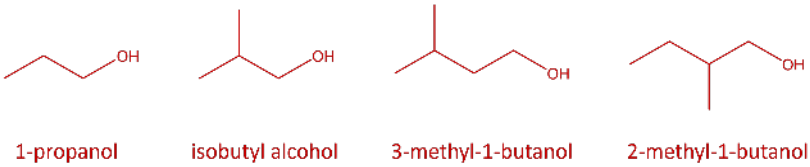
6. The amino acid cysteine has the formula $HSCH_2CH(NH_2)COOH$. What is the sulfur-containing functional group in the cysteine molecule?
7. The amino acid methionine has the formula $CH_3SCH_2CH_2CH(NH_2)COOH$. What is the sulfur-containing functional group are in methionine?
8. Tetrahydrocannabinol is the principal active ingredient in marijuana. What functional groups are present in this molecule?



9. Name each compound.
   a. $(CH_3CH_2)_3N$
   b. $(CH_3CH_2)_2NCH_3$
10. Draw the structure for each compound.
    a. dimethylammonium chloride
    b. anilinium chloride
11. Name each compound.
    a. $CH_3CH_2CH_2CH_2OCH_3$
    b. $CH_3CH_2OCH_2CH_2CH_3$
12. Draw the structure for each compound.
    a. methyl ethyl ether
    b. diisopropyl ether
13. Draw the structure for each alcohol.
    a. cyclopentanol
    b. 4-methyl-2-hexanol
    c. 4,5-dimethyl-3-heptanol

Answers

1. a. primary alcohol
   b. secondary alcohol
   c. phenol
   d. ether

3. 

1-propanol isobutyl alcohol 3-methyl-1-butanol 2-methyl-1-butanol

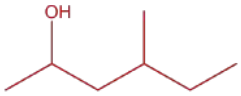
5. a. Menthol is a cyclic alcohol (secondary) and thymol is a phenol.
   b. 2-isopropyl-5-methylphenol

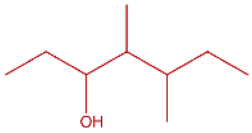
7. Thioether

9. a. triethylamine
   b. diethylmethylamine

11. a. butyl methyl ether
    b. ethyl propyl ether

13. a. 

    b. 

    c. 

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3.S: Functional Groups (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the summary and ask yourself how they relate to the topics in the chapter.

A **functional group** is any atom or atom group that confers characteristic properties to a family of compounds.

The hydroxyl group (OH) is the functional group of the **alcohols**. The alcohols are represented by the general formula ROH. Alcohols are derived from alkanes by replacing one or more hydrogen atoms by an OH group. A **primary (1°) alcohol** (RCH_2OH) has the OH group on a carbon atom attached to one other carbon atom; a **secondary (2°) alcohol** (R_2CHOH) has the OH group on a carbon atom attached to two other carbon atoms; and a **tertiary (3°) alcohol** (R_3COH) has the OH group on a carbon atom attached to three other carbon atoms.

The ability to engage in hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. Alcohols can also engage in hydrogen bonding with water molecules, and those with up to about four carbon atoms are soluble in water.

Rubbing alcohol is usually a 70% aqueous solution of isopropyl alcohol. Ethanol is also used in some rubbing alcohol formulations.

Alcohols can be named using the IUPAC or common systems. The IUPAC nomenclature of alcohols is determined as: location and identity of substituents + parent prefix (with location of functional group) + ol suffix. The common name of alcohols is identified as: identity of alkyl group + alcohol .

Phenols (ArOH) are compounds having the OH group attached to an aromatic ring. IUPAC nomenclature of phenols: location and identity of substituents + phenol

Ethers (R–O–R′, R–O–Ar, Ar–O–Ar) are compounds in which an oxygen atom is joined to two organic groups. Ether molecules have no OH group and thus no hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it. To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*.

A **thiol** is a compound with a sulhydryl (SH) functional group. **Thioethers** are sulfur analogs of ethers that have the form general formula R–S–R′. The name of thiols is determined by: location and identity of substituents + parent alkane + thiol suffix (with location of functional group).

Amines are derivatives of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. A **primary (1°) amine** (RNH_2) has one carbon atom attached to the nitrogen of the functional group; a **secondary (2°) amine** (R_2NH) has two carbon atoms attached to the nitrogen; and a **tertiary (3°) amine** (R_3N) has three carbon atoms attached to the nitrogen. Common names of amines indicate the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

The physical properties of the the amines may vary depending on the classification. Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative. The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass. Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

Amines are weak bases, so they are able to accept protons from acids. When an amine reacts with water, a **protonated amine** is produced. If the amine reacts with a strong acid, a salt, often referred to as an **amine salt**, is produced.

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CHAPTER OVERVIEW

4: Organic Nomenclature - Carbonyl-Containing Compounds

4.1: Aldehydes and Ketones
4.2: Properties of Aldehydes and Ketones
4.3: Carboxylic Acids
4.4: Physical Properties of Carboxylic Acids
4.5: Esters
4.6: Physical Properties of Esters
4.7: Amides
4.8: Physical Properties of Amides
4.E: Carbonyl-Containing Compounds (Exercises)
4.S: Carbonyl-Containing Compounds (Summary)

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4.1: Aldehydes and Ketones

Learning Objectives

- Identify the general structure for an aldehyde and a ketone.
- Use common names to name aldehydes and ketones.
- Use the IUPAC system to name aldehydes and ketones.

The next group we consider, the **carbonyl group**, represents a carbon-oxygen double bond. The carbon of the carbonyl group also has two single bonds to other atoms/groups. One of the bonds is usually to another R group and the other bond distinguishes the functional group.



Figure 4.1.1: Structure of the carbonyl group.

> *The carbonyl group is ubiquitous in biological compounds. It is found in carbohydrates, fats, proteins, nucleic acids, hormones, and vitamins—organic compounds critical to living systems.*

Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones. In an **aldehyde**, at least one of the groups attached to the carbonyl carbon must be a hydrogen atom. The following general formulas, in which R represents an alkyl group and Ar stands for an aryl (aromatic) group, are aldehydes:

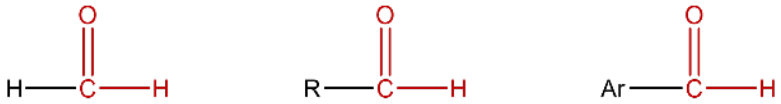


Figure 4.1.2: General structures of aldehydes.

In a **ketone**, two carbon groups are attached to the carbonyl carbon atom. The carbon groups can be identical or different. The following general formulas represent ketones.

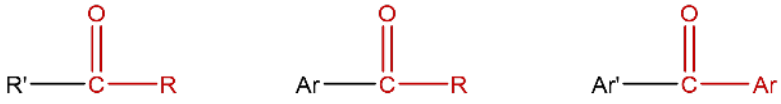


Figure 4.1.3: General structures of ketones.

In condensed formulas, we use CHO to identify an aldehyde rather than COH, which might be confused with an alcohol. This follows the general rule that in condensed structural formulas H comes after the atom it is attached to (usually C, N, or O). The carbon-oxygen double bond is not shown but understood to be present. Because they contain the same functional group, aldehydes and ketones share many common properties, but they still differ enough to warrant their classification into two families.



Figure 4.1.4: Condensed structures of aldehydes and ketones.

Naming Aldehydes and Ketones

Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.

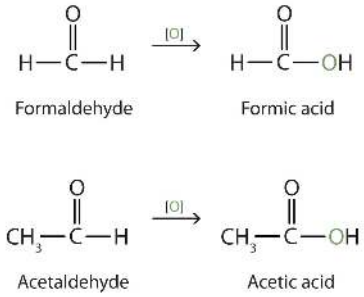


Figure **4.1.5**: Aldehydes with common names and the organic acid they can form.

The stems for the common names of the first four aldehydes are as follows:

- 1 carbon atom: *form-*
- 2 carbon atoms: *acet-*
- 3 carbon atoms: *propion-*
- 4 carbon atoms: *butyr-*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as ***acetone***, a unique name unrelated to other common names for ketones.

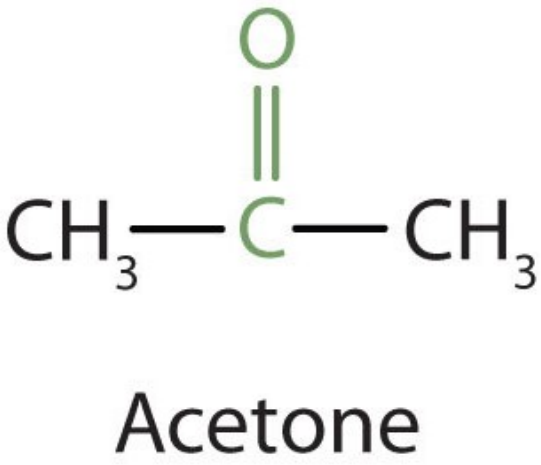


Figure **4.1.6**: Structure of acetone.

Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone (Figure **4.1.7**:) .

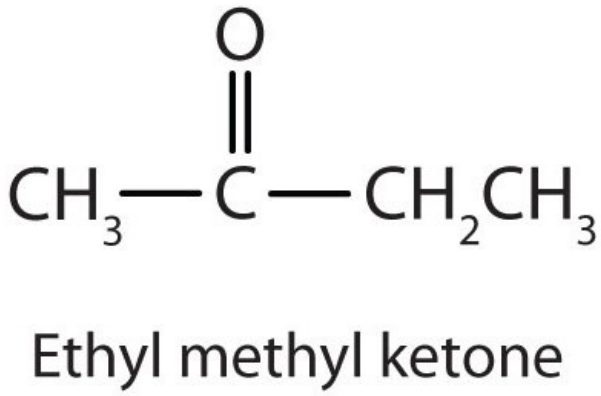
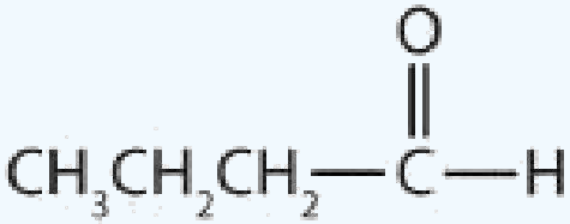


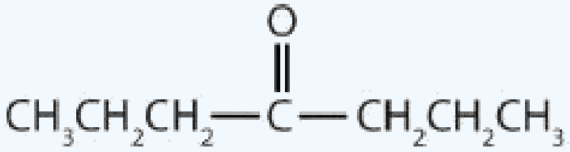
Figure 4.1.7: Structure of ethyl methyl ketone.

Example 4.1.1

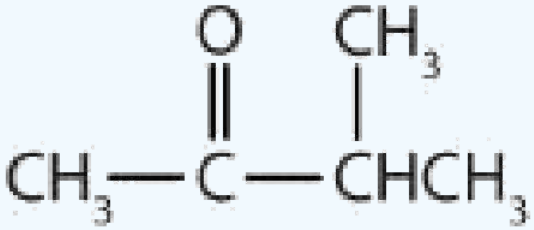
Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.



a.



b.



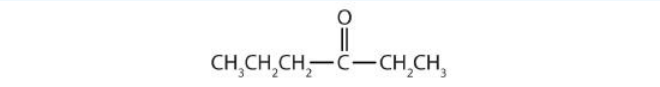
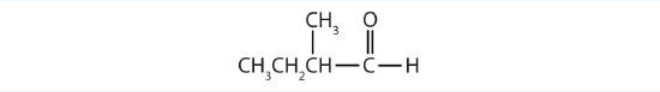
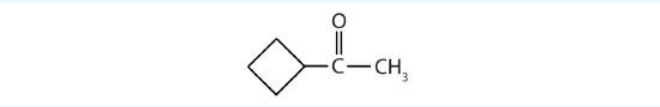
c.

Solution

1. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.
2. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.
3. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

Exercise 4.1.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

1. 
2. 
3. 

Here are some simple IUPAC rules for naming aldehydes and ketones:

1. The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the **longest continuous chain (LCC) of carbon atoms that contains the functional group**.
   a. For an **aldehyde**, drop the *-e* from the alkane name and add the ending ***-al.*** Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
   b. For a **ketone**, drop the *-e* from the alkane name and add the ending ***-one***. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
2. **Number the parent chain** to determine the location of atoms present in the molecule.
   a. To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
   b. To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.
3. **Substituents are named and numbered** as in alkanes. These groups are listed in alphabetical order prior to the parent name. *According to these rules, the IUPAC name for the molecule shown below in Figure* **4.1.8** *is 5-methylhexanal.*

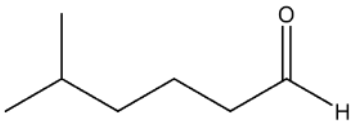
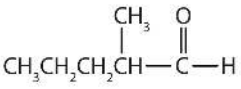
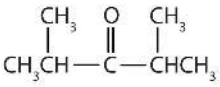


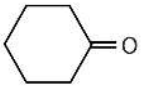
Figure **4.1.8**: Skeletal structure of an aldehyde named using IUPAC rules.

Example 4.1.2

Give the IUPAC name for each compound.

a. 

b. 

c. 

Solution

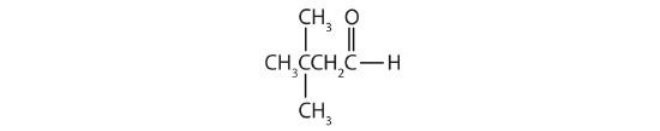
a. There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.

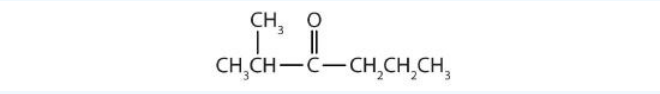
b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.

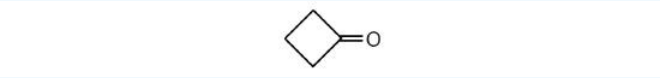
c. There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

Exercise 4.1.2

Give the IUPAC name for each compound.

a. 

b. 

c. 

Example 4.1.3

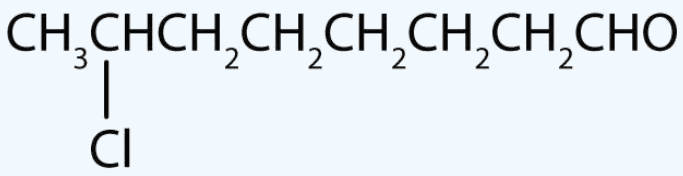
Draw the structure for each compound.

a. 7-chlorooctanal

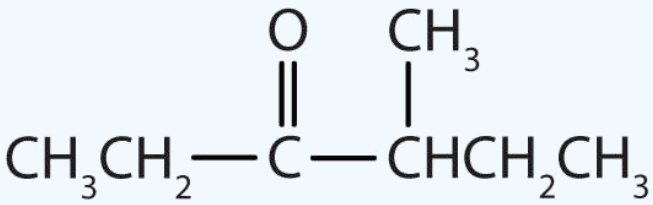
b. 4-methyl–3-hexanone

Solution

a. The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.



b. The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH_3) group at C4:



? Exercise 4.1.3

Draw the structure for each compound.

a. 5-bromo-3-iodoheptanal
b. 5-bromo-4-ethyl-2-heptanone

Summary

- IUPAC names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.
  - aldehydes: location and identity of substituents + parent stem name + al suffix
  - ketones: location and identity of substituents + parent stem name (with location of functional group) + one suffix
- The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. Common name of aldehydes: name based on number of carbon in alkyl group + aldehyde.
  - 1 carbon atom: *form-*
  - 2 carbon atoms: *acet-*
  - 3 carbon atoms: *propion-*
  - 4 carbon atoms: *butyr-*
- The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Common name of ketones: identities of alkyl groups (in alphabetical order) + aldehyde.

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4.2: Properties of Aldehydes and Ketones

Learning Objectives

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Describe some of the uses of common aldehydes and ketones.

The carbon-oxygen double bond is quite polar, more polar than a carbon-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge:

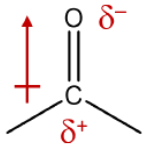


Figure 4.2.1: Polarity of the carbonyl group.

In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 4.2.1 shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

Table 4.2.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass (g/mol)	Type of Intermolecular Forces	Boiling Point (°C)
$CH_3CH_2CH_2CH_3$	alkane	58	dispersion only	–1
$CH_3OCH_2CH_3$	ether	60	weak dipole	6
CH_3CH_2CHO	aldehyde	58	strong dipole	49
$CH_3CH_2CH_2OH$	alcohol	60	hydrogen bonding	97

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.

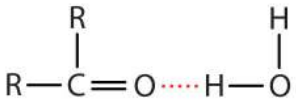


Figure 4.2.2: Hydrogen bonding between the carbonyl and water.

The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about

four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

Some Common Carbonyl Compounds

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms.

> *The odor of green leaves is due in part to a carbonyl compound, cis-3-hexenal, which with related compounds is used to impart a "green" herbal odor to shampoos and other products.*

Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure **4.2.3**).

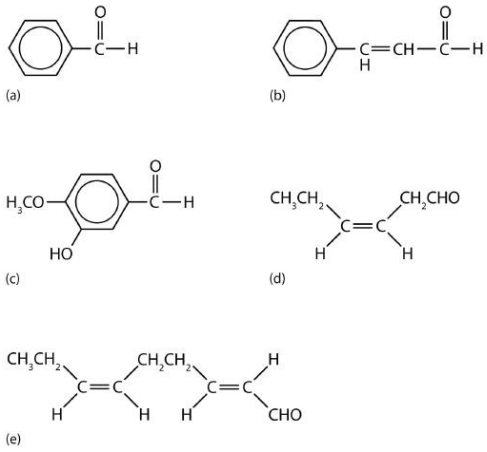


Figure **4.2.3** Some common carbonyl-containing compounds. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

Acetone is the simplest and most important ketone. Because it is miscible (mixes with) with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail polish remover.

To Your Health: Acetone in Blood, Urine, and Breath

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.

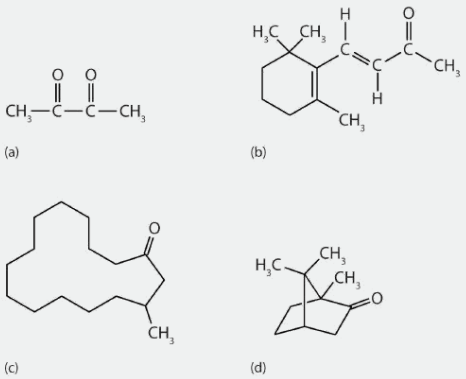


Figure **4.2.4**: Some ketones have interesting properties: (a) Butter flavoring comes from 2,3-butanedione; (b) β-ionone is responsible for the odor of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents.

Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone and testosterone (Figure **4.2.5**).

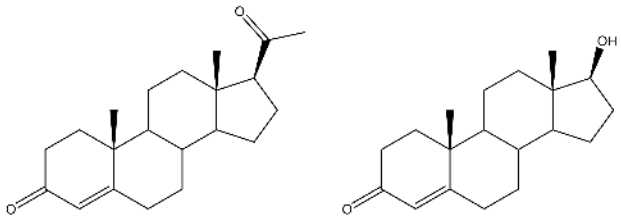


Figure **4.2.5**: Structures of progesterone (left) and testosterone (right).

Progesterone is a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg. Testosterone is the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

✔ Example 4.2.1

Which compound in each pair has the higher boiling point?

a. acetone or 2-propanol

b. dimethyl ether or acetaldehyde

Solution

a. 2-propanol. Acetone is a ketone and has dipole-dipole intermolecular forces as its strongest force of attraction. However, 2-propanol is an alcohol and will participate in hydrogen bonding. Since hydrogen bonding is a stronger force, the alcohol will require more energy (heat) to disrupt those forces.

b. Acetaldehyde. Both molecules will participate in dipole-dipole forces. However, the dipole-dipole attractions are stronger in the aldehyde due to the presence of the carbon-oxygen double bond (which is more polar than the carbon-oxygen single bond).

? Exercise 4.2.1

Which compound in each pair has the higher boiling point?

a. butanal or 1-butanol

b. acetone or isobutane

Summary

The polar carbon-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols that engage in intermolecular hydrogen bonding.

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4.3: Carboxylic Acids

Learning Objectives

- Name carboxylic acids with common names.
- Name carboxylic acids according to IUPAC nomenclature.

A common carbonyl-containing organic molecule is the **carboxylic acid.** A carboxylic acid contains a **carboxyl group**, which is formed when a hydroxyl group (–OH) is attached to the carbon of a carbonyl group.

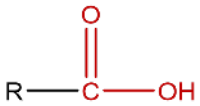


Figure **4.3.1**: General structure of a carboxylic acid with the carboxyl group shown in red.

Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure **4.3.2**). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



Figure **4.3.2**: Carboxylic Acids in the Home. Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock

Common Carboxylic Acids

The simplest carboxylic acid, formic acid (HCOOH), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).



Figure **4.3.3**: Structure of formic acid.

The next higher homolog is acetic acid, which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Figure **4.3.4**: Structure of acetic acid.

> Pure acetic acid solidifies at 16.6°C, only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often "froze" on the storage shelf. For that reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid (CH_3CH_2COOH), is seldom encountered in everyday life. The fourth homolog, butyric acid ($CH_3CH_2CH_2COOH$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives.

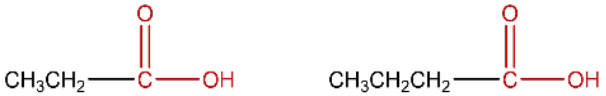


Figure **4.3.5**: Structures of propionic acid (left) and butyric acid (right).

The acid with the carboxyl group attached directly to a benzene ring is called benzoic acid (C_6H_5COOH).



Figure **4.3.6**: Structure of benzoic acid.

Naming Carboxylic Acids

Both common and International Union of Pure and Applied Chemistry (IUPAC) names are used for carboxylic acids. The common names of carboxylic acids use Greek letters (α, β, γ, δ, and so forth), not numbers, to designate the position of substituents in acids. These letters refer to the position of the carbon atom in relation to the carboxyl carbon atom.

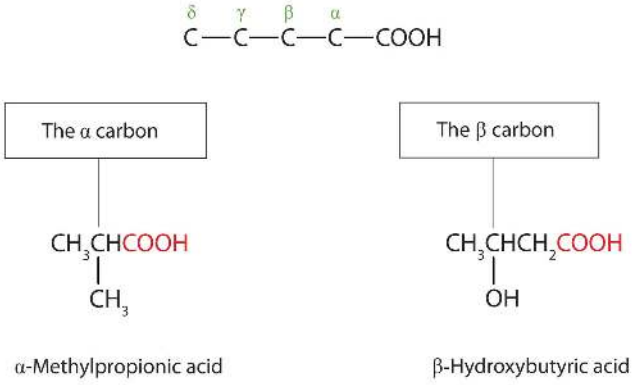


Figure **4.3.7**: Locator guidelines used in common names of carboxylic acids.

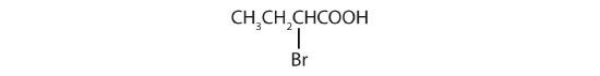
Here are some simple IUPAC rules for naming carboxylic acids:

1. The parent hydrocarbon is the one that corresponds to the **longest continuous chain (LCC) containing the carboxyl group**. The parent name is determining by replacing the *-e* ending of the parent alkane with the **suffix *-oic* and the word *acid* *(-oic acid)***.
2. **Number the parent chain** to determine the location of atoms present in the molecule. As with aldehydes, the **carboxyl carbon atom is always assigned to C1**. It is unnecessary to designate this group by number.
3. **Substituents are named and numbered** as in alkanes. These groups are listed in alphabetical order prior to the parent name. *According to these rules, the IUPAC name for the molecules shown above in* Figure **4.3.7** are 2-methylpropanoic acid (left) and 3-hydroxybutanoic acid (right).

Greek letters are used with common names; numbers are used with IUPAC names.

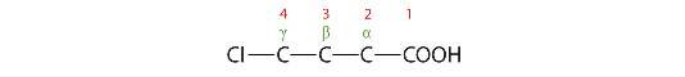
✔ Example 4.3.1

Give the common and IUPAC names for each compound.

1. $ClCH_2CH_2CH_2COOH$
2. 

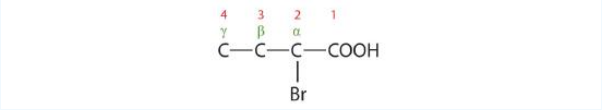
Solution

1. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The chlorine atom is attached to the γ-carbon in the common system or C4 in the IUPAC system. The compound is γ-chlorobutyric acid or 4-chlorobutanoic acid.

2. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The bromine (Br) atom is at the α-carbon in the common system or C2 in the IUPAC system. The compound is α-bromobutyric acid or 2-bromobutanoic acid.

? Exercise 4.3.1

Give the IUPAC name for each compound.

a. $ClCH_2CH_2CH_2CH_2COOH$
b. $(CH_3)_2CHCH_2CHBrCOOH$

✔ Example 4.3.2

Write the condensed structural formula for β-chloropropionic acid.

Solution

Propionic acid has three carbon atoms: C–C–COOH. Attach a chlorine (Cl) atom to the parent chain at the beta carbon atom, the second one from the carboxyl group: Cl–C–C–COOH. Then add enough hydrogen atoms to give each carbon atom four bonds: $ClCH_2CH_2COOH$.

? Exercise 4.3.2

Write the condensed structural formula for 4-bromo-5-methylhexanoic acid.

Key Takeaways

- Simple carboxylic acids are best known by common names based on Latin and Greek words that describe their source (e.g., formic acid, Latin *formica*, meaning “ant”).
- Greek letters, not numbers, designate the position of substituted acids in the common naming convention.
- IUPAC names are derived from the LCC of the parent hydrocarbon with the *-e* ending of the parent alkane replaced by the suffix *-oic* and the word *acid*.

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4.4: Physical Properties of Carboxylic Acids

Learning Objectives

- Compare the boiling points of carboxylic acids with alcohols of similar molar mass.
- Compare the solubilities of carboxylic acids in water with the solubilities of comparable alkanes and alcohols in water.

Many carboxylic acids are colorless liquids with disagreeable odors. The carboxylic acids with 5 to 10 carbon atoms all have "goaty" odors (explaining the odor of Limburger cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated locker rooms. The acids with more than 10 carbon atoms are waxlike solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility.

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass.

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure **4.4.1**). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid [$CH_3(CH_2)_4COOH$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$CH_3(CH_2)_{14}COOH$], with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

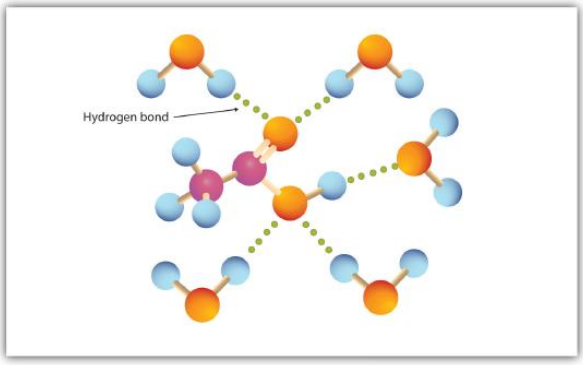


Figure **4.4.1**: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table **4.4.1** lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

Table **4.4.1**: Physical Constants of Carboxylic Acids

Condensed Structure	Name of Acid	Melting Point (°C)	Boiling Point (°C)	Solubility (g/100 g of Water)
HCOOH	formic acid	8	100	miscible
CH_3COOH	acetic acid	17	118	miscible
CH_3CH_2COOH	propionic acid	–22	141	miscible
$CH_3(CH_2)_2COOH$	butyric acid	–5	163	miscible
$CH_3(CH_2)_3COOH$	valeric acid	–35	187	5
$CH_3(CH_2)_4COOH$	caproic acid	–3	205	1.1
C_6H_5COOH	benzoic acid	122	249	0.29

Example 4.4.1

1. Which compound has the higher boiling point—butanoic acid or 2-pentanone? Explain.
2. Would you expect butyric acid to be more or less soluble than 1-butanol in water? Explain.

Solution

1. The compounds have comparable molar mass values, 88 g/mol for butanoic acid and 86 g/mol for 2-pentanone. However, only butanoic acids will form hydrogen bonding. Therefore, butanoic acid will have a higher boiling point.
2. Although butyric acid (butanoic acid) and 1-butanol can both form hydrogen bonds, it is expected that butyric acid is more soluble because it forms more extensive hydrogen bonding.

Exercise 4.4.1

1. Which compound has the higher boiling point—$CH_3CH_2CH_2OCH_2CH_3$ or $CH_3CH_2CH_2COOH$? Explain
2. Which compound is more soluble in water—CH_3COOH or $CH_3CH_2CH_2CH_3$? Explain.

Key Takeaways

- Carboxylic acids have high boiling points compared to other substances of comparable molar mass. Boiling points increase with molar mass.
- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

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4.5: Esters

Learning Objectives

- Identify the general structure for an ester.
- Use common names to name esters.
- Name esters according to the IUPAC system.

Esters are carboxylic acid derivatives formed by replacing the H in the hydroxyl group with a carbon group. Esters have the general formula RCOOR′, where R may be a hydrogen atom, an alkyl group, or an aryl group, and R′ may be an alkyl group or an aryl group but *not* a hydrogen atom (if it were a hydrogen atom, the compound would be a carboxylic acid). Figure **4.5.1** shows the general structure for an ester, with the functional group shown in red.

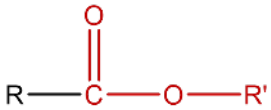


Figure **4.5.1**: The structure of an ester. Esters feature a carbon-oxygen double bond that is also singly bonded to a second oxygen atom, which is then joined to an alkyl or an aryl group.

Esters occur widely in nature. Unlike carboxylic acids, esters generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers. Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.

Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

Naming Esters

Although esters are covalent compounds and salts are ionic, esters are named in a manner similar to that used for naming salts.

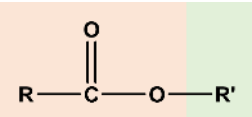
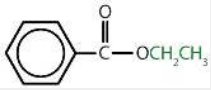


Figure **4.5.2**: Guide for naming esters.

The common and International Union of Pure and Applied Chemistry (IUPAC) rules for naming esters are similar. In both systems, the identity of the R' carbon group (that replaced the hydrogen) is given and is followed by the name of the acid portion. Another similarity among the systems is that the *-ic acid* ending of the parent acid is replaced by the suffix *-ate* (Table **4.5.1**).

If the ester molecule has substituents, as with carboxylic acids, the carbonyl carbon atom is always assigned to C1. It is unnecessary to designate this group by number.

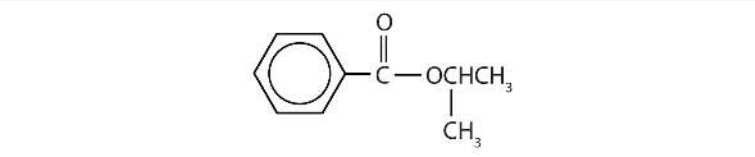
Table **4.5.1**: Nomenclature of Esters

Condensed Structural Formula	Common Name	IUPAC Name
$HCOOCH_3$	methyl formate	methyl methanoate
CH_3COOCH_3	methyl acetate	methyl ethanoate
$CH_3COOCH_2CH_3$	ethyl acetate	ethyl ethanoate
$CH_3CH_2COOCH_2CH_3$	ethyl propionate	ethyl propanoate
$CH_3CH_2CH_2COOCH(CH_3)_2$	isopropyl butyrate	isopropyl butanoate
	ethyl benzoate	ethyl benzoate

Example 4.5.1

Give the common and IUPAC names for each compound.

a. 

b. 

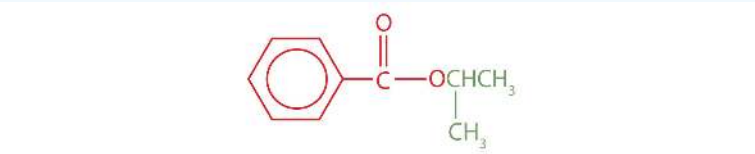
Solution

a. The alkyl group attached directly to the oxygen atom is a butyl group (in green).



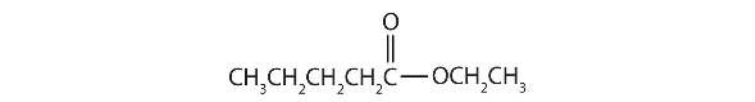
The part of the molecule derived from the carboxylic acid (in red) has three carbon atoms. It is called propionate (common) or propanoate (IUPAC). The ester is therefore butyl propionate or butyl propanoate.

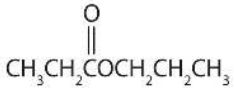
b. An alkyl group (in green) is attached directly to the oxygen atom by its middle carbon atom; it is an isopropyl group. The part derived from the acid (that is, the benzene ring and the carbonyl group, in red) is benzoate. The ester is therefore isopropyl benzoate (both the common name and the IUPAC name).



Exercise 4.5.1

Give the common and IUPAC names for each compound.

a. 

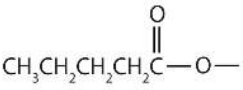
b. 

Example 4.5.2

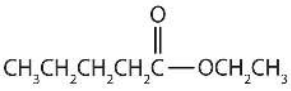
Draw the structure for ethyl pentanoate.

Solution

Start with the portion from the acid. Draw the pentanoate (five carbon atoms) group first; keeping in mind that the last carbon atom is a part of the carboxyl group.



Then attach the ethyl group to the bond that ordinarily holds the hydrogen atom in the carboxyl group.



Exercise 4.5.2

Draw the structure for phenyl pentanoate.

Key Takeaway

- An ester has an OR' group attached to the carbon atom of a carbonyl group.
- The R' cannot be H, because this will represent a carboxylic acid.
- The common and IUPAC names for esters identify the R' group that replaced the H followed by the name of the acid portion of the molecule.

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4.6: Physical Properties of Esters

Learning Objectives

- Compare the boiling points of esters with alcohols of similar molar mass.
- Compare the solubilities of esters in water with the solubilities of comparable alkanes and alcohols in water.

Ester molecules are polar but have no hydrogen atom attached directly to an oxygen atom. They are therefore incapable of engaging in intermolecular hydrogen bonding with one another and thus have considerably lower boiling points than their isomeric carboxylic acids counterparts. Because ester molecules can engage in hydrogen bonding with water molecules, however, esters of low molar mass are somewhat soluble in water. Borderline solubility occurs in those molecules that have three to five carbon atoms. Table **4.6.1** lists the physical properties of some common esters.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer "dries," leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Table **4.6.1**: Physical Properties of Some Esters

Condensed Structure	Name	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)	Aroma
$HCOOCH_3$	methyl formate	60	−99	32	
$HCOOCH_2CH_3$	ethyl formate	74	−80	54	rum
CH_3COOCH_3	methyl acetate	74	−98	57	
$CH_3COOCH_2CH_3$	ethyl acetate	88	−84	77	
$CH_3CH_2CH_2COOCH_3$	methyl butyrate	102	−85	102	apple
$CH_3CH_2CH_2COOCH_2CH_3$	ethyl butyrate	116	−101	121	pineapple
$CH_3COO(CH_2)_4CH_3$	pentyl acetate	130	−71	148	pear
$CH_3COOCH_2CH_2CH(CH_3)_2$	isopentyl acetate	130	−79	142	banana
$CH_3COOCH_2C_6H_5$	benzyl acetate	150	−51	215	jasmine
$CH_3CH_2CH_2COO(CH_2)_4CH_3$	pentyl butyrate	158	−73	185	apricot
$CH_3COO(CH_2)_7CH_3$	octyl acetate	172	−39	210	orange

Example 4.6.1

a. Which compound has the higher boiling point—$CH_3CH_2CH_2CH_2OH$ or CH_3COOCH_3? Explain.
b. Which compound is more soluble in water—methyl butyrate or butyric acid? Explain.

Solution

a. $CH_3CH_2CH_2CH_2OH$ has the higher boiling point because there is hydrogen bonding and there is no hydrogen bonding in CH_3COOCH_3.

b. Butyric acid is more soluble in water because of hydrogen bonding with water.

? Exercise 4.6.1

a. Which compound has the higher boiling point—$CH_3CH_2CH_2CH_2OH$ or CH_3COOCH_3? Explain.

b. Which compound is more soluble in water—methyl butyrate or butyric acid? Explain.

Summary

Esters have polar bonds but do not engage in hydrogen bonding and are therefore intermediate in boiling points between the nonpolar alkanes and the alcohols, which engage in hydrogen bonding. Ester molecules can engage in hydrogen bonding with water, so esters of low molar mass are therefore somewhat soluble in water.

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4.7: Amides

Learning Objectives

- Identify the general structure for an amide.
- Identify the functional group for an amide.
- Names amides with common names.
- Name amides according to the IUPAC system.

Amides are carboxylic acid derivatives that contain a functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*.

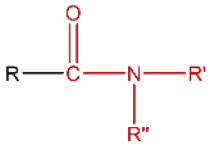


Figure **4.7.1**: General structure of an amide. If R' and R" are both hydrogen atoms, the compound is a simple amide. If not, it is a substituted amide.

The carbonyl carbon-nitrogen bond is called an **amide linkage**. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

Naming Amides

Simple amides are named as derivatives of carboxylic acids. The *-ic acid* ending of the common name or the *-oic acid* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.



Figure **4.7.2**: Structures of a carboxylic acid (left) and amide (right) along with common (top) and IUPAC (bottom) names.

The names of substituted amides, include the identity of the R' or R" (of N–R) substituents. Instead of locator numbers, N– is used to indicate the location of these groups (Figure **4.7.3**).

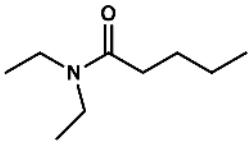
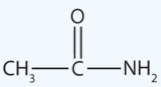
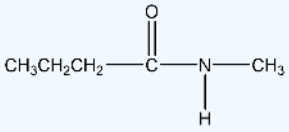


Figure **4.7.3**: Skeletal structure of N,N-diethylpentanamide.

Example 4.7.1

Name each compound with the common name, the IUPAC name, or both.

a. 

b. 

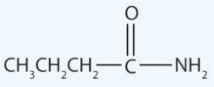
Solution

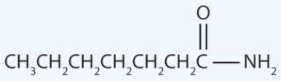
a. This amide has two carbon atoms and is thus derived from acetic acid. The OH of acetic acid is replaced by an NH_2 group. The *-ic acid* from *acetic acid* (or *-oic acid* from ethanoic acid) is dropped, and *-amide* is added to give *acetamide* (or ethanamide in the IUPAC system).

b. This is a substituted amide since there is a methyl group bonded to the nitrogen. The parent portion of the molecule is derived from butanoic acid. The *-oic acid* is dropped, and *-amide* is added to give butanamide. The methyl group is attached to the nitrogen (N) of the functional group, so the location is indicated as N-methyl. Therefore the name of the molecule is N-methylbutanamide.

Exercise 4.7.1

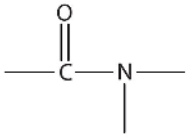
Name each compound with the common name, the IUPAC name, or both.

a. 

b. 

Key Takeaways

- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.
- The functional group for an amide is as follows:



- In names for amides, the *-ic acid* of the common name or the *-oic acid* ending of the IUPAC for the corresponding carboxylic acid is replaced by *-amide*.

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4.8: Physical Properties of Amides

Learning Objectives

- Compare the boiling points of amides with alcohols of similar molar mass.
- Compare the solubilities in water of amides of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

With the exception of formamide ($HCONH_2$), which is a liquid, all simple amides are solids (Table **4.8.1**). The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms. Like the esters, solutions of amides in water usually are neutral—neither acidic nor basic.

Table **4.8.1**: *Physical Constants of Some Unsubstituted Amides*

Condensed Structure	Name	Melting Point (°C)	Boiling Point (°C)	Solubility in Water
$HCONH_2$	formamide	2	193	soluble
CH_3CONH_2	acetamide	82	222	soluble
$CH_3CH_2CONH_2$	propionamide	81	213	soluble
$CH_3CH_2CH_2CONH_2$	butyramide	115	216	soluble
$C_6H_5CONH_2$	benzamide	132	290	slightly soluble

The amides generally have high boiling points and melting points. These characteristics and their solubility in water result from the polar nature of the amide group and hydrogen bonding (Figure **4.8.1**). Similar hydrogen bonding plays a critical role in determining the structure and properties of proteins, deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and other giant molecules so important to life processes.

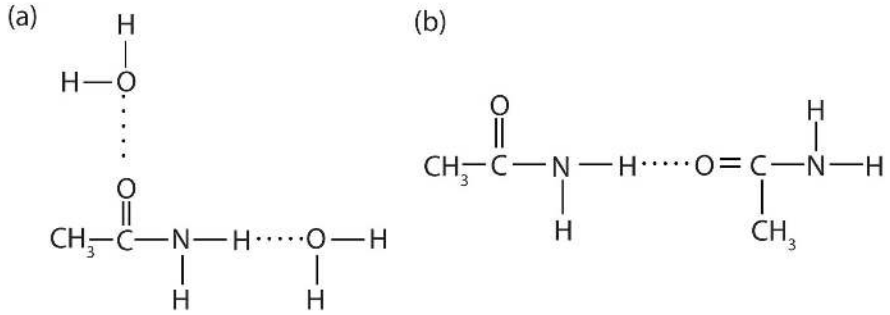


Figure **4.8.1**: Hydrogen Bonding in Amides. Amide molecules can engage in hydrogen bonding with water molecules (a). Those amides with a hydrogen atom on the nitrogen atom can also engage in hydrogen bonding (b). Both hydrogen bonding networks extend in all directions.

Example 4.8.1

a. Which compound has the higher boiling point—pentanamide or propyl acetate? Explain.

b. Which compound is more soluble in water—propanamide or 1-pentene? Explain.

Solution

a. Pentanamide ($CH_3CH_2CH_2CH_2CONH_2$) has the higher boiling point because the nitrogen-hydrogen (N–H) and the carbon-oxygen double (C=O) bonds can engage in hydrogen bonding. Propyl acetate ($CH_3COOCH_2CH_2CH_3$) cannot engage in hydrogen bonding.

b. Propanamide ($CH_3CH_2CONH_2$) is more soluble in water because the N–H and C=O bonds can engage in hydrogen bonding with water. 1-pentene ($CH_2=CHCH_2CH_2CH_3$) cannot engage in hydrogen bonding with water

? Exercise 4.8.1

a. Which compound has the higher boiling point—butyramide or dimethylacetamide [$CH_3CON(CH_3)_2$]? Explain.

b. Which compound is more soluble in water—acetamide (CH_3CONH_2) or 1-butene ($CH_2=CHCH_2CH_3$)? Explain.

Key Takeaways

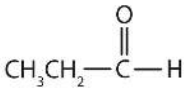
- Most amides are solids at room temperature; the boiling points of amides are much higher than those of alcohols of similar molar mass.
- Amides of five or fewer carbon atoms are soluble in water.

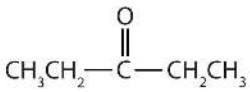
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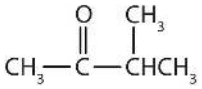
4.E: Carbonyl-Containing Compounds (Exercises)

Additional Exercises

1. Name each compound.

a. 

b. 

c. 

2. Draw the structure for each compound.
   a. butyraldehyde
   b. 2-hexanone
   c. *p*-nitrobenzaldehyde

3. Which compound in each pair has the higher boiling point?
   a. hexanal or 2-hexanol
   b. butane or 2-propanone

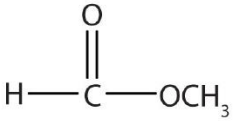
4. Draw the structure for each compound.
   a. *o*-nitrobenzoic acid
   b. *p*-chlorobenzoic acid
   c. 3-chloropentanoic acid
   d. α-chloropropionic acid

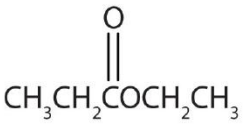
5. Name each compound with either the IUPAC name, the common name, or both.
   a. $(CH_3)_2CHCH_2COOH$
   b. $(CH_3)_3CCH(CH_3)CH_2COOH$
   c. $CH_2BrCH_2CH_2COOH$

6. Which compound has the higher boiling point: 1-pentanol or butanoic acid? Explain.

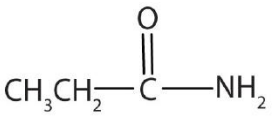
7. Which compound is more soluble in water: propanoic acid or hexanoic acid? Explain.

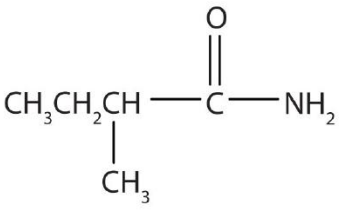
8. Name each compound with both the common name and the IUPAC name.

a. 

b. 

9. Draw the structure for each compound.
   a. ethyl hexanoate
   b. ethyl benzoate
   c. ethyl 3-methylhexanoate
10. Which compound has the higher boiling point: 1-octanol or ethyl hexanoate? Explain.
11. Which compound is more soluble in water: methyl ethanoate or propanoic acid? Explain.
12. Draw the structure for each compound.
   a. propionamide
   b. butanamide
13. Name each compound with the common name, the IUPAC name, or both.

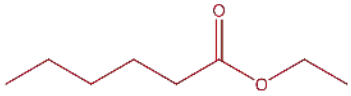
a. 

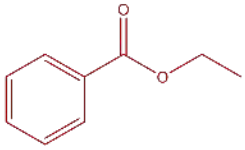
b. 

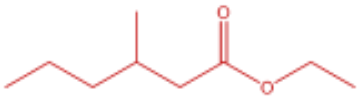
14. Which compound has the higher boiling point—butyramide or dimethylacetamide? Explain.
15. Which compound is more soluble in water: N-methylethanamide or 2-methylbutane? Explain.

Answers

1. a. IUPAC: propanal; Common: propionaldehyde
   b. IUPAC: 3-pentanone; Common: diethyl ketone
   c. IUPAC: 3-methyl-2-butanone; Common: isopropyl methyl ketone
3. a. 2-hexanol
   b. 2-propanone
5. a. IUPAC: 3-methylbutanoic acid; Common: β-methylbutyric acid
   b. IUPAC: 3,4,4-trimethylpentanoic acid; no common name
   c. IUPAC: 4-bromobutanoic acid; Common: γ- bromobutyric acid
7. Propanoic acid because both molecules can form hydrogen bonds, but this compound is more polar. As the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant.

9. a. 

b. 

c. 

11. Propanoic acid because it can form hydrogen bonds with water.

13. a. common: propionamide; IUPAC: propanamide
    b. common: α-methylbutyramide; IUPAC: 2-methylbutanamide

15. N-methylethanamide because it can form hydrogen bonds with water.

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4.S: Carbonyl-Containing Compounds (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the summary and ask yourself how they relate to the topics in the chapter.

The **carbonyl group**, a carbon-oxygen double bond, is the defining feature of **aldehydes** (RCHO)and **ketones** (RCOR'). In aldehydes at least one bond on the carbonyl group is a carbon-hydrogen bond; in ketones, both available bonds on the carbonyl carbon atom are carbon-carbon bonds.

A **carboxylic acid** (RCOOH) contains the COOH functional group, called the **carboxyl group**. A carboxyl group has a hydroxyl attached to a carbonyl carbon atom. There are many familiar carboxylic acids. The R group may be a hydrogen atom (as in formic acid, HCOOH), an alkyl group (as in acetic acid, CH_2COOH), or an aryl group (as in benzoic acid, C_6H_5COOH). The location of substituents along the carbon chain is indicated by a Greek letter (for common names) or a number (for names from the International Union of Pure and Applied Chemistry). Carboxylic acids are weak acids that have strong, often disagreeable, odors. They are highly polar molecules and readily engage in hydrogen bonding, so they have relatively high boiling points.

An **ester** (RCOOR′) is a carboxylic acid derivative that has an OR′ group attached to a carbonyl carbon atom. Esters are pleasant-smelling compounds that are responsible for the fragrances of flowers and fruits. They have lower boiling points than comparable carboxylic acids because, even though ester molecules are somewhat polar, they cannot engage in hydrogen bonding. However, with water, esters can engage in hydrogen bonding; consequently, the low molar mass esters are soluble in water. Some of the most important esters in biochemistry are those formed from phosphoric acid.

Amides are also carboxylic acid derivatives. These compounds contain a functional group that has the carbon of a carbonyl group bonded to a nitrogen atom from NH_3 or an amine. A compound is considered a simple amide when the nitrogen of the functional group has two hydrogen atoms attached. If one of the hydrogen atoms is replaced with an alkyl or aryl group, the compound is referred to as a substituted amide. The carbon-nitrogen bond is referred to as an amide linkage (or a peptide linkage). Most amides are colorless and odorless, and the lighter ones are soluble in water. Because they are polar molecules, amides have comparatively high boiling points and melting points. The IUPAC names for substituted amides use N- as a locator for substituents bonded to the nitrogen of the functional groups instead of numbers.

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CHAPTER OVERVIEW

5: Organic Chemical Reactions

5.1: Organic Redox Reactions
5.2: Alkene Reactions
5.3: Condensation Reactions
5.4: Hydrolysis Reactions
5.E: Organic Chemical Reactions (Exercises)
5.S: Organic Chemical Reactions (Summary)

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5.1: Organic Redox Reactions

Learning Objectives

- Identify oxidation-reduction reactions with organic compounds.

Oxidation and reduction (redox) reactions are essential to energy production and transfer in living systems. To understand these electron-transfer reactions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called **oxidation**. The gain of electrons is called **reduction**. Because any loss of electrons by one substance must be accompanied by a gain in electrons by something else, oxidation and reduction always occur together. As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species being oxidized is called the **reducing agent**, and the species being reduced is called the **oxidizing agent**.

Redox reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.



Figure 5.1.1: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. from Wikipedia.

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure 5.1.1).

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{5.1.1}$$

In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($\mathrm{C_6H_{12}O_6}$), a simple sugar:

$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O} \tag{5.1.2}$$

Functional Group Oxidation

Redox reactions involving organic molecules are characterized by the addition or removal of oxygen and/or hydrogen. Organic chemists use a variety of redox reactions. For example, potassium dichromate ($\mathrm{K_2Cr_2O_7}$) is a common oxidizing agent that can be used to oxidize alcohols (symbolized by the general formula ROH). The product of the reaction depends on the location of the OH functional group in the alcohol molecule, the relative proportions of alcohol and the dichromate ion, and reaction conditions such as temperature. If the OH group is attached to a terminal carbon atom (primary alcohol) and the product is distilled off as it forms, the product is an aldehyde, which has a terminal carbonyl group (C=O) and is often written as RCHO. One example is the reaction used by the Breathalyzer to detect ethyl alcohol ($\mathrm{CH_3CH_2OH}$) in a person's breath:

$$\mathrm{3\,CH_3CH_2OH + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O} \tag{5.1.3}$$

If the product acetaldehyde ($\mathrm{CH_3CHO}$) is not removed as it forms, it is further oxidized to acetic acid ($\mathrm{CH_3COOH}$). In this case, the overall reaction is as follows:

$$3\,CH_3CH_2OH + 2\,Cr_2O_7^{2-} + 16\,H^+ \rightarrow 3\,CH_3COOH + 4\,Cr^{3+} + 11\,H_2O \qquad (5.1.4)$$

In this reaction, the chromium atom is reduced because it went from $Cr_2O_7^{2-}$ to Cr^{3+}. On the other hand, the carbon atom in ethanol is oxidized. In the **oxidation** of ethyl alcohol (CH_3CH_2OH, a.k.a. ethanol) to form acetaldehyde (CH_3CHO, a.k.a. ethanal), the **number of bonds to oxygen has increased and the number of hydrogen atoms has decreased** from six to four. Either or both of these indicate that an oxidation has occurred.

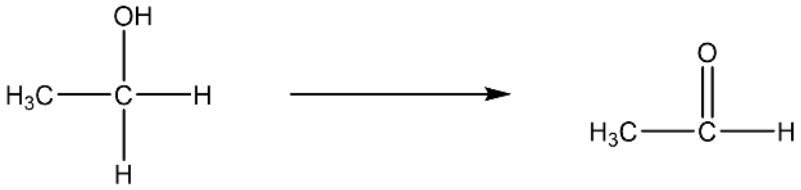


Figure 5.1.2: Simple oxidation of a primary alcohol to an aldehyde.

In the oxidation of acetaldehyde to acetic acid (a.k.a. ethanoic acid), the carbon atom that gained an additional oxygen is the element oxidized.

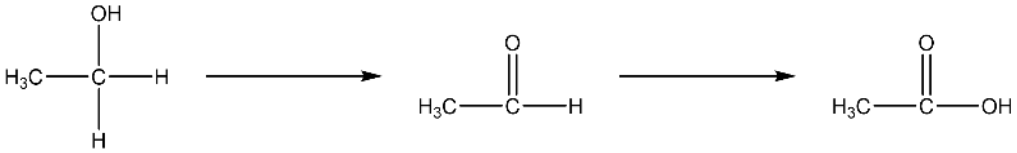


Figure 5.1.3: Complete oxidation of a primary alcohol to an aldehyde to a carboxylic acid.

When the alcohol represents a secondary alcohol, the oxidation will produce a ketone (the formulas of ketones are often written as RCOR, and the carbon–oxygen bond is a double bond). The simplest ketone is derived from the oxidation of 2-propanol ($CH_3CHOHCH_3$). It is the common solvent acetone [$(CH_3)_2CO$], which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:

$$3\,CH_3CHOHCH_3 + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,(CH_3)_2CO + 2\,Cr^{3+} + 7\,H_2O \qquad (5.1.5)$$

Tertiary alcohols (R_3COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-hydrogen bonding is easily broken under oxidative conditions, but carbon-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

Functional Group Reduction

As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. In the **reduction** of an organic compound, the **number of bonds to oxygen decreases and the number of hydrogen atoms increases**. Either or both of these indicate that a reduction has occurred. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid ($CH_3COCOOH$) is reduced to lactic acid ($CH_3CHOHCOOH$) in the muscles.

$$CH_3COCOOH \rightarrow CH_3CHOHCOOH \qquad (5.1.6)$$

(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

Oxidation and reduction also occur with hydrocarbon molecules. Alkynes can be reduced to alkenes, which can be further reduced to alkanes. The opposite transitions represent the oxidation of alkanes to alkenes, which are further oxidized to alkynes.

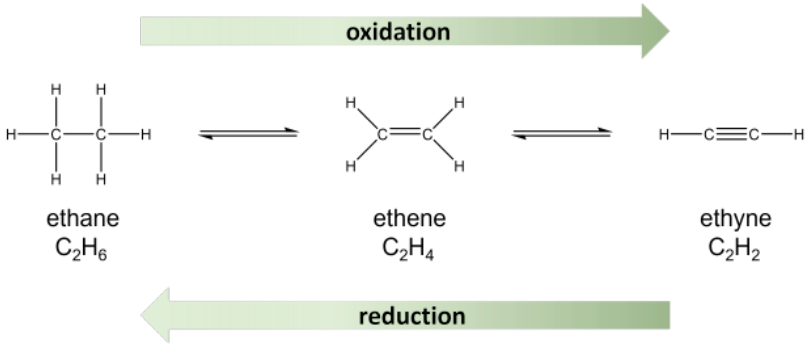


Figure 5.1.4: Oxidation and reduction of hydrocarbons.

Redox Reactions in Food Chemistry

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $C_6H_8O_6$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($C_6H_6O_6$). In the stomach, ascorbic acid reduces the nitrite ion (NO_2^-) to nitric oxide (NO):

$$C_6H_8O_6 + 2\,H^+ + 2\,NO_2^- \rightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO \tag{5.1.7}$$

> *If reaction in Equation 5.1.7 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.*

Tocopherol (vitamin E) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure 5.1.5).



Figure 5.1.5: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. Wedges of pink grapefruit, lime, and lemon, and a half orange (clockwise from top) from Wikipedia.

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called **photosynthesis**, in which carbon dioxide and water are converted to glucose ($C_6H_{12}O_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy. The overall change that occurs is as follows:

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{5.1.8}$$

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.



Figure 5.1.6: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

Example 5.1.1

A typical respiratory reaction discussed in the text is the oxidation of glucose ($C_6H_{12}O_6$):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

Is this a redox reaction? If so, what are the oxidizing and reducing agents?

Solution

Yes; oxidizing agent: O_2; reducing agent: $C_6H_{12}O_6$

Exercise 5.1.1

What alcohol is produced in the reduction of propanal (CH_3CH_2CHO)?

Summary

- Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.
- Redox reactions involving organic compounds are characterized by the addition or removal of atoms/bonds:
  - oxidation - increase in oxygen and/or decrease in hydrogen
  - reduction - decrease in oxygen and/or increase in hydrogen
- Primary alcohols are oxidized to form aldehydes, which are further oxidized to form carboxylic acids.
- Secondary alcohols are oxidized to form ketones.
- Tertiary alcohols are not readily oxidized.

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5.2: Alkene Reactions

Learning Outcomes

- Identify and describe addition and elimination reactions.
- Distinguish between the types of addition reactions.
- Predict products of each reaction type.
- Predict products based on Markovnikov's rule.
- Define "polymer".

Organic reactions require the breaking of strong covalent bonds, which takes a considerable input of energy. In order for relatively stable organic molecules to react at a reasonable rate, they often must be modified with the use of highly reactive materials or in the presence of a catalyst. In this lesson, you will learn about several general categories of organic reactions.

Addition Reactions

Addition reactions are useful ways to introduce a new functional group into an organic molecule. An **addition reaction** is a reaction in which an atom or molecule is added to an unsaturated molecule, making a single product. An addition reaction can often be thought of as adding a molecule across the double bond of an alkene or across the triple bond of an alkyne.

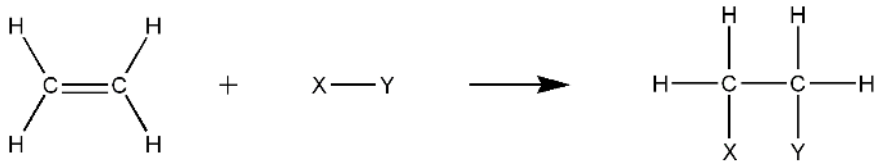


Figure 5.2.1: Reaction scheme of a general alkene addition reaction.

Knowing that "ation" means to add, the specific names of these reactions, such as hydrogenation, hydration, or halogination (bromination or chlorination), should make sense. Note that hydrogenation (adding H_2) and hydration (adding H_2O) are very different processes.

Hydrogenation

One type of addition reaction is called **hydrogenation**. Hydrogenation is a reaction that occurs when molecular hydrogen (H_2) is added to an alkene to produce an alkane or hydrogen is added to an alkyne to produce an alkene or alkane. The reaction is typically performed in the presence of a metal catalyst such as nickel (Ni) or platinum (Pt). For example, ethene reacts with hydrogen to form ethane.

$$\mathrm{CH_2{=}CH_2}\,(g) + \mathrm{H_2}\,(g) \xrightarrow{\mathrm{Pt}} \mathrm{CH_3CH_3}\,(g) \qquad (5.2.1)$$

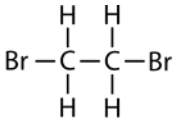
Note that the hydrogenation reaction is also a redox reaction. Ethene is reduced, because the oxidation numbers of the carbon atoms change from -2 to -3 as a result of the reaction.

Vegetable oils consist of long carbon chains with carboxyl groups on the end; these molecules are referred to as fatty acids. The carbon chains of the fatty acids in vegetable oils are unsaturated, usually containing multiple double bonds. When hydrogen gas is blown through a sample of the oil, hydrogen atoms add across the double bonds. This conversion changes the substance from a liquid oil into a solid fat. The "hydrogenated" on a food product is an indication that oil (liquid) has been converted into fat (solid) by this process. Margarine is manufactured from unsaturated vegetable oil in this way by hydrogenating some of the double bonds making it a "partially hydrogenated vegetable oil".

Halogenation/Hydrohalogenation

Alkyl halides can be produced from an alkene by the addition of either the elemental halogen or the hydrogen halide. When the reactant is the diatomic halogen, the reaction is known as a **halogenation reaction**. The product of a halogenation addition reaction is a disubstituted alkyl halide as in the addition of bromine to ethene.

$$\mathrm{CH_2{=}CH_2}\,(g) + \mathrm{Br_2}\,(l) \rightarrow \mathrm{CH_2BrCH_2Br}\,(g) \qquad (5.2.2)$$



1,2-dibromoethane

The addition of bromine to an unknown organic compound can be used as a test for unsaturation in the compound. Bromine has a distinctive brownish-orange color, while most bromoalkanes are colorless. When bromine is slowly added to a solution of the compound, the orange color will fade if it undergoes an addition reaction to produce an alkyl halide. If the orange color remains, then the original compound was already saturated, and no reaction occurred.

A monosubstituted alkyl halide can be produced by the addition of a hydrogen halide to an alkene in a **hydrohalogenation reaction**. Shown below is the formation of chloroethane.

$$\mathrm{CH_2{=}CH_2}\,(g) + \mathrm{HCl}\,(g) \rightarrow \mathrm{CH_3CH_2Cl}\,(g) \qquad (5.2.3)$$

Unlike addition reactions involving $\mathbf{H_2}$, $\mathbf{Br_2}$, or $\mathbf{Cl_2}$, the addition of a hydrogen halide can have two possible products because an $\mathbf{-H}$ and a $\mathbf{-Br}$ or $\mathbf{-Cl}$ are being added to the carbons in the double bond. **Markovnikov's rule** helps predict the major (main) product in an addition reaction involving an asymmetric alkene double bond. The rule states that the hydrogen atom from the hydrogen halide will add to the carbon that originally had more hydrogen atoms. For example, look at the reaction representing the addition of HBr to propene (Figure $\mathbf{5.2.2}$).

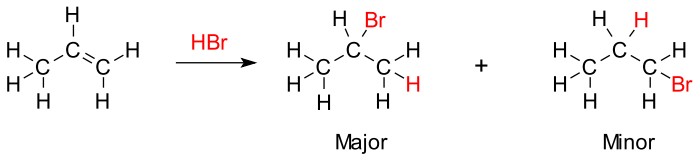


Figure $\mathbf{5.2.2}$: Reaction scheme showing the addition of HBr to propene. V8rik, CC BY-SA 3.0, via Wikimedia Commons

Note that the first carbon in propene started with two hydrogen atoms and the second carbon started with one hydrogen. Therefore, the major product is formed when the hydrogen from HBr is added to the first carbon and the $\mathbf{-Br}$ is added to the second carbon. When there are equal numbers of hydrogen atoms on both carbons in a double bond then the two products will form in approximately equal amounts. For example, the hydrohalogenation of 2-pentene results in two products. In the first product, the $\mathbf{-Br}$ group is on the second carbon and in the second product, the $\mathbf{-Br}$ group is on the third carbon. While these two molecules will have similar properties, there will be differences.

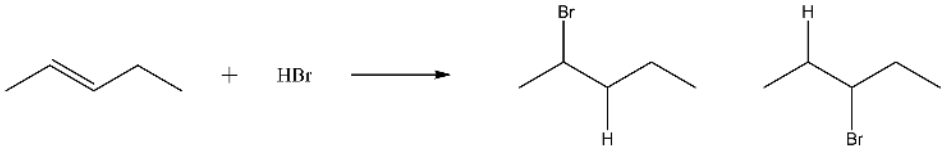


Figure $\mathbf{5.2.3}$: Reaction scheme showing the addition of HBr to 2-pentene.

Hydration

A **hydration reaction** is a reaction in which water is added to an alkene. Hydration reactions can take place when the alkene and water are heated to near $\mathbf{100°C}$ in the presence of a strong acid, which acts as a catalyst. Shown below is the hydration of ethene to produce ethanol.

$$\mathrm{CH_2{=}CH_2}\,(g) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{CH_3CH_2OH}\,(g) \qquad (5.2.4)$$

As with hydrohalogenation reactions, the addition of water can have two possible products because an $\mathbf{-H}$ and an $\mathbf{-OH}$ are being added to the carbons in the double bond. Therefore, Markovnikov's rule is also used to help predict the major product in a hydration reaction.

The rule states that the hydrogen atom from water will add to the carbon that originally had more hydrogen atoms. For example, look at the hydration of 1-butene.

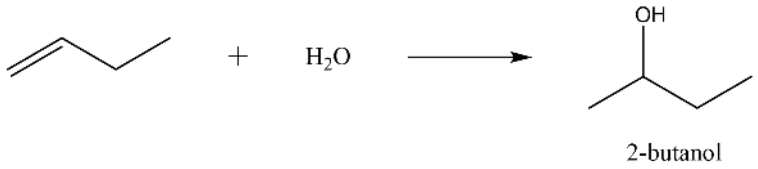


Figure **5.2.4**: Reaction scheme showing the hydration of 2-butene.

Note that the first carbon in 1-butene started with two hydrogen atoms and the second carbon started with one hydrogen. Therefore, the hydrogen from water adds to the first carbon and the **–OH** group adds to the second carbon.

Elimination Reactions

An **elimination reaction** involves the removal of adjacent atoms from a molecule. This results in the formation of a multiple bond and the release of a small molecule, so they are called elimination reactions. They have the general form:

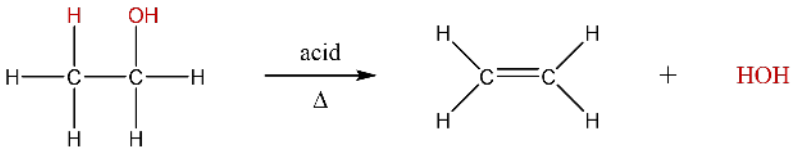


Figure **5.2.5**: Elimination reaction of the conversion of an alcohol to an alkene.

A typical example is the conversion of ethyl chloride to ethylene:

$$CH_3CH_2Cl \rightarrow CH_2 = CH_2 + HCl \tag{5.2.5}$$

Much of the approximately 26 million tons of ethylene produced per year in the United States is used to synthesize plastics, such as polyethylene. In the above reaction, the A–B molecule eliminated is HCl, whose components are eliminated as H^+ from the carbon atom on the left and Cl^- from the carbon on the right. When an acid is produced, as occurs here, the reaction is generally carried out in the presence of a base (such as NaOH) to neutralize the acid. Other elimination reactions will produce H_2, X_2 (where X = halogen), or H_2O. These reactions are often referred to by more descriptive terms such as **dehydration** (removing water), **dehydrogenation** (removing hydrogen), or **dehalogenation** (removing a halogen).

Polymerization

Polymers are very different than the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A **polymer** is a large molecule formed of many smaller molecules covalently bonded to one another in a repeating pattern. The small molecules that make up the polymer are called **monomers**. Polymers are generally formed by either addition or condensation reactions (discussed later in the chapter). Teflon (see figure below) is a non-reactive, non-stick coating used on cookware as well as in containers and pipes for reactive or corrosive chemicals.

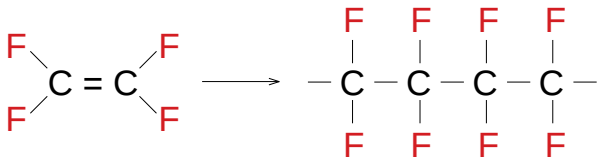


Figure **5.2.6**: Polytetrafluoroethylene (also known as Teflon) is formed from the polymerization of tetrafluoroethylene. 4C, CC BY-SA 3.0, via Wikimedia Commons

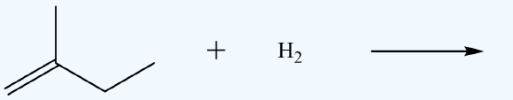
Example 5.2.1

Complete each equation.

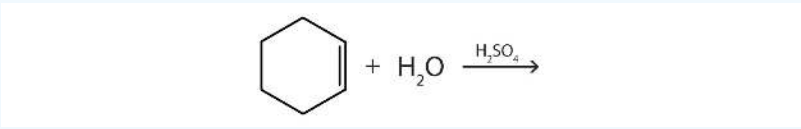
a.

$(CH_3)_2C=CH_2 + Br_2 \rightarrow$

b.



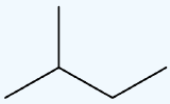
c.



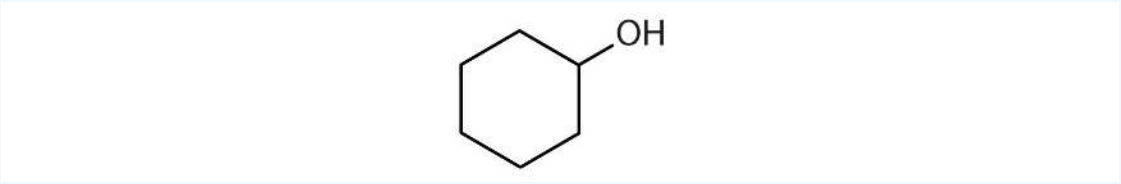
Solution

a. $(CH_3)_2CBrCH_2Br$

b.



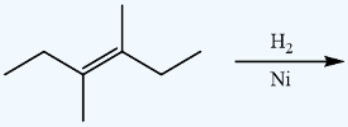
c.



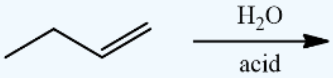
? Exercise 5.2.1

Complete each equation.

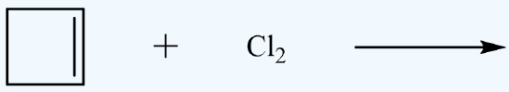
a.



b.



c.



KEY TAKEAWAYS

- Alkenes undergo addition reactions, adding such substances as hydrogen, bromine, and water across the carbon-to-carbon double bond.
- Elimination reactions remove groups to form alkenes.

Contributors and Attributions

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- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

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5.3: Condensation Reactions

Learning Objectives

- Construct products of condensation reactions.

In a **condensation reaction**, two (or more) molecules combine to form a single molecule. A small molecule, often water, is usually removed during a condensation reaction. Amino acids are important biological molecules that have an amine functional group on one end of the molecule and a carboxylic acid functional group on the other end. When two amino acids combine in a condensation reaction, a covalent bond forms between the carboxyl carbon of one amino acid and the amine nitrogen of the second amino acid. A molecule of water is then removed as a second product.

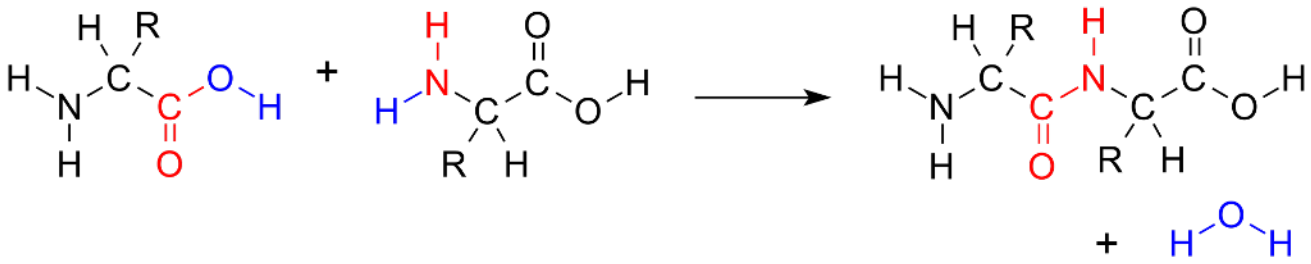


Figure 5.3.1: Amino acids join together to form a molecule called a dipeptide. The **–OH** from the carboxyl group of one amino acid combines with a hydrogen atom from the amine group of the other amino acid to produce water (blue).

This reaction forms a molecule called a dipeptide and the carbon-nitrogen covalent bond is called a peptide bond or amide bond. When repeated numerous times, a long molecule called a protein is eventually produced.

Esterification

An **esterification reaction** is a condensation reaction in which reactants (typically an alcohol and carboxylic acid) combine to produce an ester.

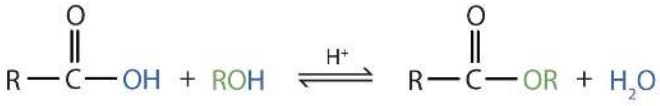


Figure 5.3.2: Reaction scheme for a condensation reaction.

Esterification is a subcategory of condensation reactions because a water molecule is produced in the reaction. The reaction is catalyzed by a strong acid, usually sulfuric acid. When the carboxylic acid butanoic acid is heated with an excess of methanol and a few drops of sulfuric acid, the ester methyl butanoate is produced. Methyl butanoate has the scent of pineapples.

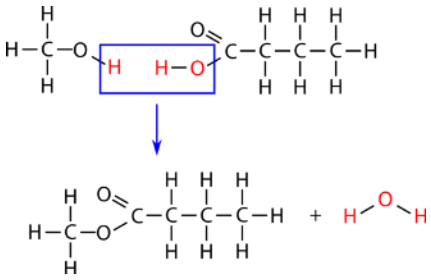
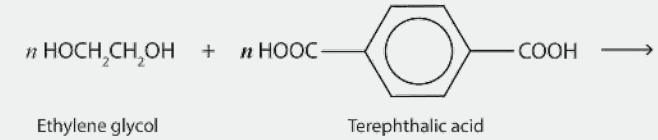


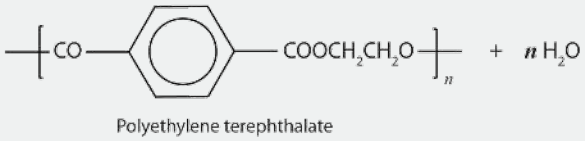
Figure 5.3.3: Esterification reaction between methanol and butanoic acid to produce methyl butanoate.

A Closer Look: Condensation Polymers

A commercially important esterification reaction is condensation polymerization, in which a reaction occurs between a dicarboxylic acid and a dihydric alcohol (diol), with the elimination of water. Such a reaction yields an ester that contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other end. Further condensation reactions then occur, producing polyester polymers.

The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:





Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes. Synthetic arteries can be made from PET, polytetrafluoroethylene, and other polymers.

Amidation

An **amidation reaction** is a condensation reaction in which reactants (typically an amine and carboxylic acid) combine to produce an amide. The addition of ammonia (NH_3) to a carboxylic acid forms an amide, but the reaction is very slow in the laboratory at room temperature. Water molecules are split out, and a bond is formed between the nitrogen atom and the carbonyl carbon atom.

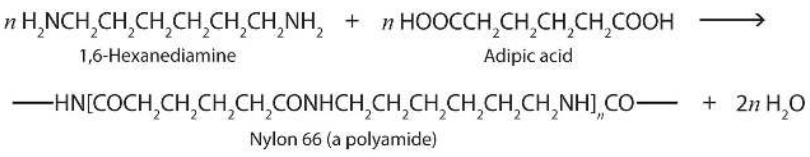


Figure 5.3.4: Amidation reaction between ammonia and acetic acid to produce acetamide.

In living cells, amide formation is catalyzed by enzymes. Proteins are polyamides; they are formed by joining amino acids into long chains. In proteins, the amide functional group is called a *peptide bond*.

Polyamides

Just as the reaction of a diol and a diacid forms a polyester, the reaction of a diacid and a diamine yields a polyamide. The two difunctional monomers often employed are adipic acid and 1,6-hexanediamine. The monomers condense by splitting out water to form a new product, which is still difunctional and thus can react further to yield a polyamide polymer.



Some polyamides are known as *nylons*. Nylons are among the most widely used synthetic fibers—for example, they are used in ropes, sails, carpets, clothing, tires, brushes, and parachutes. They also can be molded into blocks for use in electrical equipment, gears, bearings, and valves.

Example 5.3.1

a. From what carboxylic acid and what alcohol can isopropyl nonanoate be made?
b. From what carboxylic acid and what amine can N-propylhexanamide be made?

Solution

a. nonanoic acid and isopropyl alcohol
b. hexanoic acid and propylamine

Exercise 5.3.1

a. From what carboxylic acid and what alcohol can cyclobutyl butyrate be made?
b. From what carboxylic acid and what amine can butanamide be made?

Summary

- A condensation reaction is a reaction in which two molecules combine to form a single molecule.
- An esterification is a condensation reaction in which an ester is formed from an alcohol and a carboxylic acid.
- An amidation is a condensation reaction in which an amid is formed from an amine and a carboxylic acid.

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5.4: Hydrolysis Reactions

Learning Objectives

- Distinguish between condensation and hydrolysis reactions.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.
- Generate products of the hydrolysis of amides.

Condensation and hydrolysis reactions are chemical reactions involving organic compounds. These opposite reactions involve the building up or breaking down of organic molecules. As with other chemical reactions involving organic compounds, these processes result in a change in the class of organic compound represented.

Hydrolysis reactions are the reverse of condensation reactions. In a **hydrolysis reaction**, a larger molecule forms two (or more) smaller molecules and water is consumed as a reactant. Hydrolysis ("hydro" = water and "lysis" = break) involves adding water to one large molecule to break it into multiple smaller molecules.



Figure 5.4.1: General reaction scheme of a hydrolysis reaction. FrozenMan, CC BY-SA 4.0, via Wikimedia Commons

Hydrolysis of Esters

The esterification reaction is reversible. The formation of the ester represents a condensation reaction, but the reverse reaction represents the hydrolysis of the ester. This hydrolysis can occur under acidic or basic conditions.

Acidic hydrolysis is simply the reverse of esterification. The ester is heated with a large excess of water containing a strong-acid catalyst. Like esterification, the reaction is reversible and does not go to completion.

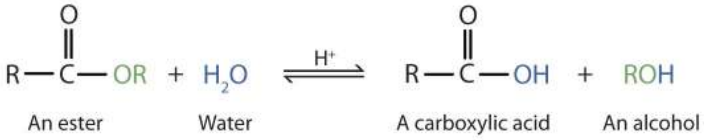


Figure 5.4.2: Reaction scheme for the acid-catalyzed hydrolysis of an ester.

As a specific example, butyl acetate and water react to form acetic acid and 1-butanol. The reaction is reversible and does not go to completion.

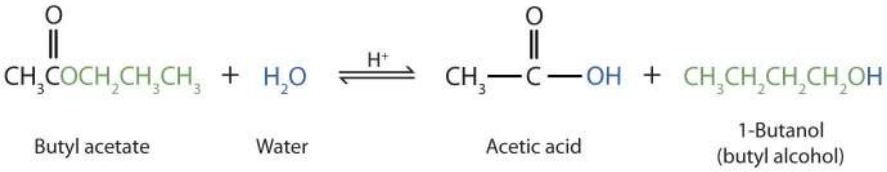


Figure 5.4.3: Acid-catalyzed hydrolysis of butyl acetate.

When an ester is heated in the presence of a strong base (such as sodium hydroxide [NaOH] or potassium hydroxide [KOH]), the ester breaks down. The products are an alcohol and the carboxylate salt.

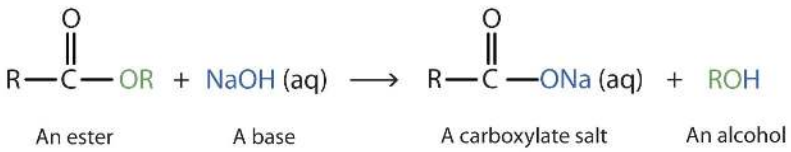


Figure 5.4.4: Reaction scheme for the base-catalyzed hydrolysis of an ester.

As a specific example, butyl acetate and water react to form acetic acid and 1-butanol. The reaction is reversible and does not go to completion.

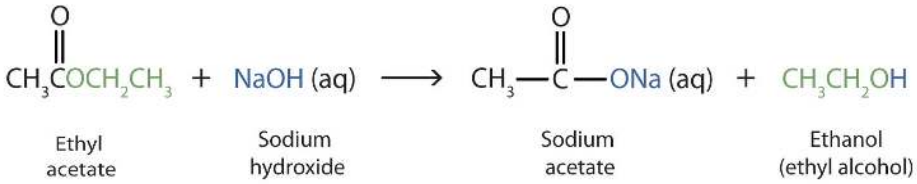


Figure 5.4.5: Base-catalyzed hydrolysis of ethyl acetate.

The strong base is not acting as a catalyst, but is consumed as a reactant in the reaction. This alkaline hydrolysis of an ester is referred to as **saponification** (Latin *sapon*, meaning "soap," and *facere*, meaning "to make"). The term saponification originally described the hydrolysis of long-chain esters called fatty acid esters to produce soap molecules, which are the salts of fatty acids. One such soap molecule is sodium stearate, formed from the hydrolysis of ethyl stearate.

$$\underset{\text{ethyl stearate}}{C_{17}H_{35}COOC_2H_5} + NaOH \rightarrow \underset{\text{sodium stearate (soap)}}{C_{17}H_{35}COO^- Na^+} + C_2H_5OH \tag{5.4.1}$$

Hydrolysis of Amides

Generally, amides resist hydrolysis in plain water, even after prolonged heating. In the presence of added acid or base, however, hydrolysis proceeds at a moderate rate. In living cells, amide hydrolysis is catalyzed by enzymes. Amide hydrolysis is illustrated in the following example:

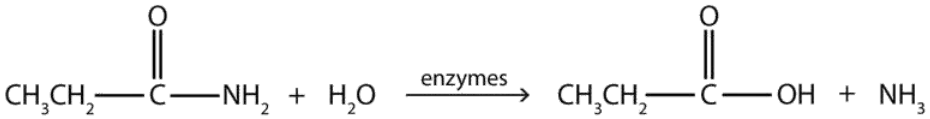


Figure 5.4.6: Reaction scheme for the hydrolysis of an amide.

> *Hydrolysis of an amide in acid solution actually gives a carboxylic acid and the salt of ammonia or an amine (the ammonia or amine initially formed is neutralized by the acid). Basic hydrolysis gives a salt of the carboxylic acid and ammonia or an amine.*

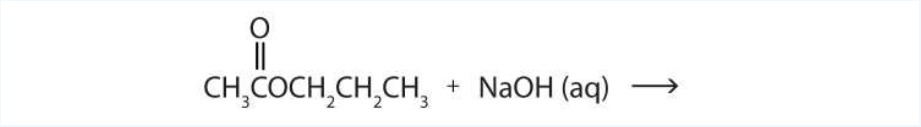
Career Focus: Athletic Trainer

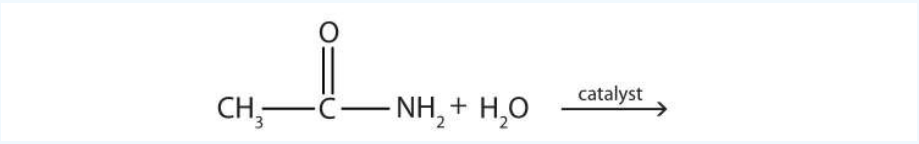
Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology, chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.

Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

Example 5.4.1

Complete each equation.

a. 

b. 

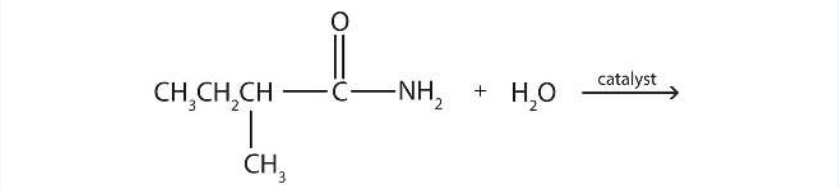
Solution

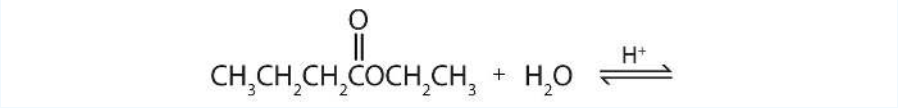
a. $CH_3COONa(aq) + CH_3CH_2CH_2OH$

b. $CH_3COOH + NH_3$

Exercise 5.4.1

Complete each equation.

a. 

b. 

Summary

- A hydrolysis reaction is a reaction in which one molecule breaks apart to form multiple smaller molecules.
- Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol.
- Basic hydrolysis (saponification) of an ester gives a carboxylate salt and an alcohol.
- The hydrolysis of an amide produces a carboxylic acid and ammonia or an amine.

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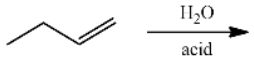
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5.E: Organic Chemical Reactions (Exercises)

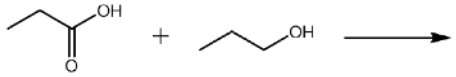
Additional Exercises

1. What would be the ultimate organic product if $CH_3CH_2CH_2OH$ were to react with a solution of $K_2Cr_2O_7$?
2. What would be the major organic product if $CH_3CH_2CHOHCH_2CH_3$ were to react with a solution of $K_2Cr_2O_7$?
3. What alcohol is produced in the reduction of propanal (CH_3CH_2CHO)?
4. Complete each equation.

   a.

   b.

   c.

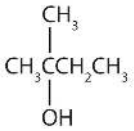
   

5. Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write “no reaction” after the arrow.

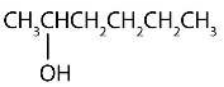
   a.

   $CH_3CH_2CH_2CH_2CH_2OH$

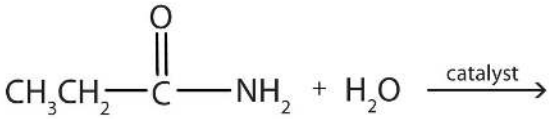
   b.

   c.

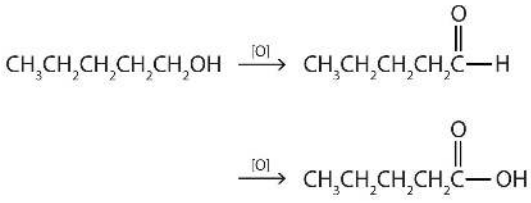
   

6. Write the equation for the reaction of acetic acid with each compound.
   a. ethanol
   b. 1-butanol in the presence of a mineral acid catalyst
7. How do acidic hydrolysis and basic hydrolysis of an ester differ in terms of
   a. products obtained?
   b. the extent of reaction?
8. Write an equation for the acid-catalyzed hydrolysis of ethyl acetate.
9. Write the condensed structural formulas and names of the two compounds from which pentanamide is formed.
10. Complete the following equation.

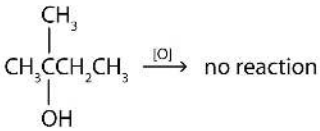


Answers

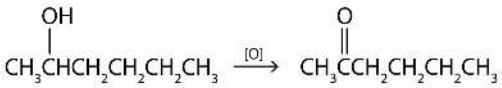
1. CH_3CH_2COOH
3. $CH_3CH_2CH_2OH$
5. a.



b.



c.



7. a. acidic hydrolysis: carboxylic acid + alcohol; basic hydrolysis: carboxylate salt + alcohol
   b. basic hydrolysis: completion; acidic hydrolysis: incomplete reaction
9. $CH_3CH_2CH_2CH_2COOH$ (pentanoic acid) and NH_3 (ammonia)

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5.S: Organic Chemical Reactions (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Oxidation reactions are reactions in which an atom loses an electron. **Reduction reactions** are reactions in which an atom gains an electron. These two processes always occur together, so they are collectively referred to as **oxidation-reduction** (or **redox**) **reactions**. The species being oxidized it called the **reducing agent**, while the species being reduced is the **oxidizing agent**. Alternate definitions of oxidation and reduction focus on the gain or loss of oxygen atoms, or the loss or gain of hydrogen atoms. Redox reactions are easily balanced if the overall reaction is first separated into **half reactions**, which are individually balanced.

Oxidation-reduction reactions are common in organic and biological chemistry. **Respiration**, the process by which we inhale and metabolize oxygen, is a series of redox reactions. In the absence of oxygen, redox reactions still occur in a process called **anaerobic metabolism**. **Antioxidants** such as ascorbic acid also play a part in the human diet, acting as reducing agents in various biochemical reactions. **Photosynthesis**, the process by which plants convert water and carbon dioxide to glucose, is also based on redox reactions.

More reactive than alkanes, alkenes undergo **addition reactions** across the double bond:

- Addition of hydrogen (**hydrogenation**):

  $CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$

- Addition of halogen (**halogenation**):

  $CH_2{=}CH_2 + X_2 \rightarrow XCH_2CH_2X$

  where X = F, Cl, Br, or I.

- Addition of a hydrogen halide (**hydrohalogenation**):

  $CH_2{=}CH_2 + HX \rightarrow HCH_2CH_2X$

  where X = F, Cl, Br, or I.

- Addition of water (**hydration**):

  $CH_2{=}CH_2 + HOH \rightarrow HCH_2CH_2OH$

If the alkene double bond is asymmetric, **Markovnikov's Rule** is used to determine the major product. This rule states that the –H bonds to carbon of the alkene with more hydrogen atoms and the –OH bonds to carbon of the alkene with more carbon groups attached.

Alkenes also undergo **addition polymerization**, molecules joining together to form long-chain molecules.

$\ldots CH_2{=}CH_2 + CH_2{=}CH_2 + CH_2{=}CH_2 + \ldots \rightarrow \ldots CH_2CH_2{-}CH_2CH_2{-}CH_2CH_2{-}\ldots$

The reactant units are **monomers**, and the product is a **polymer**.

Many alcohols can be synthesized by the **hydration** of alkenes. Common alcohols include methanol, ethanol, and isopropyl alcohol. When water is removed from an alcohol in a **dehydration** step, the result is either an alkene or an ether, depending on the reaction conditions. **Aldehydes** are synthesized by the oxidation of **primary alcohols**. Mild oxidizing agents can be further oxidized the aldehyde to a **carboxylic acid**. **Ketones** are prepared by the oxidation of **secondary alcohols**. Ketones are not oxidized by these reagents. **Tertiary alcohols** are not easily oxidized.

Another type of reaction that occurs with organic compounds is the condensation reaction. A **condensation reaction** is a reaction in which two molecules combine to form a single molecule. An **esterification reaction** is a condensation reaction in which a carboxylic acid and an alcohol are combined under acidic conditions. Esters are neutral compounds that undergo **hydrolysis**, a reaction with water. Under acidic conditions, hydrolysis is essentially the reverse of esterification. When carried out under basic conditions, the process is called **saponification**.

An **amidation reaction** is a condensation reaction in which an amide is formed from an amine and a carboxylic acid. Amides are neutral compounds. They resist hydrolysis in water, but acids, bases, and enzymes catalyze the reaction.

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CHAPTER OVERVIEW

6: Carbohydrates

6.1: Overview of Carbohydrates
6.2: Stereoisomers
6.3: Classifying Monosaccharides
6.4: Important Monosaccharides
6.5: Reactions of Monosaccharides
6.6: Disaccharides
6.7: Oligosaccharides
6.8: Polysaccharides
6.E: Carbohydrates (Exercises)
6.S: Carbohydrates (Summary)

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6.1: Overview of Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, oligo- or polysaccharides.

Carbohydrates are biological molecules composed of carbon, hydrogen and oxygen atoms. The term carbohydrate is generally applied to the group of polyhydroxy aldehydes or polyhydroxy ketones commonly known as sugars.

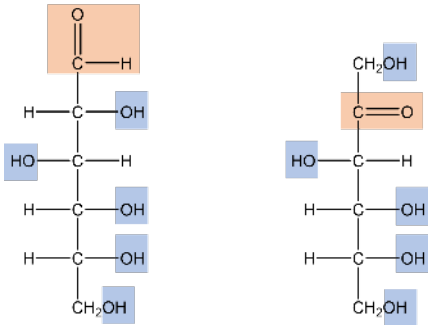


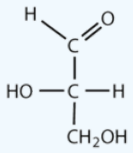
Figure **6.1.1**: Structures of a polyhydroxy aldehyde (left) and polyhydroxy ketone (right).

Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a "carbon hydrate" with the structure $C_n{\cdot}(H_2O)_n$ or $C_6{\cdot}6H_2O$ molecular formula.

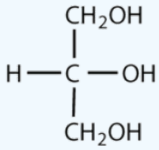
Example 6.1.1

Which compounds would be classified as carbohydrates?

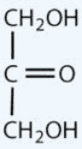
a.



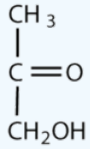
b.



c.



d.

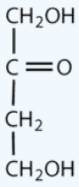


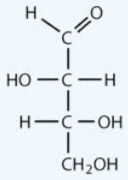
Solution

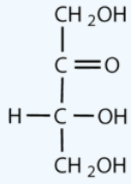
a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.
d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

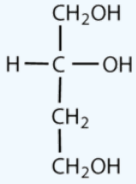
? Exercise 6.1.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as **photosynthesis**:

$$6\,CO_2 + 6\,H_2O + 686\ \text{kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{6.1.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

Carbohydrates are classified based on the number of sugar units combined to make the molecule. The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called **monosaccharides**. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. **Disaccharides** (meaning two sugars) consist of two monosaccharides joined together; **oligosaccharides** (meaning a few sugars) contain anywhere from three to nine monosaccharides; and **polysaccharides** (meaning many sugars) are biological polymers containing 10 or more monosaccharide units. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

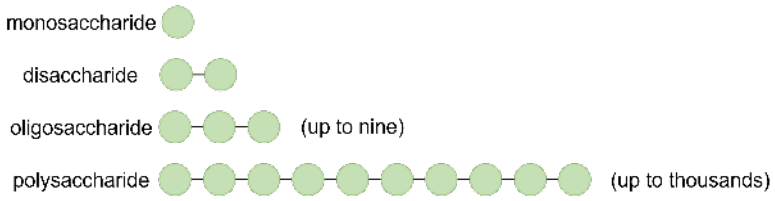


Figure **6.1.2**: Types of carbohydrates categorized based on the number of sugar units present.

> *Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.*

Example 6.1.1

When an aqueous solution of trehalose is hydrolyzed, two molecules of glucose are produced for each molecule of trehalose. Is trehalose a monosaccharide, a disaccharide, an oligosaccharide, or a polysaccharide?

Solution

Trehalose is a disaccharide because it is hydrolyzed into two molecules of glucose (a monosaccharide)

Exercise 6.1.1

When an aqueous solution of arabinose is hydrolyzed, no other molecules are produced. Is arabinose a monosaccharide, a disaccharide, an oligosaccharide, or a polysaccharide

Summary

- Carbohydrates are an important group of biological molecules that includes sugars and starches.
- Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates.
- Carbohydrates are classified based on the number of sugar units. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, oligosaccharides contain between three and nine monosaccharide units, and polysaccharides contain ten or more monosaccharide units.

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6.2: Stereoisomers

Learning Outcomes

- Determine the isomeric relationship between a pair of molecules.
- Identify the chiral centers in a molecule.
- Describe different types of isomers.

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged - the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers**. Isomers are molecules with the same molecular formulas, but different arrangements of atoms. There are several different types of isomers (some previously discussed and some being introduced):

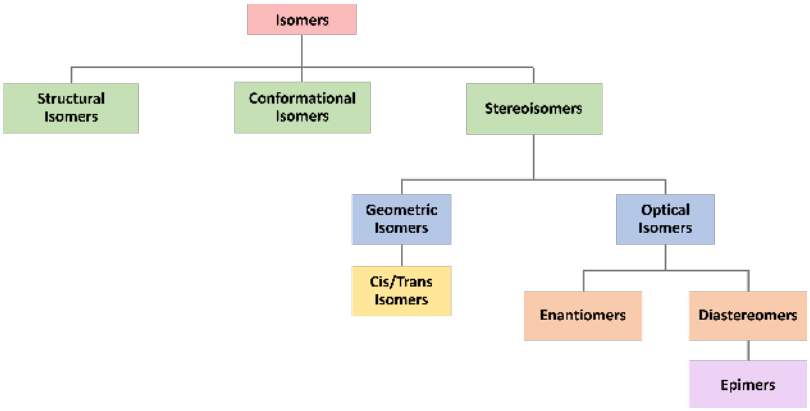


Figure **6.2.1**: Different types of isomers.

Structural Isomers

Structural isomers are molecules that have the same molecular formula, but the atoms are connected/bonded differently. As a result, these compounds will have different IUPAC names.

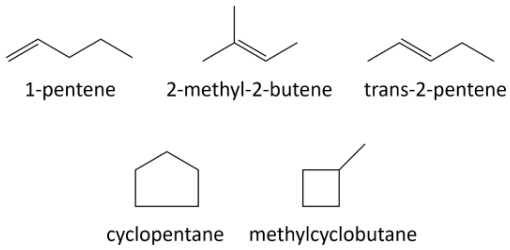


Figure **6.2.2**: Structural isomers with the C_5H_{10} molecular formula.

Conformational Isomers

Conformational isomers are molecules with the same molecular formula and the same connectivity/bonding between the atoms. However, due to the rotation of one or more single bonds, the molecules look as if they are bonded differently. Conformational isomers will have the same IUPAC name.

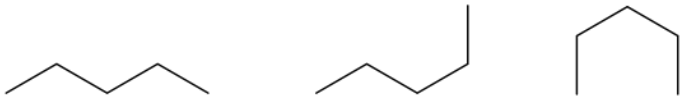


Figure **6.2.3**: Conformational isomers of pentane.

Stereoisomers

Stereoisomers also have the same molecular formula and same connectivity/bonding between the atoms. However, these isomers have different three-dimensional arrangements. Stereoisomers can be further categorized based on how the 3-D arrangements differ.

Geometric Isomers

Geometric isomers, also called **cis-trans isomers,** have different configurations due to the restricted rotation of double bonds or cyclic molecules. The **cis isomer** occurs when the groups are on the same side of the molecule. The **trans isomer** occurs when the groups are on the opposite side of the molecule. Geometric isomers will have the same IUPAC name, except for the cis/trans designation at the beginning of the name.

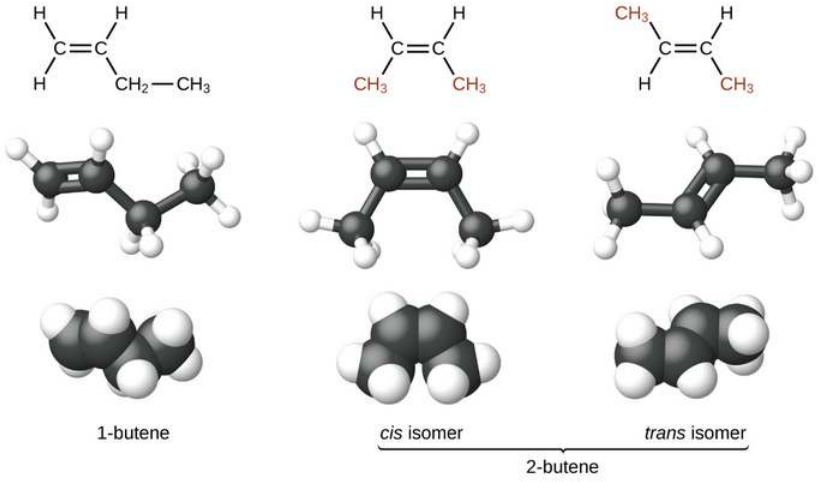


Figure \(\PageIndex{4}\): Structural and Geometric isomers of butene. OpenStax, CC BY 4.0 <https://creativecommons.org/licenses/by/4.0>, via Wikimedia Commons

Optical Isomers

Stereoisomers that are not geometric isomers are known as **optical isomers**. Optical isomers, which were given their name because of their interactions with plane-polarized light, differ in the placement of substituted groups around one or more atoms of the molecule. These types of isomers are labeled as **enantiomers** or **diastereomers**.

Enantiomers are non-superimposable (no symmetry) mirror images. Your hands are a common example of a pair of enantiomers. Your left hand and right hand are mirror images of one another, but no matter how you turn, twist, or rotate them, they are not superimposable.

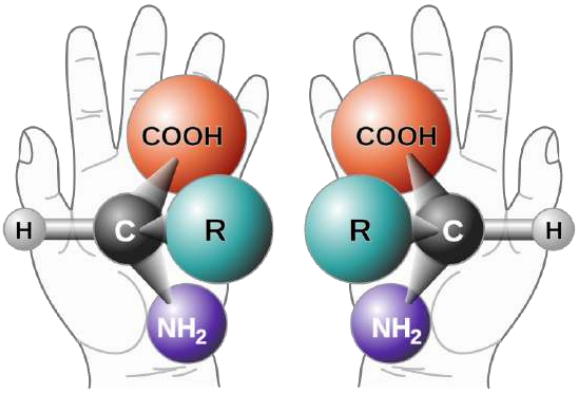


Figure **6.2.5**: Your hands and some molecules are mirror images that are not superimposable. These pairs of objects or molecules are enantiomers.

Objects or molecules that have non-superimposable mirror images are called **chiral**. Chiral molecules contain a **chiral (or chirality) center**. A chiral center is a tetrahedral carbon (carbon with four single bonds) bonded to four different atoms or group of atoms. Note that we have to look beyond the first atom attached to the central carbon atom. The four shaded areas shown below (Figure **6.2.6**) indicate the four unique groups attached to the central carbon atom, which is a chiral center.

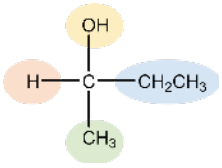


Figure **6.2.6**: A chiral carbon has four unique groups attached to it.

If you look back at the molecule shown above in Figure **6.2.5**, three distinct groups are present. If the R group is anything other than the three groups shown, the molecule is chiral. However, if the R group is the same as one of the groups shown (H, NH_2, or COOH), the molecule will be considered **achiral**. Achiral objects or molecules have symmetry because they have superimposable (identical) mirror images.

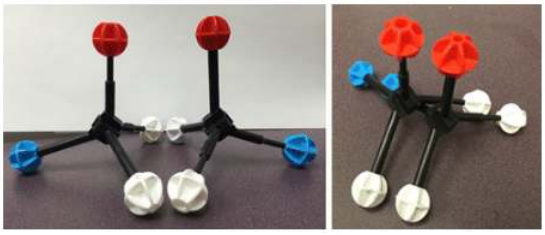


Figure **6.2.7**: Two models that are mirror images and superimposable. Since they are superimposable, they are achiral and do not represent enantiomers.

Another type of optical isomers are **diastereomers**. Diastereomers are non-mirror image isomers that have a different arrangement around one or more chiral centers while some of the atoms have the same arrangement. As shown in the figure below, note that the orientation of groups on the first and third carbons are different but those on the second one remains the same. Therefore, these do not represent the same molecule. The solid wedge indicates a group coming out of the page/screen towards you and the dashed line indicates that a group is going away from you "behind" the page/screen.

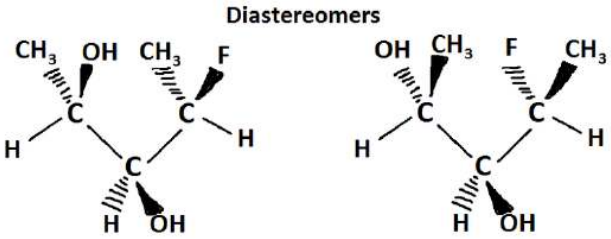


Figure **6.2.8**: Diastereomers differ at one or more atom. These molecules are not mirror images and they are not superimposable. Rhannosh, CC BY-SA 3.0 <https://creativecommons.org/licenses/by-sa/3.0>, via Wikimedia Commons

Epimers are a sub-group of diastereomers that differ at only one chiral center. All epimers are diastereomers but not all diastereomers are epimers. As shown in the figure below, the orientation of the groups on the first and second carbons are the same and only the third carbon changes.

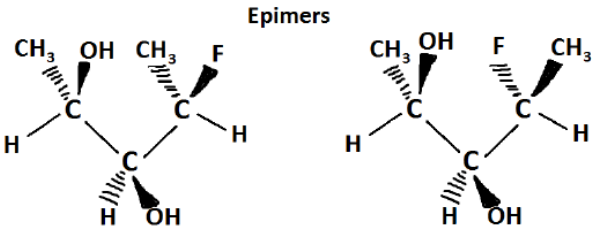
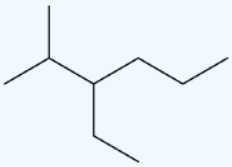


Figure **6.2.9**: Epimers have a different arrangement around only one chiral center, while arrangements around the other atoms are the same.

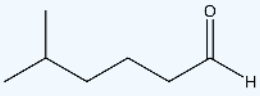
Example 6.2.1

Indicate whether the following molecule has a chiral center. If so, identify the carbon.

a.



b.



Solution

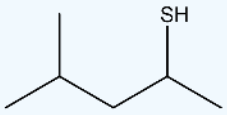
a. This molecule has one chiral center, carbon 3 of the parent chain. When identifying chiral centers, eliminate the carbon atoms that cannot be chiral centers. This includes CH_2 groups, CH_3 groups, and any carbon that is part of a double or triple bond. Then check to see if each of the remaining carbon atoms have four different groups attached. Carbon 2 has two CH_3 groups attached, so it is not chiral.

b. This molecule does not have a chiral center. Carbon 1 is not tetrahedral since it has a double bond to the oxygen. Carbons 2, 3, 4, and 6 have multiple hydrogen atoms. Carbon 5 has two CH_3 groups.

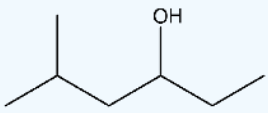
Example 6.2.1

Indicate whether the following molecule has a chiral center. If so, identify the carbon.

a.



b.



Key Takeaway

- Stereoisomers have the same connectivity, but a different 3D structure.
- Enantiomers are non-superimposable mirror images (referred to as chiral molecules).
- Chiral centers, which are present in chiral molecules, are carbon atoms that have four different groups of atoms attached to it.
- Diastereomers are non-mirror image stereoisomers.
- Epimers are stereoisomers that differ around only one chiral center.

Contributors and Attributions

-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

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6.3: Classifying Monosaccharides

Learning Objectives

- Classify monosaccharides based on the carbonyl group.
- Classify monosaccharides based on the number of carbon atoms.
- Distinguish between a D sugar and an L sugar.

Types of Monosaccharides

The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix ***-ose***. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms.

Monosaccharides are also classified as **aldoses** or **ketoses** to indicate the carbonyl-containing group that is present. Those that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.

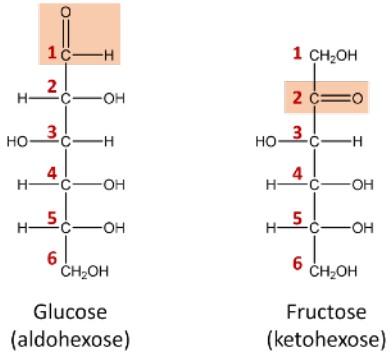


Figure **6.3.1**: Structures of glucose (left) and fructose.

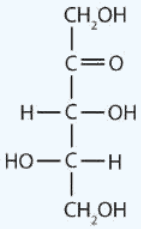
Example 6.3.1

Draw an example of each type of compound.

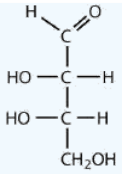
a. a ketopentose
b. an aldotetrose

Solution

a. The structure must have five carbon atoms with the second carbon atom being a carbonyl group and the other four carbon atoms each having an OH group attached. Several structures are possible, but one example is shown.



b. The structure must have four carbon atoms with the first carbon atom part of the aldehyde functional group. The other three carbon atoms each have an OH group attached. Several structures are possible, but one example is shown.



Exercise 6.3.1

Draw an example of each type of compound.

a. an aldohexose
b. a ketotetrose

Stereochemistry of Monosaccharides

The simplest sugars are the trioses. The possible trioses are shown in part (a) of Figure **6.3.2**; glyceraldehyde is an aldotriose, while dihydroxyacetone is a ketotriose. Notice that two structures are shown for glyceraldehyde. These structures are stereoisomers, and hence are isomers having the same structural formula but differing in the arrangement of atoms or groups of atoms in three-dimensional space. If you make models of the two stereoisomers of glyceraldehyde, you will find that you cannot place one model on top of the other and have each functional group point in the same direction. However, if you place one of the models in front of a mirror, the image in the mirror will be identical to the second stereoisomer in part (b) of Figure **6.3.2**. Since these molecules are nonsuperimposable mirror images of each other, they represent enantiomers.

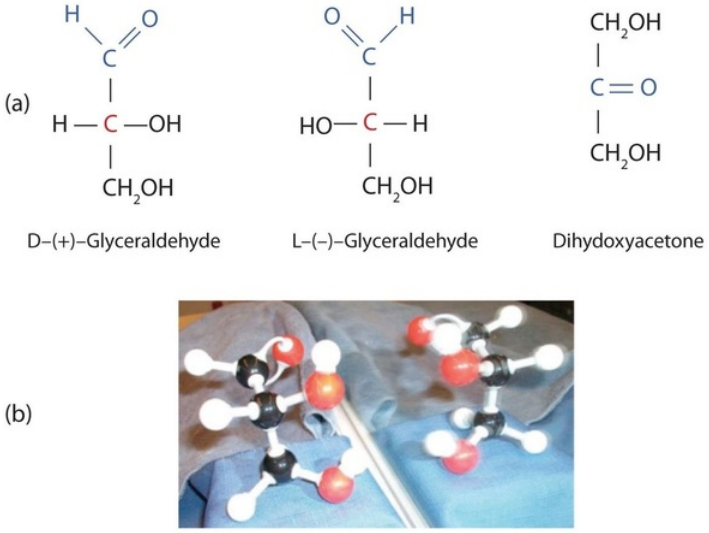


Figure **6.3.2**: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

A key characteristic of enantiomers is that they have a chiral carbon. If a molecule contains one or more chiral carbons, it is likely to exist as two or more stereoisomers. Dihydroxyacetone does not contain a chiral carbon and thus does not exist as a pair of stereoisomers. Glyceraldehyde, however, has a chiral carbon and exists as a pair of enantiomers. Except for the direction in which each enantiomer rotates plane-polarized light, these two molecules have identical physical properties. One enantiomer has a specific rotation of +8.7°, while the other has a specific rotation of −8.7°.

H. Emil Fischer, a German chemist, developed the convention commonly used for drawing monosaccharides. These structural formulas, known as **Fischer projections**, use horizontal and vertical lines to indicate the three–dimensional structure of a molecule. The horizontal lines project forward (coming towards you), while the vertical lines project backward (going away from you). Where the lines intersect represents a carbon atom that is usually chiral.

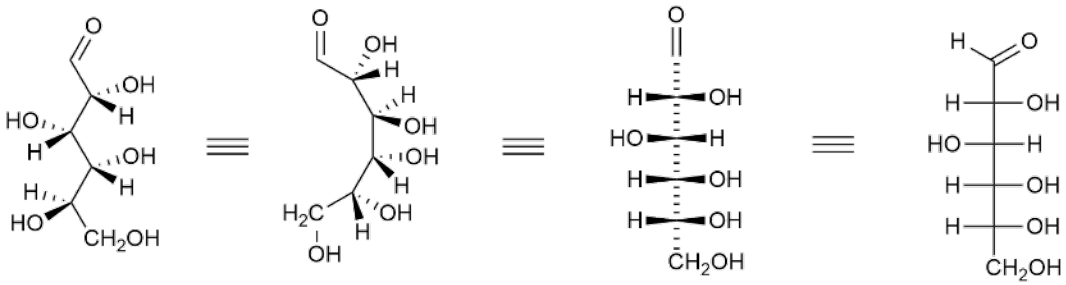


Figure 6.3.3: Projection of Glucose to the Fischer Projection. Choutkaj, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons

When drawing Fischer projections, the aldehyde group is written at the top, and the H and OH groups that are attached to each chiral carbon are written to the right or left. The arrange of the atoms distinguishes one stereoisomer from the other.

The two enantiomers of glyceraldehyde are especially important because monosaccharides with more than three carbon atoms can be considered as being derived from them. Thus, D- and L-glyceraldehyde provide reference points for designating and drawing all other monosaccharides. Sugars whose Fischer projections terminate in the same configuration as D-glyceraldehyde are designated as **D sugars**; those derived from L-glyceraldehyde are designated as **L sugars**. D and L designations of sugars are based on the position of the hydroxyl on the chiral carbon farthest from the carbonyl group in the Fischer projection of the molecule. All D-sugars have the –OH on the right side and L-sugars have the –OH on the left side.

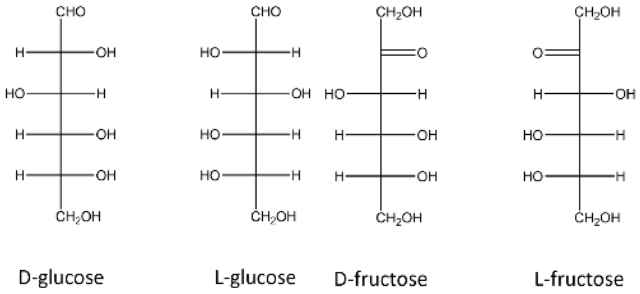


Figure 6.3.4: Fischer projections of enantiomers of glucose (left) and fructose (right).

> *By convention, the penultimate (next-to-last) carbon atom has been chosen as the carbon atom that determines if a sugar is D or L. It is the chiral carbon farthest from the aldehyde or ketone functional group.*

D and L sugars of the same monosaccharide are enantiomers of one another (Figure 6.3.4). When comparing the Fischer projections of monosaccharides, if the arrangement around all of the chiral centers (horizontal lines) are the exact opposite, then the molecules are enantiomers. However, molecules are not “perfect” mirror images are diastereomers. When comparing Fischer projections of monosaccharides, if the arrangement is different at one or more (but not all) chiral centers, then the molecules are diastereomers (Figure 6.3.5).

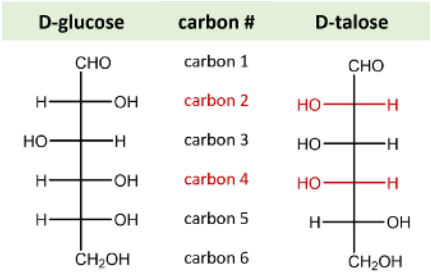


Figure 6.3.5: Fischer projections of diastereomers: D-glucose and D-talose.

The arrangement of H and OH around each chiral center gives the identity of the carbohydrate. Since diastereomers have different arrangements, they will also have different names. Since epimers are a type of diastereomers, they will also have dfiferent names. When comparing Fischer projections, if the arrangement is different at only one chiral center, the molecules are epimers. For example, D-glucose and D-galactose are epimers because the molecules are identical, except for the arrangement of the H and OH around carbon 4 Figure 6.3.6.

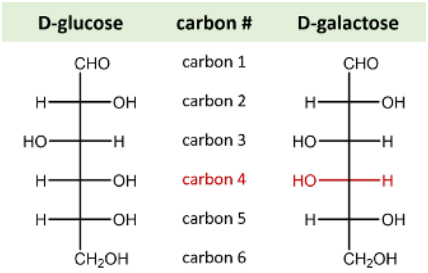
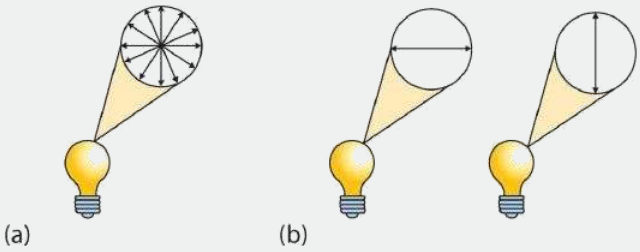


Figure 6.3.1: Fischer projections of epimers: D-glucose and D-galactose.

The general formula for determining the maximum number of stereoisomers of a molecule is 2^n, where n is the number of chiral centers present in the molecule. IN the case of glucose, carbons 2, 3, 4, and 5 are chiral centers. Therefore, there are 2^4 = 2 x 2 x 2 x 2 = 16 stereoisomers of the molecule. Only two can represent enatiomers, while the others would represent diastereomers (or epimers).

Looking Closer: Polarized Light

A beam of ordinary light can be pictured as a bundle of waves; some move up and down, some sideways, and others at all other conceivable angles. When a beam of light has been polarized, however, the waves in the bundle all vibrate in a single plane. Light altered in this way is called *plane-polarized light*. Much of what chemists know about stereoisomers comes from studying the effects they have on plane-polarized light. In this illustration, the light on the left is not polarized, while that on the right is polarized.



Sunlight, in general, is not polarized; light from an ordinary light bulb or an ordinary flashlight is not polarized. One way to polarize ordinary light is to pass it through Polaroid sheets, special plastic sheets containing carefully oriented organic compounds that permit only light vibrating in a single plane to pass through. To the eye, polarized light doesn't "look" any different from nonpolarized light. We can detect polarized light, however, by using a second sheet of polarizing material, as shown here.



In the photo on the left, two Polaroid sheets are aligned in the same direction; plane-polarized light from the first Polaroid sheet can pass through the second sheet. In the photo on the right, the top Polaroid sheet has been rotated 90° and now blocks the plane-polarized light that comes through the first Polaroid sheet.

Certain substances act on polarized light by rotating the plane of vibration. Such substances are said to be optically active. The extent of optical activity is measured by a polarimeter, an instrument that contains two polarizing lenses separated by a sample tube, as shown in the accompanying figure. With the sample tube empty, maximum light reaches the observer's eye when the two lenses are aligned so that both pass light vibrating in the same plane. When an optically active substance is placed in the sample tube, that substance rotates the plane of polarization of the light passing through it, so that the polarized light emerging from the sample tube is vibrating in a different direction than when it entered the tube. To see the maximum amount of light when the sample is in place, the observer must rotate one lens to accommodate the change in the plane of polarization.

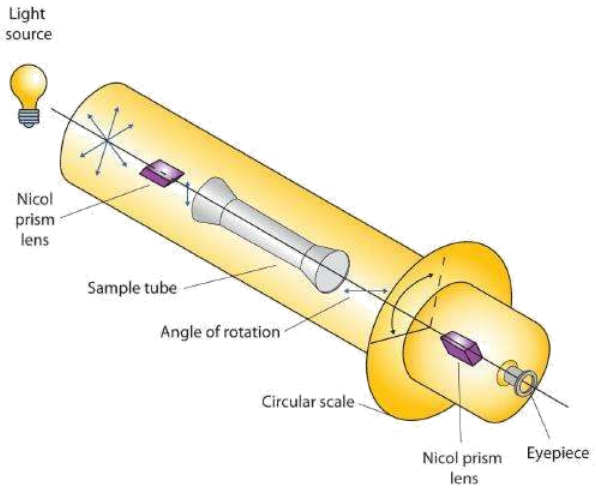


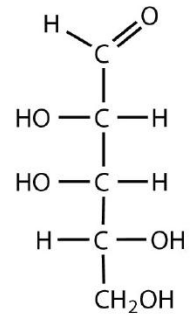
Figure **6.3.5**: Diagram of a Polarimeter

Some optically active substances rotate the plane of polarized light to the right (clockwise) from the observer's point of view. These compounds are said to be **dextrorotatory (d)** and the direction of rotation is denoted with a positive sign (+). Substances that rotate light to the left (counterclockwise) are said to be **levorotatory (l)** and the direction of rotation is denoted with a negative sign (−). Achiral compounds are optically inactive because they do not rotate plane-polarized light. **Racemic mixtures**, mixtures containing a 50:50 mix of both enantiomers, are also optically inactive.

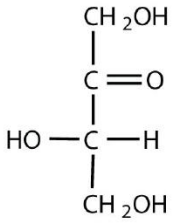
✔ Example **6.3.2**

Identify each sugar as an aldose or a ketose and then as a D sugar or an L sugar.

a.



b.



Solution

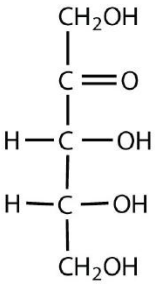
a. aldose; D sugar. The carbonyl group is on carbon 1 which indicates the presence of an aldehyde. The hydroxyl on the chiral carbon farthest from the carbonyl group is pointing to the right, making it a D-sugar.

b. ketose; L sugar. The carbonyl group is on carbon 2 which indicates the presence of an ketone. The hydroxyl on the chiral carbon farthest from the carbonyl group is pointing to the left, making it an L-sugar.

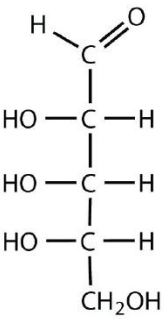
? Exercise 6.3.2

Identify each sugar as an aldose or a ketose and then as a D sugar or an L sugar.

a.



b.



Summary

- Monosaccharides can be classified based on their chemical composition (number of carbon atoms and/or the type of carbonyl group).
- Fischer projections are commonly used to draw monosaccharides. The intersection of the horizontal and veritical lines represents a carbon, which is typically a chiral center.
- Most monosaccharides contain at least one chiral carbon and can form 2^n possible stereoisomers.
- Three types of stereoisomers present in monosaccharides can be identified by comparing the chiral centers in Fischer Projections:
  o all opposite = enantiomers
  o only 1 opposite = epimers
  o more than 1, but less than all opposite = diastereomers
- Enantiomers are a specific type of stereoisomers that are mirror images of each other and rotate plane polarized light in opposite directions.

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6.4: Important Monosaccharides

Learning Objectives

- Identify the structures of glucose, galactose, and fructose.
- Contrast structures of the important monosaccharides.
- Classify monosaccharides as D- or L-sugars.

Important Hexoses

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure **6.4.1**). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

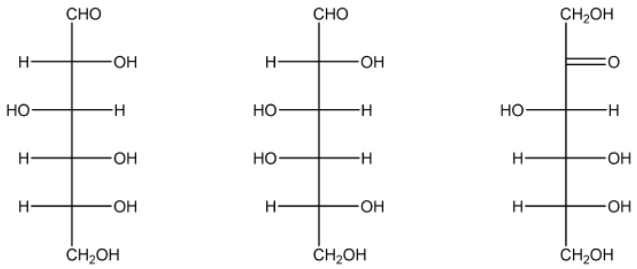


Figure \(\PageIndex{1}\): Structures of three important hexoses: D-glucose (left), D-galactose (middle), and D-fructose (right).

Glucose

D-Glucose, generally referred to simply as glucose, is the most abundant sugar found in nature. Most of the carbohydrates we eat are eventually converted to glucose in a series of biochemical reactions that produce energy for our cells. Glucose is also known by three other names: *dextrose*, from the fact that it rotates plane-polarized light in a dextrorotatory (clockwise) direction; *corn sugar* because in the United States cornstarch is used in the commercial process that produces glucose from the hydrolysis of starch; and *blood sugar* because it is the carbohydrate found in the circulatory system of animals. Normal blood sugar values range from 70 to 105 mg glucose/dL plasma, and normal urine may contain anywhere from a trace to 20 mg glucose/dL urine.

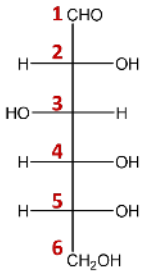


Figure **6.4.2**: Fischer projection of D-glucose

The Fischer projection of D-glucose is given in Figure **6.4.2**. Glucose is a D sugar because the OH group on the fifth carbon atom (the chiral center farthest from the carbonyl group) is on the right. In fact, all the OH groups except the one on the third carbon atom are to the right. If the direction of any of these groups change, it will no longer represent D-glucose.

Galactose

D-Galactose does not occur in nature in the uncombined state. It is released when lactose, a disaccharide found in milk, is hydrolyzed. The galactose needed by the human body for the synthesis of lactose is obtained by the metabolic conversion of D-glucose to D-galactose. Galactose is also an important constituent of the glycolipids that occur in the brain and the myelin sheath of nerve cells. For this reason it is also known as *brain sugar*.

Galactose is an epimer of glucose because the arrangement of the molecules are identical, except around one chiral center (Figure **6.4.3**).

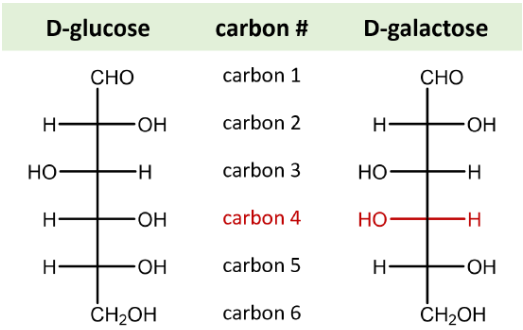


Figure **6.4.3**: Fischer projections of D-Glucose and D-Galactose.

Fructose

D-Fructose, also shown in Figure **6.4.1**, is the most abundant ketohexose. Glucose and fructose are not epimers. Instead, these molecules are structural isomers of one another. They both have the $C_6H_{12}O_6$ molecular formula, but differ in the arrangement of atoms around carbons 1 and 2. Note that from the third through the sixth carbon atoms, the structures are the same.

Fructose occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. D-fructose (from the Latin *fructus*, meaning "fruit") is also referred to as *levulose* because it has a specific rotation that is strongly levorotatory (−92.4°). Fructose is the sweetest sugar, being 1.7 times sweeter than sucrose (table sugar), although many nonsugars are several hundred or several thousand times as sweet (Table **6.4.1**).

Table **6.4.1**: The Relative Sweetness of Some Compounds (Sucrose = 100)

Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000
sucralose	60,000

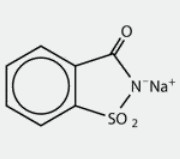
Looking Closer: Artificial Sweeteners

Although sweetness is commonly associated with mono- and disaccharides, it is not a property found only in sugars. Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake. The synthetic compounds are noncaloric or used in such small quantities that they do not add significantly to the caloric value of food.

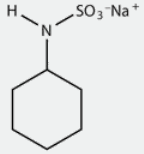
The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short years of World War I, the ban was lifted and was not reinstated at

the war's end. One drawback to the use of saccharin is its bitter, metallic aftertaste. The initial solution to this problem was to combine saccharin with cyclamate, a second artificial sweetener discovered in 1937.

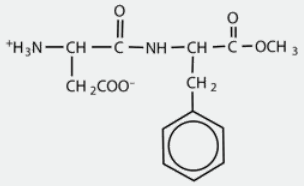
In the 1960s and 1970s, several clinical tests with laboratory animals implicated both cyclamate and saccharin as carcinogenic (cancer-causing) substances. The results from the cyclamate tests were completed first, and cyclamate was banned in the United States in 1969. Then a major study was released in Canada in 1977 indicating that saccharin increased the incidence of bladder cancer in rats. The US Food and Drug Administration (FDA) proposed a ban on saccharin that raised immediate public opposition because saccharin was the only artificial sweetener still available. In response, Congress passed the Saccharin Study and Labeling Act in 1977, permitting the use of saccharin as long as any product containing it was labeled with a consumer warning regarding the possible elevation of the risk of bladder cancer. Today this warning is no longer required; moreover, the FDA is currently reviewing the ban on cyclamate, as 75 additional studies and years of usage in other countries, such as Canada, have failed to show that it has any carcinogenic effect.



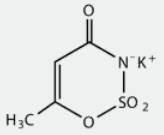
Saccharin



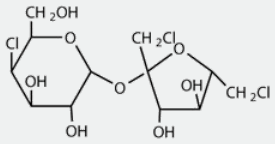
Cyclamate



Aspartame



Acesulfame K



Sucralose

A third artificial sweetener, aspartame, was discovered in 1965. This white crystalline compound is about 180 times sweeter than sucrose and has no aftertaste. It was approved for use in 1981 and is used to sweeten a wide variety of foods because it blends well with other food flavors. Aspartame is not used in baked goods, however, because it is not heat stable.

In the body (or when heated), aspartame is initially hydrolyzed to three molecules: the amino acids aspartic acid and phenylalanine and an alcohol methanol. Repeated controversy regarding the safety of aspartame arises partly from the fact that the body metabolizes the released methanol to formaldehyde. It should be noted, though, that a glass of tomato juice has six times as much methanol as a similar amount of a diet soda containing aspartame. The only documented risk connected to aspartame use is for individuals with the genetic disease *phenylketonuria* (PKU); these individuals lack the enzyme needed to metabolize the phenylalanine released when aspartame is broken down by the body. Because of the danger to people with PKU, all products containing aspartame must carry a warning label.

Acesulfame K, discovered just two years after aspartame (1967), was approved for use in the United States in 1988. It is 200 times sweeter than sugar and, unlike aspartame, is heat stable. It has no lingering aftertaste.

One of the newest artificial sweeteners to gain FDA approval (April 1998) for use in the United States is sucralose, a white crystalline solid approximately 600 times sweeter than sucrose. Sucralose is synthesized from sucrose and has three chlorine atoms substituted for three OH groups. It is noncaloric because it passes through the body unchanged. It can be used in baking because it is heat stable.

All of the extensive clinical studies completed to date have indicated that these artificial sweeteners approved for use in the United States are safe for consumption by healthy individuals in moderate amounts.

Important Pentoses

Ribose and 2-deoxyribose are pentoses which are parts of larger biomolecules that make up our genetic material called nucleic acids. Ribonucleic acid (RNA) contains the sugar ribose and deoxyribonucleic acid (DNA) contains 2-deoxyribose.

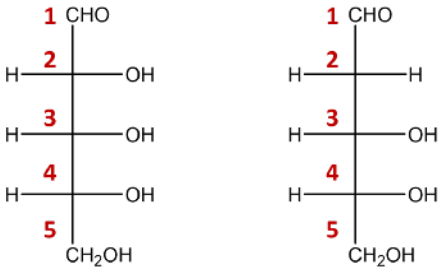


Figure 6.4.1: Fischer projections of D-ribose (left) and D-2-deoxyribose (right).

Example 6.4.1

Describe the similarities and differences in the structures of D-glucose and D-galactose.

Solution

D-glucose and D-galactose are similar because they are both monosaccharides that are classified as aldohexoses. However, these two monosaccharides differ in the arrangement of the H and OH around the fourth carbon atom.

Exercise 6.4.1

Describe similarities and differences in the structures of D-glucose and D-fructose

Summary

- Three abundant hexoses in living organisms are the aldohexoses D-glucose and D-galactose and the ketohexose D-fructose.
- D-glucose and D-galactose are epimers because the molecules are identical, except at C4.
- D-glucose and D-fructose are structural isomers that both have the $C_6H_{12}O_6$ molecular formula.

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6.5: Reactions of Monosaccharides

Learning Objectives

- Distinguish between the oxidation and reduction of monosaccharides.
- Define what is meant by anomers.
- Predict the product of the ring formation of a monosaccharide.

Monosaccharide Redox Reactions

The chemical reactions of carbohydrates are largely that of the hydroxyl and carbonyl groups. The aldehyde and ketone groups in sugars undergo redox reactions to produce new substances. Recall, redox (reduction-oxidation) reactions involve a transfer of electrons. The substance losing electrons is said to undergo oxidation, while the substance gaining electrons is said to undergo reduction. In the case of organic molecules, this process is often distinguished based on the change in hydrogen and/or oxygen atoms. An increase in O and/or decrease in H represents oxidation. While a decrease in O and/or increase in H represents reduction. These processes result in a change in the carbonyl functional group present in the molecule Figure **6.5.1**.

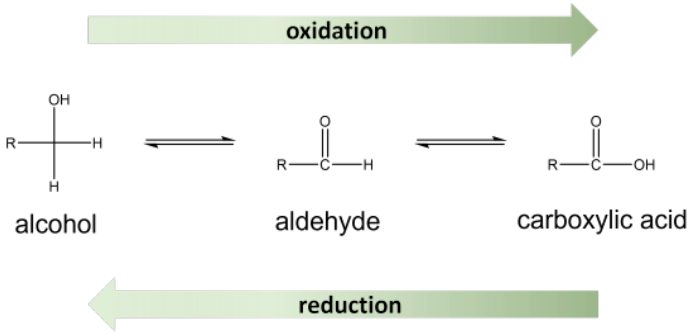


Figure **6.5.1**: Oxidation and reduction of organic functional groups.

The oxidation of monosaccharides, results in the aldehyde functional group being converted into a carboxylic acid. This compound is then referred to as a **sugar acid**. The same process will occur if the monosaccharide is a ketose. In the presence of an oxidizing agent, the ketose can rearrange to an aldose and then undergo oxidation to form the sugar acid. Carbohydrates that are able to undergo oxidation are referred to as **reducing sugars** (sugars that are reducing agents). The **Benedict's test** is a useful test to determine the presence of reducing sugars. In the reaction between a reducing sugar and Benedict's reagent, copper (II) ion is reduced to copper (I) by the aldehyde functional group Figure **6.5.2**:.

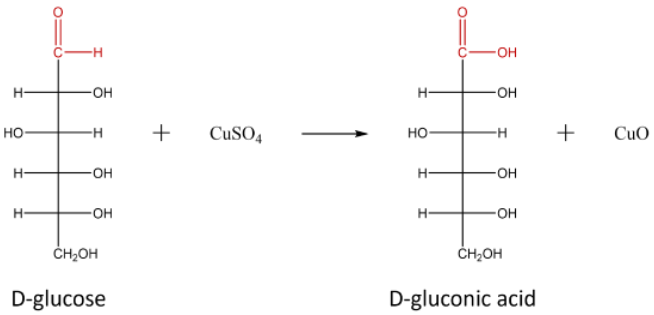


Figure **6.5.2**: Chemical reaction for the reduction of Cu (II) by glucose. Note the oxidation of the aldehyde to a carboxylic acid.

The reduction of monosaccharides can also occur. This reaction results in the aldehyde functional group being converted to an alcohol, in a compound referred to as a **sugar alcohol**.

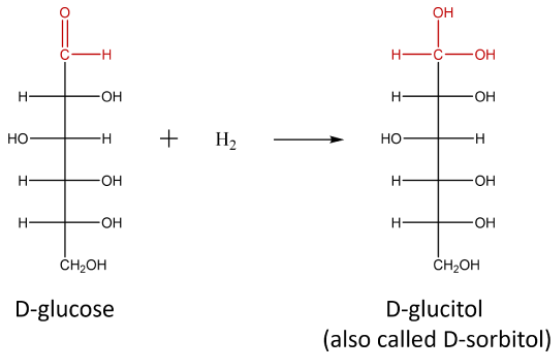


Figure 6.5.3: Copy and Paste Caption here. (Copyright; author via source)

Monosaccharide Ring Formation

So far we have represented monosaccharides as linear molecules, but many of them also adopt cyclic structures. This conversion occurs because of the ability of aldehydes and ketones to react with alcohols. When the alcohol and aldehyde combine, a **hemiacetal** is formed. When an alcohol and ketone combine, a **hemiketal** is formed.

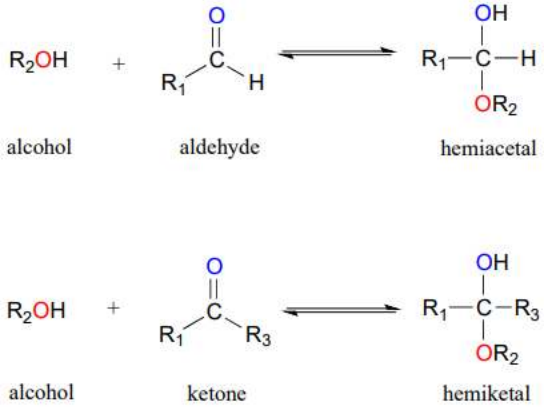


Figure 6.5.4: Formation of a hemiacetal and hemiketal. " Hemiacetals, Hemiketals, and Hydrates" by Tim Soderberg, LibreTexts is licensed under CC BY-NC-SA .

You might wonder why the aldehyde reacts with the OH group on the fifth carbon atom rather than the OH group on the second carbon atom next to it. Recall that cyclic alkanes containing five or six carbon atoms in the ring are the most stable. The same is true for monosaccharides that form cyclic structures: rings consisting of five or six carbon atoms are the most stable.

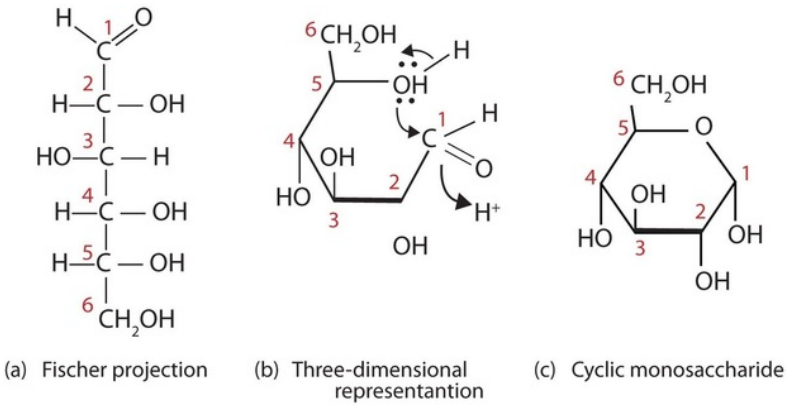


Figure 6.5.5: Ring formation of D-glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two **anomers**. Anomers are a type of diastereomer (technically epimer) that differ only around the **anomeric carbon**. The anomeric carbon is the carbonyl carbon that reacts to form the cyclic structure. The two possible arrangements, termed *anomers*, are referred to as the alpha (α) and beta (β) anomers. The **a anomer** is formed when the hydroxyl group bonded to the anomeric carbon is trans (opposite side) to the carbon outside the ring (carbon 6). The **β anomer** is formed when the hydroxyl group bonded to the anomeric carbon is cis (same side) to the carbon outside the ring. Note that this hydroxyl group on the anomeric carbon is formed during the hemiacetal/hemiketal reaction.

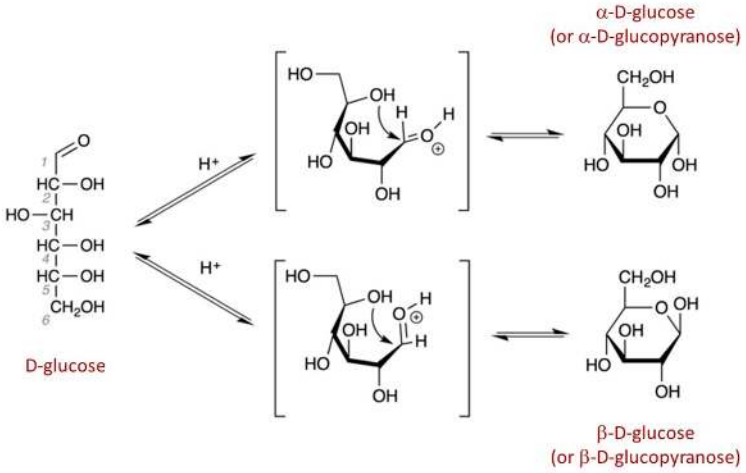


Figure 6.5.6: . Ring formation in D–glucose (left) to form α–D–glucose (top) and β–D–glucose (bottom). Steff-X, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons (changes made to include molecule names).

It is possible to obtain a sample of crystalline glucose in which all the molecules have the α structure or all have the β structure. The α form melts at 146°C and has a specific rotation of +112°, while the β form melts at 150°C and has a specific rotation of +18.7°. When the sample is dissolved in water, however, a mixture is soon produced containing both anomers as well as the straight-chain form, in dynamic equilibrium (part (a) of Figure 6.5.7). You can start with a pure crystalline sample of glucose consisting entirely of either anomer, but as soon as the molecules dissolve in water, they open to form the carbonyl group and then reclose to form either the α or the β anomer. The opening and closing repeats continuously in an ongoing interconversion between anomeric forms and is referred to as **mutarotation** (Latin *mutare*, meaning "to change"). At equilibrium, the mixture consists of about 36% α-D-glucose, 64% β-D-glucose, and less than 0.02% of the open-chain aldehyde form. The observed rotation of this solution is +52.7°.

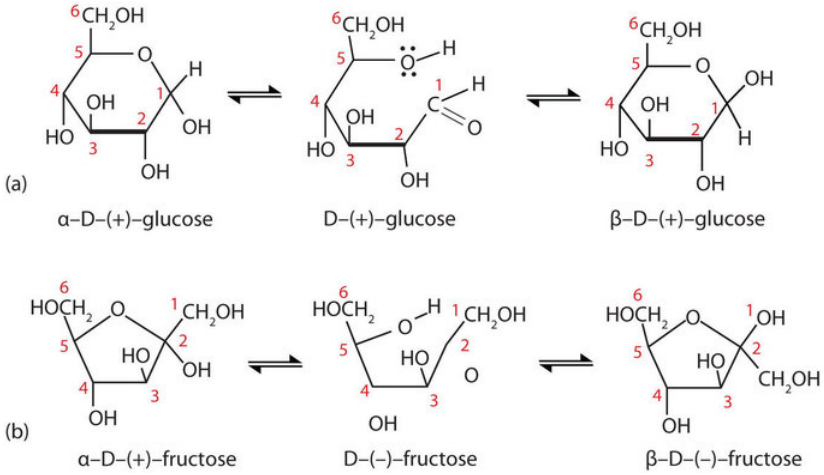


Figure 6.5.7: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

Even though only a small percentage of the molecules are in the open-chain aldehyde form at any time, the solution will nevertheless exhibit the characteristic reactions of an aldehyde. As the small amount of free aldehyde is used up in a reaction, there is a shift in the equilibrium to yield more aldehyde. Thus, all the molecules may eventually react, even though very little free aldehyde is present at a time.

Drawing Cyclic Structures of Monosaccharides

The cyclic forms of sugars are commonly depicted as **Haworth projections**. This convention, first suggested by the Englis chemist Walter N. Haworth, shows molecules drawn as planar rings with darkened edges representing the side facing toward the viewer. The structure is simplified to show only the functional groups attached to the carbon atoms. Any group written to the *right* in a Fischer projection appears *below (bottom face)* the plane of the ring in a Haworth projection, and any group written to the *left* in a Fischer projection appears *above* (top face) the plane in a Haworth projection.

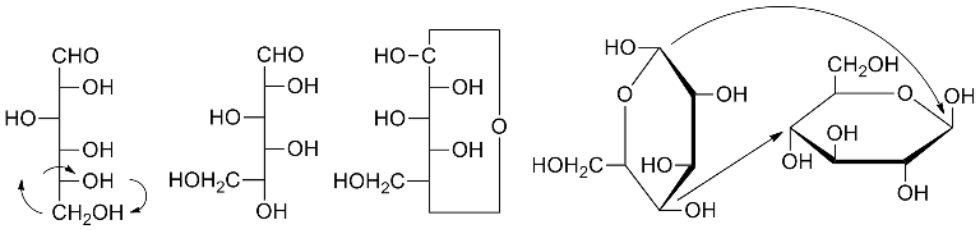


Figure 6.5.8: Conversion of the Fischer projection of D-glucose to the Haworth projection of ß-D-glucose.

1. When converting a Fischer projection (line) to a Haworth projection, you must first identify the type of monosaccharide involved. If the carbohydrate represents an aldohexose, the **pyranose** ring is typically used. A pyranose is a cyclic structure that contains five carbon atoms and an oxygen. If the carbohydrate represents a ketohexose, the **furanose** ring is typically used. The furanose ring contains four carbon atoms and an oxygen.

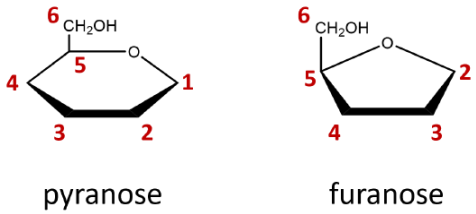


Figure 6.5.9: Haworth projections of a pyranose and furanose ring.

2. Indicate the arrangement of the hydroxyl group attached to the anomeric carbon to identify the sugar as an alpha or beta anomer. The α and β anomers are determined with respect to carbon 6. If the molecule represents a D-sugar, carbon 6 will be above the plane of the ring (top face) and forn an L-sugar, carbon 6 will be below the plane of the ring (ring). The α anomer occurs when the OH on the anomeric carbon is trans to carbon 6 and the β anomer occurs when the OH on the anomeric carbon is cis to carbon 6. If the cyclic structure contains a furanose, since carbon 1 is not included within the ring, that carbon group would be arranged in the opposite direction of the OH group (Figure \(\PageIndex{10}\)).

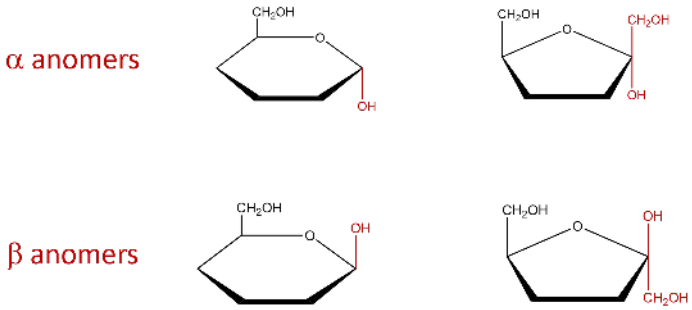


Figure 6.5.10: Arrangement of groups around the anomeric carbon to designate the molecule as an alpha or beta anomer.

3. The remaining chiral centers (carbons 2, 3 and 4 of the pyranose or carbons 3 and 4 of the furanose) are arranged based on the directions of the hydroxyl from the Fischer projection structures. Groups to the left of the Fischer projection would point up (top face), while groups to the right would point down (bottom face).

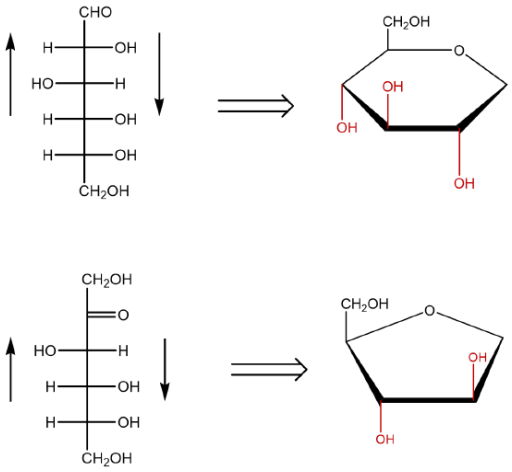


Figure 6.5.11: Fischer projections (left) and incomplete Haworth projections (right) of D-glucose (top) and D-fructose (bottom).

Since the Fischer Projection of any given carbohydrate is always the same, the Haworth Projection is essentially always the same. The only differences between the Haworth Projection of the alpha or beta form of a single carbohydrate, is how the OH (and carbon 1 if a furanose ring) is arranged around the anomeric carbon to determine whether the molecule is alpha or beta.

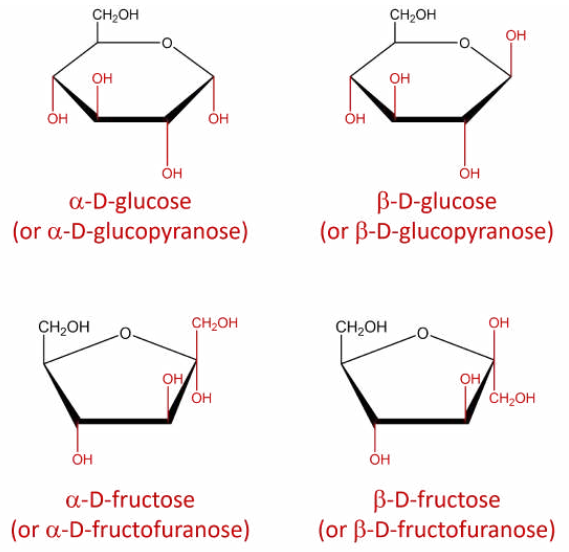


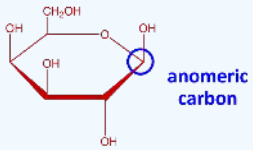
Figure 6.5.12: Haworth projections of D-glucose (top) and D-fructose (bottom).

The difference between the α and the β forms of sugars may seem trivial, but such structural differences are often crucial in biochemical reactions. This explains why we can get energy from the starch in potatoes and other plants but not from cellulose, even though both starch and cellulose are polysaccharides composed of glucose molecules linked together.

Example 6.5.1

Draw the cyclic structure for β-D-galactose. Identify the anomeric carbon.

Solution



To identify the structure, we should first start with the Fischer projection of D-galactose. Since it is an aldohexose, we will start with the pyranose ring. The beta anomer was requested, so the OH on the anomeric carbon (C1) is cis to C6. Since C6 is top face (pointing up), the OH will be top face. Carbons 2, 3, and 4 are then arranged based on the Fischer projection arrangement at those carbons (C2 right, C3 left, and C4 left).

Exercise 6.5.1

Draw the cyclic structure for α-D-galactose. Identify the anomeric carbon

Summary

- Monosaccharides can be oxidized to produce sugar acids or reduced to form sugar alcohols.
- Monosaccharides commonly exist in the cyclic form and are shown as Haworth projections.
- Two cyclic stereoisomers can form from each straight-chain monosaccharide; these are known as anomers. The alpha (α) anomer is trans to carbon 6 and the beta (ß) anomer is cis to carbon 6.

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6.6: Disaccharides

Learning Objectives

- Identify the structures of sucrose, lactose, and maltose.
- Identify the monosaccharides that are needed to form sucrose, lactose, and maltose

Previously, you learned that monosaccharides can form cyclic structures by the reaction of the carbonyl group with an OH group. These cyclic molecules can in turn react with another alcohol. **Disaccharides** ($C_{12}H_{22}O_{11}$) are sugars composed of two monosaccharide units that are joined by a carbon–oxygen-carbon linkage known as a **glycosidic linkage (or glycosidic bond)**. This linkage is formed from the reaction of the anomeric carbon of one cyclic monosaccharide with the OH group of a second monosaccharide. If one anomeric carbon is free (not part of a glycosidicbond), the sugar is a reducing sugar. If there is no free anomeric carbon, the sugar is a nonreducing sugar.

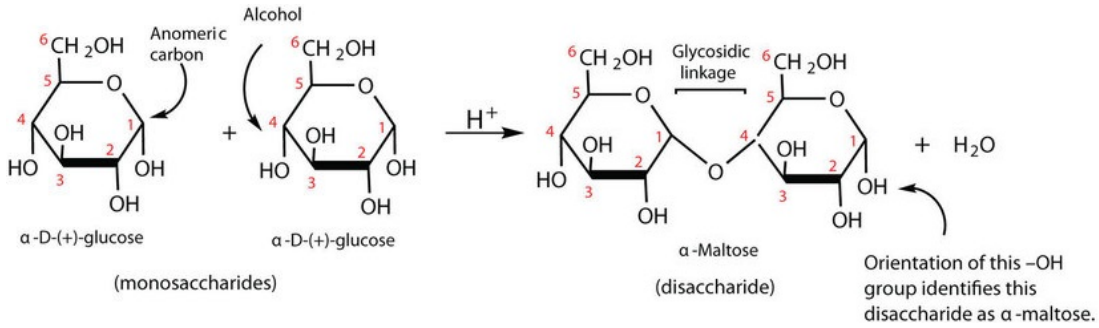


Figure 6.6.1: Formation of the maltose disaccharide.

The disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water. We'll consider each sugar in more detail.

Maltose

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units.

In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*. The same reactions can be carried out in the laboratory with dilute acid as a catalyst, although in that case the rate is much slower, and high temperatures are required. Whether it occurs in the body or a glass beaker, the hydrolysis of maltose produces two molecules of D-glucose.

$$\text{maltose} \xrightarrow{H^+ \text{ or maltase}} 2\ \text{D-glucose} \tag{16.6.2}$$

Maltose is a reducing sugar. Thus, its two glucose molecules must be linked in such a way as to leave one anomeric carbon that can open to form an aldehyde group. The glucose units in maltose are joined in a *head-to-tail* fashion through an α-linkage from the first carbon atom of one glucose molecule to the fourth carbon atom of the second glucose molecule (that is, an α-1,4-glycosidic linkage; see Figure 6.6.1). The bond from the anomeric carbon of the first monosaccharide unit is directed downward, which is why this is known as an α-glycosidic linkage. The OH group on the anomeric carbon of the second glucose can be in either the α or the β position, as shown in Figure 6.6.2.

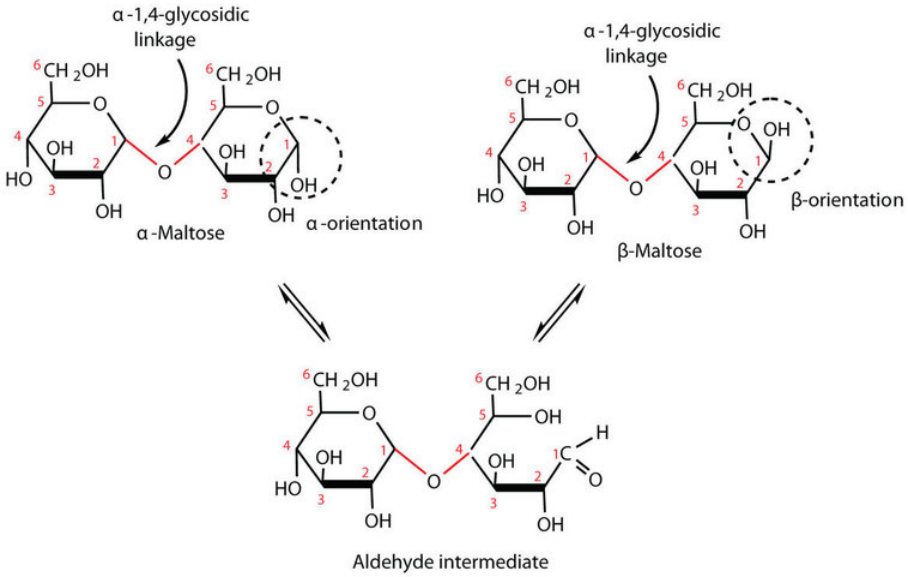


Figure 6.6.2: An Equilibrium Mixture of Maltose Isomers.

Lactose

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow's milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

Lactose is a reducing sugar composed of one molecule of ß-D-galactose and one molecule of D-glucose joined by a β-1,4-glycosidic bond (the bond from the anomeric carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic action of the enzyme *lactase*:

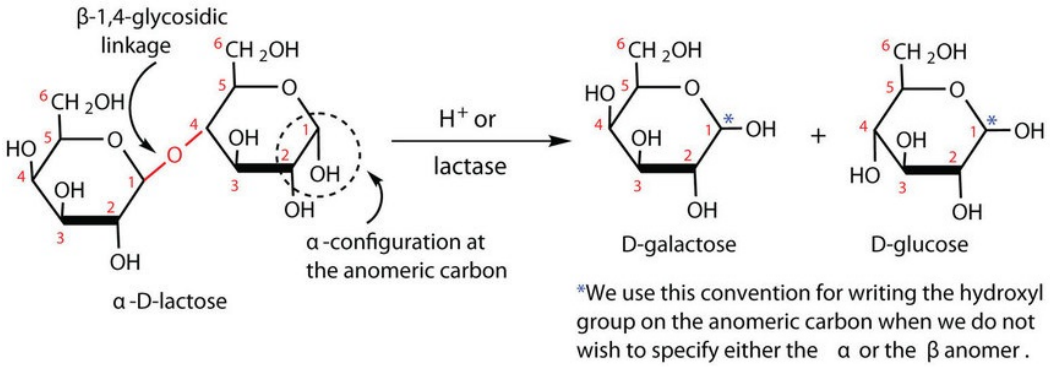
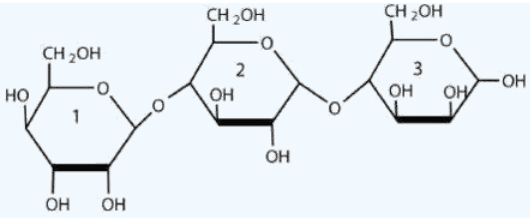


Figure 6.6.3: Hydrolysis of of the alpha lactose disaccharide.

Many adults and some children suffer from a deficiency of lactase. These individuals are said to be lactose intolerant because they cannot digest the lactose found in milk. A more serious problem is the genetic disease galactosemia, which results from the absence of an enzyme needed to convert galactose to glucose. Certain bacteria can metabolize lactose, forming lactic acid as one of the products. This reaction is responsible for the "souring" of milk.

Example 6.6.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.

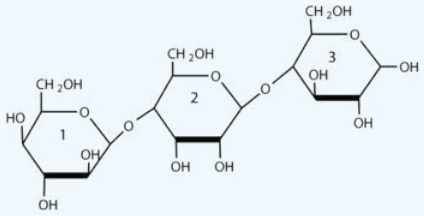


Solution

The glycosidic linkage between sugars 1 and 2 is β because the bond is directed up from the anomeric carbon. The glycosidic linkage between sugars 2 and 3 is α because the bond is directed down from the anomeric carbon.

Exercise 6.6.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.



To Your Health: Lactose Intolerance and Galactosemia

Lactose makes up about 40% of an infant's diet during the first year of life. Infants and small children have one form of the enzyme lactase in their small intestines and can digest the sugar easily; however, adults usually have a less active form of the enzyme, and about 70% of the world's adult population has some deficiency in its production. As a result, many adults experience a reduction in the ability to hydrolyze lactose to galactose and glucose in their small intestine. For some people the inability to synthesize sufficient enzyme increases with age. Up to 20% of the US population suffers some degree of lactose intolerance.

In people with lactose intolerance, some of the unhydrolyzed lactose passes into the colon, where it tends to draw water from the interstitial fluid into the intestinal lumen by osmosis. At the same time, intestinal bacteria may act on the lactose to produce organic acids and gases. The buildup of water and bacterial decay products leads to abdominal distention, cramps, and diarrhea, which are symptoms of the condition.

The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis of the lactose, so some people with lactose intolerance are still able to enjoy cheese, yogurt, or cooked foods containing milk. The most common treatment for lactose intolerance, however, is the use of lactase preparations (e.g., Lactaid), which are available in liquid and tablet form at drugstores and grocery stores. These are taken orally with dairy foods—or may be added to them directly—to assist in their digestion.

Galactosemia is a condition in which one of the enzymes needed to convert galactose to glucose is missing. Consequently, the blood galactose level is markedly elevated, and galactose is found in the urine. An infant with galactosemia experiences a lack of appetite, weight loss, diarrhea, and jaundice. The disease may result in impaired liver function, cataracts, mental retardation, and even death. If galactosemia is recognized in early infancy, its effects can be prevented by the exclusion of milk and all other sources of galactose from the diet. As a child with galactosemia grows older, he or she usually develops an alternate pathway for metabolizing galactose, so the need to restrict milk is not permanent. The incidence of galactosemia in the United States is 1 in every 65,000 newborn babies.

Sucrose

Sucrose, probably the largest-selling pure organic compound in the world, is known as *beet sugar*, *cane sugar*, *table sugar*, or simply *sugar*. Most of the sucrose sold commercially is obtained from sugar cane and sugar beets (whose juices are 14%–20% sucrose) by evaporation of the water and recrystallization. The dark brown liquid that remains after the recrystallization of sugar is sold as molasses.

The sucrose molecule is unique among the common disaccharides in having an α-1,β-2-glycosidic (head-to-head) linkage. Because this glycosidic linkage is formed by the OH group on the anomeric carbon of α-D-glucose and the OH group on the anomeric carbon of β-D-fructose, it ties up the anomeric carbons of both glucose and fructose.

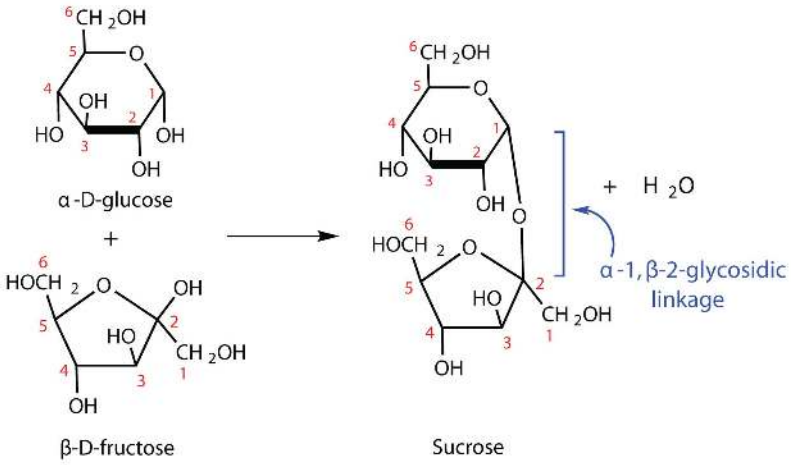


Figure **6.6.4**: Formation of the sucrose disaccharide.

This linkage gives sucrose certain properties that are quite different from those of maltose and lactose. As long as the sucrose molecule remains intact, neither monosaccharide "uncyclizes" to form an open-chain structure. Thus, sucrose is incapable of mutarotation and exists in only one form both in the solid state and in solution. In addition, sucrose does not undergo reactions that are typical of aldehydes and ketones. Therefore, sucrose is a nonreducing sugar.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as invertase) gives an equimolar mixture of glucose and fructose. This 1:1 mixture is referred to as *invert sugar* because it rotates plane-polarized light in the opposite direction than sucrose. The hydrolysis reaction has several practical applications. Sucrose readily recrystallizes from a solution, but invert sugar has a much greater tendency to remain in solution. In the manufacture of jelly and candy and in the canning of fruit, the recrystallization of sugar is undesirable. Therefore, conditions leading to the hydrolysis of sucrose are employed in these processes. Moreover, because fructose is sweeter than sucrose, the hydrolysis adds to the sweetening effect. Bees carry out this reaction when they make honey.

The average American consumes more than 100 lb of sucrose every year. About two-thirds of this amount is ingested in soft drinks, presweetened cereals, and other highly processed foods. The widespread use of sucrose is a contributing factor to obesity and tooth decay. Carbohydrates such as sucrose, are converted to fat when the caloric intake exceeds the body's requirements, and sucrose causes tooth decay by promoting the formation of plaque that sticks to teeth.

✔ Example **6.6.2**

Identify each sugar by its common chemical name.

a. milk sugar

b. table sugar

Solution

a. lactose
b. sucrose

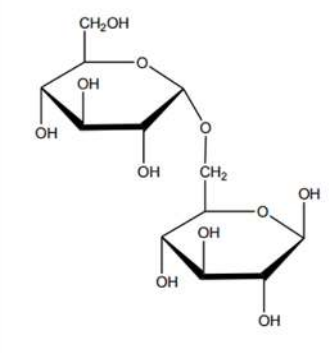
? Exercise 6.6.2

Identify each sugar by its common chemical name.

a. cane sugar
b. malt sugar

✓ Example 6.6.3

Using the structure of the discaccharide shown below to answer the questions that follow:



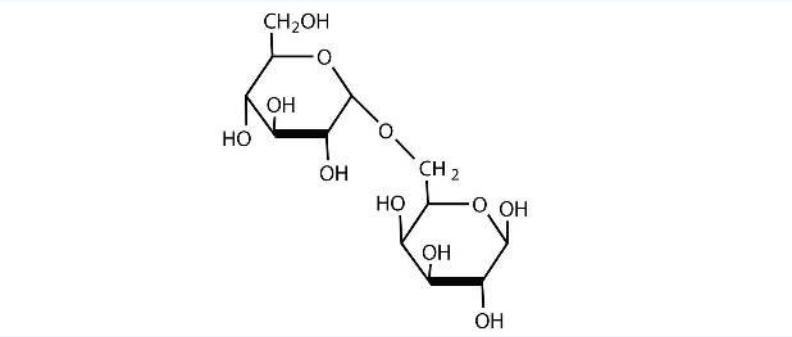
a. What are the identities of the monosaccharides present in the molecule?
b. What type of glycosidic linkage is present?
c. Would this be a reducing sugar?

Solution

a. These are both D-glucose molecules. The monosaccharide to the left is α-D-glucose and the right unit is β-D-glucose.
b. The glycosidic linkage present in the disaccharide is an α-1,6-glycosidic linkage.
c. This molecule would be a reducing sugar, because the anomeric carbon on the glucose to the right is free.

? Exercise 6.6.1

Using the structure of the discaccharide shown below to answer the questions that follow:



a. What are the identities of the monosaccharides present in the molecule?
b. What type of glycosidic linkage is present?
c. Would this be a reducing sugar?

Summary

- Maltose is composed of two molecules of D-glucose (one has to be alpha and the other can be either) joined by an α-1,4-glycosidic linkage. It is a reducing sugar that is found in sprouting grain.
- Lactose is composed of a molecule of ß-D-galactose joined to a molecule of glucose (either alpha or beta) by a β-1,4-glycosidic linkage. It is a reducing sugar that is found in milk.
- Sucrose is composed of a molecule of α-D-glucose joined to a molecule of β-fructose by an α-1,β-2-glycosidic linkage. It is a nonreducing sugar that is found in sugar cane and sugar beets.

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6.7: Oligosaccharides

Learning Objectives

- Describe the role of carbohydrates as cell markers.
- Identify the blood type classified as the universal donor/acceptor.

Oligosaccharides

An **oligosaccharide** is a saccharide polymer containing a small number (typically two to ten) of monosaccharides. Oligosaccharides can have many functions; for example, they are commonly found on the plasma membrane of animal cells where they can play a role in cell-cell recognition. In general, they are found attached to compatible amino acid side-chains in proteins or to lipids.

Oligosaccharides are often found as a component of **glycoproteins** or **glycolipids**. They are often used as chemical markers on the outside of cells, often for cell recognition. Oligosaccharides are also responsible for determining blood type.

Blood Type

Cell markers are carbohydrate chains on the surface of cells where they act as “road signs” allowing molecules to distinguish one cell from another. ABO blood markers found on red blood cells are made up of oligosaccharides that contain either three or four sugar units (Figure 6.7.1).

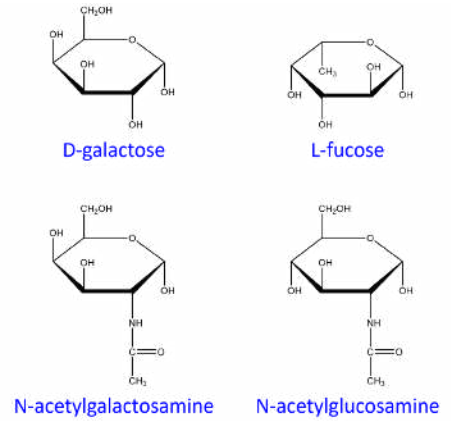


Figure **6.7.1**: Structures of monosaccharide units present in ABO blood markers.

Carbohydrates attached to red blood cells determine the ABO blood type (Figure 6.7.2).

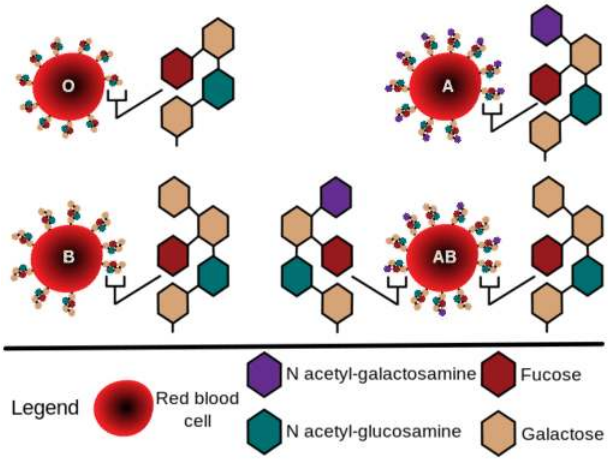


Figure 6.7.2: ABO blood types.

Of the four blood types, type O has the fewest types of saccharides attached to it while type AB has the most. As a result, type O blood is considered the **universal donor** because it doesn't have any saccharides present that will appear as foreign when transfused into blood of another type. The reverse is not true. For example, if type A blood is given to a patient with type O blood, it will be rejected by the body because there is an unknown species being introduced to the body. Type A blood cells contain N-acetylgalactosamine which is not present in type O blood. A person with type O blood would undergo rejection upon receiving type A blood. Since type AB blood has all possible saccharides, type AB blood is considered the **universal acceptor**. The Rhesus factor (Rh) in blood also affects donor and acceptor properties but it does not depend on carbohydrates. The Rh factor is determined by the presence (Rh+) or absence (Rh-) of a specific protein on the surface of red blood cells.

✔ Example 6.7.1

Indicate whether the following blood types could be accepted by a person with type A blood:

a. Type AB
b. Type O

Solution

a. No, because type AB blood has saccharides that are not present in type A blood. Therefore, the presence of this foreign substance would be rejected.
b. Yes, this is the universal donor. Although it does not have all of the same saccharides as type A, no foreign substances are introduced.

? Exercise 6.7.1

Indicate whether the following blood types could be accepted by a person with type AB blood:

a. Type B
b. Type O

Summary

- All blood types include the N-acetylglucosamine, galactose, and fucose; but differ in the absence or presence of additional units.
- Type O blood is considered the universal donor.
- Type AB blood is considered the universal acceptor.

Contributors and Attributions

-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

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6.8: Polysaccharides

Learning Objectives

- Compare and contrast the structures and uses of starch, glycogen, and cellulose.

Polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as ***homopolymers*** because each yields only one type of monosaccharide (glucose) after complete hydrolysis. ***Heteropolymers*** may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. We often think of potatoes as a "starchy" food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polysaccharides: **amylose** and **amylopectin**. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a straight-chain polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (Figure **6.8.1*a***). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (Figure **6.8.1*b***). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

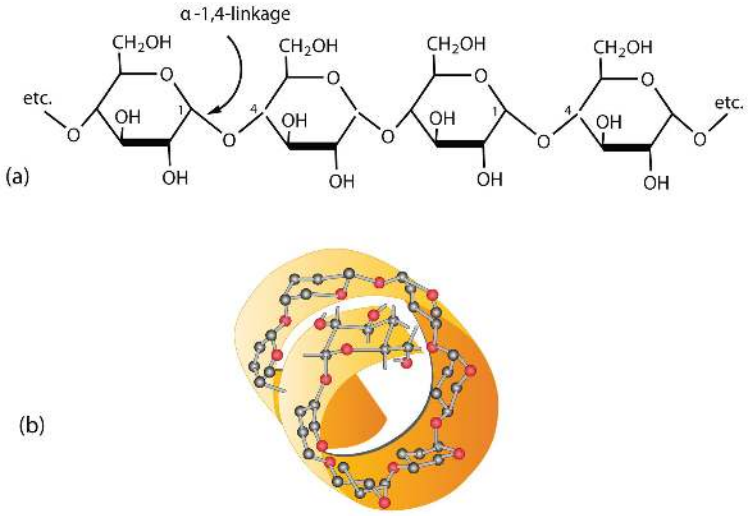


Figure **6.8.1**: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure **6.8.2**). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

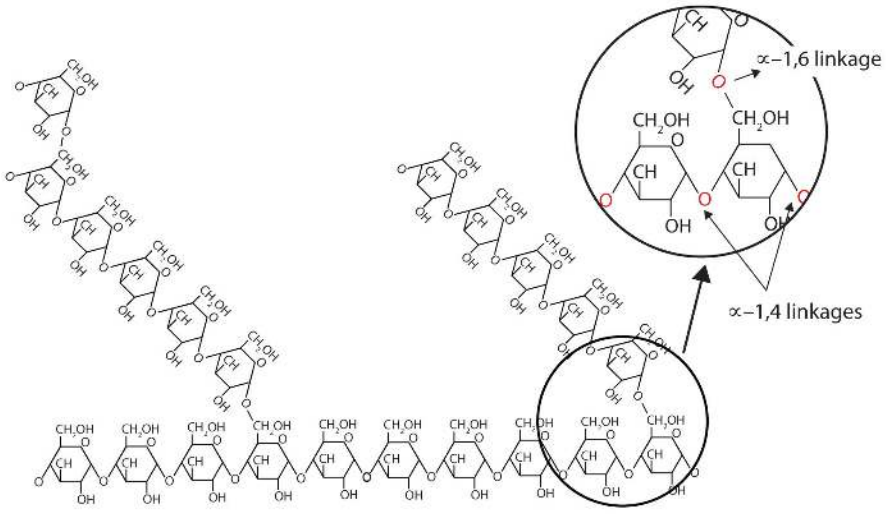


Figure **6.8.2**: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy storage carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

> *About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.*

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (Figures **6.8.3**). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (Figure **6.8.3**). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

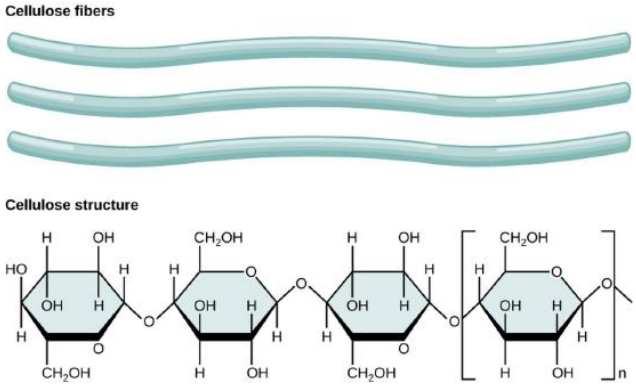


Figure **6.8.3**: Cellulose. In cellulose, glucose monomers are linked in unbranched chains by *β-1*,4 glycosidic linkages. Because of the way the glucose subunits are joined, every glucose monomer is flipped relative to the next one resulting in a linear, fibrous structure.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Career Focus: Certified Diabetes Educator

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.



A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

Example 6.8.1

What monosaccharide is obtained from the hydrolysis of cellulose?

Solution

Glucose (more specifically, *β-D-glucose)*

Exercise 6.8.1

What monosaccharide is obtained from the hydrolysis of each carbohydrate?

a. starch
b. cellulose

Summary

- Starch is a storage form of energy in plants. It contains two polysaccharides composed of alpha-D-glucose units:
  - amylose - linear with α-1,4-glycosidic bonds.
  - amylopectin - branched polysaccharide with α-1,4 and α-1,6-glycosidic bonds.
- Glycogen is a storage form of energy in animals. It is a branched polysaccharide composed of alpha-D-glucose units with α-1,4 and α-1,6-glycosidic bonds. It is more highly branched than amylopectin.
- Cellulose is a structural polysaccharide of glucose units found in plants. It is a linear polysaccharide with the glucose units linked through β-1,4-glycosidic bonds.

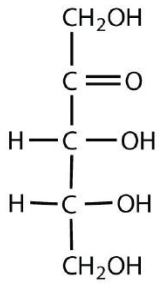
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6.E: Carbohydrates (Exercises)

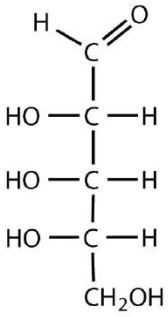
Additional Exercises

1. When an aqueous solution of an unknown carbohydrate was heated, four molecules of glucose were produced. What type of carbohydrate does this compound represent?
2. Classify the following based on the chemical composition (functional group and number of carbon) and then as a D sugar or an L sugar.

a.



b.



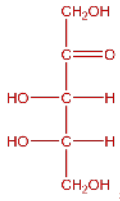
3. Use the structures shown above in problem 2 to answer the following problems:
   a. How many chiral centers are present in the molecule shown in 2a?
   b. What is the maximum number of stereoisomers possible for the molecule shown in 2a?
   c. Draw the enantiomer of the molecule shown in 2a. Is this a D-sugar or L-sugar?
4. What hexose would you expect to be most abundant in each food?
   a. honey
   b. milk
5. Given that the aldohexose D-mannose differs from D-glucose only in the configuration at the second carbon atom, draw the cyclic structure for α-D-mannose.
6. Indicate whether the following would yield a positive Benedict's test
   a. L-galactose
   b. levulose
   c. D-glucose
7. Cellobiose is a disaccharide composed of two glucose units joined by a β-1,4-glycosidic linkage.
   a. Draw the structures of α-cellobiose and β-cellobiose.

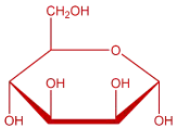
b. Is cellobiose a reducing or nonreducing sugar? Justify your answer.

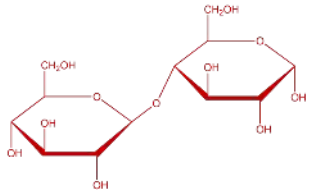
8. Describe the similarities and differences between amylose and cellulose.

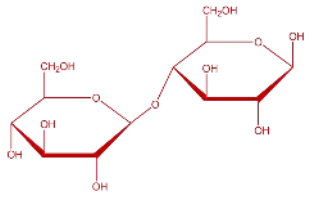
Answers

1. Oligosaccharide because four monosaccharides are present.

3. a. 2 chiral centers (carbons 3 and 4)
   b. 8 possible stereoisomers. There are 3 chiral centers and using $2^n = 2^3 = 8$ possible arrangements that will result in molecules that have the same connectivity around the chiral centers, but with different arrangements.
   c.  , this is an L-sugar.

5. 

7. a. α-cellobiose 

   β-cellobiose 

   b. Cellobiose is a reducing sugar because it has a free anomeric carbon on the second glucose molecule.

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6.S: Carbohydrates (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Carbohydrates, a large group of biological compounds containing carbon, hydrogen, and oxygen atoms, include sugars, starch, glycogen, and cellulose. All carbohydrates contain alcohol functional groups, and either an aldehyde or a ketone group (or a functional group that can be converted to an aldehyde or ketone). The simplest carbohydrates are **monosaccharides**. Monosaccharrides can be classified based on the carbonyl functional group and number of carbon atoms present. These compounds can combine to form more complex carbohydrates. Those with two monosaccharide units are **disaccharides**, those with three to nine monosaccharide units are **oligosaccharides**, and those with ten or more monosaccharide units are **polysaccharides**. Most sugars are either monosaccharides or disaccharides. Cellulose, glycogen, and starch are polysaccharides.

Many carbohydrates exist as **stereoisomers**, in which the three-dimensional spatial arrangement of the atoms in space is the only difference between the isomers. These particular stereoisomers contain at least one **chiral carbon**, a carbon atom that has four different groups bonded to it. A molecule containing a chiral carbon is nonsuperimposable on its mirror image, and two molecules that are nonsuperimposable mirror images of each other are a special type of stereoisomer called **enantiomers**. Enantiomers have the same physical properties, such as melting point, but differ in the direction they rotate polarized light.

A sugar is designated as being a D sugar or an L sugar according to how, in a Fischer projection of the molecule, the hydrogen atom and OH group are attached to the *penultimate* carbon atom, which is the carbon atom immediately before the terminal alcohol carbon atom. If the structure at this carbon atom is the same as that of D-glyceraldehyde (OH to the right), the sugar is a **D sugar**; if the configuration is the same as that of L-glyceraldehyde (OH to the left), the sugar is an **L sugar**.

Monosaccharides of five or more carbons atoms readily form cyclic structures when the carbonyl carbon atom reacts with an OH group on a carbon atom three or four carbon atoms distant. Consequently, glucose in solution exists as an equilibrium mixture of three forms, two of them cyclic (α- and β-) and one open chain. In Haworth projections, the ***alpha*** form is drawn with the OH group on the "former" carbonyl carbon atom (**anomeric carbon**) is trans (opposite) to carbon 6; the ***beta*** form, with the OH group is cis (same) to carbon 6; these two compounds are stereoisomers and are given the more specific term of **anomers**. Any solid sugar can be all alpha or all beta. Once the sample is dissolved in water, however, the ring opens up into the open-chain structure and then closes to form either the α- or the β-anomer. These interconversions occur back and forth until a dynamic equilibrium mixture is achieved in a process called **mutarotation**.

Three abundant hexoses in living organisms are the aldohexoses **D-glucose** and **D-galactose** and the ketohexose **D-fructose**. D-glucose and D-galactose are **epimers** because the molecules are identical, except at C4. D-glucose and D-fructose are structural isomers that both have the $C_6H_{12}O_6$ molecular formula.

The carbonyl group present in monosaccharides is easily oxidized by Tollens' or Benedict's reagents (as well as others). Any mono- or disaccharide containing a free anomeric carbon is a **reducing sugar**. The disaccharide *maltose* contains two glucose units joined in an α-1,4-glycosidic linkage. The disaccharide *lactose* contains a galactose unit and a glucose unit joined by a β-1,4-glycosidic linkage. Both maltose and lactose contain a free anomeric carbon that can convert to an aldehyde functional group, so they are reducing sugars; they also undergo mutarotation. Many adults, and some children, have a deficiency of the enzyme lactase (which is needed to break down lactose) and are said to be **lactose intolerant**. A more serious problem is the genetic disease **galactosemia**, which results from the absence of an enzyme needed to convert galactose to glucose.

The disaccharide ***sucrose*** (table sugar) consists of a glucose unit and a fructose unit joined by a **glycosidic linkage**. The linkage is designated as an α-1,β-2-glycosidic linkage because it involves the OH group on the first carbon atom of glucose and the OH group on the second carbon atom of fructose. Sucrose is not a reducing sugar because it has no anomeric carbon that can reform a carbonyl group, and it cannot undergo mutarotation because of the restrictions imposed by this linkage.

Oligosaccharides play important roles in the blood markers. The types of monosaccharide units present in the oligosaccharide attached to the red blood cell indicates the ABO blood type. All blood types include the N-acetylglucosamine, galactose, and fucose; but differ in the absence or presence of additional units. Type O blood is considered the **universal donor**, while Type AB blood is considered the **universal acceptor**.

Starch, the principal carbohydrate of plants, is composed of the polysaccharides **amylose** (10%–30%) and **amylopectin** (70%–90%). When ingested by humans and other animals, starch is hydrolyzed to glucose and becomes the body's energy source. *Glycogen* is the polysaccharide animals use to store excess carbohydrates from their diets. Similar in structure to amylopectin, glycogen is hydrolyzed to glucose whenever an animal needs energy for a metabolic process. The polysaccharide *cellulose* provides structure for plant cells. It is a linear polymer of glucose units joined by β-1,4-glycosidic linkages. It is indigestible in the human body but digestible by many microorganisms, including microorganisms found in the digestive tracts of many herbivores.

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CHAPTER OVERVIEW

7: Lipids

7.1: Fatty Acids
7.2: Triglycerides
7.3: Phospholipids
7.4: Osmosis and Diffusion
7.5: Steroids
7.E: Lipids (Exercises)
7.S: Lipids (Summary)

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7.1: Fatty Acids

Learning Objectives

- Recognize the structures of common fatty acids.
- Classify fatty acids based on chemical composition.
- Generate omega and delta designations for fatty acids.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-carbon double bonds. **Saturated fatty acids** contain no carbon-carbon double bonds, **monounsaturated fatty acids** contain one carbon-carbon double bond, and **polyunsaturated fatty acids** contain two or more carbon-carbon double bonds.

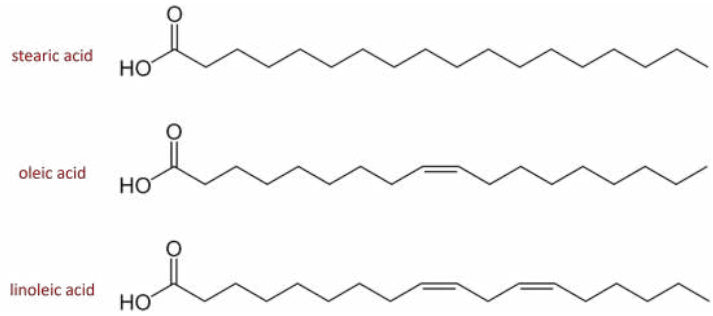


Figure 7.1.1 : Structure of an 18-carbon saturated (top), monounsaturated (middle), and polyunsaturated (bottom) fatty acid.

Table **7.1.1** lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the cis or trans isomeric form. Naturally occurring fatty acids are generally in the cis configuration.

Table **7.1.1**: Some Common Fatty Acids Found in Natural Fats

Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
palmitoleic acid	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0.5	macadamia oil
stearic acid	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COOH$	70	cocoa butter
oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16	olive oil
*linoleic acid	$C_{17}H_{31}COOH$	$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$	−5	canola oil
*α-linolenic acid	$C_{17}H_{29}COOH$	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	−11	flaxseed
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH=CH)_4(CH_2)_2COOH$	−50	liver

*Essential fatty acid.

Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed **essential fatty acids** because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

To Your Health: Prostaglandins

Prostaglandins are chemical messengers synthesized in the cells in which their physiological activity is expressed. They are unsaturated fatty acids containing 20 carbon atoms and are synthesized from arachidonic acid—a polyunsaturated fatty acid—when needed by a particular cell. They are called *prostaglandins* because they were originally isolated from semen found in the prostate gland. It is now known that they are synthesized in nearly all mammalian tissues and affect almost all organs in the body. The five major classes of prostaglandins are designated as PGA, PGB, PGE, PGF, and PGI. Subscripts are attached at the end of these abbreviations to denote the number of double bonds outside the five-carbon ring in a given prostaglandin.

The prostaglandins are among the most potent biological substances known. Slight structural differences give them highly distinct biological effects; however, all prostaglandins exhibit some ability to induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response. Aspirin and other nonsteroidal anti-inflammatory agents, such as ibuprofen, obstruct the synthesis of prostaglandins by inhibiting cyclooxygenase, the enzyme needed for the initial step in the conversion of arachidonic acid to prostaglandins.

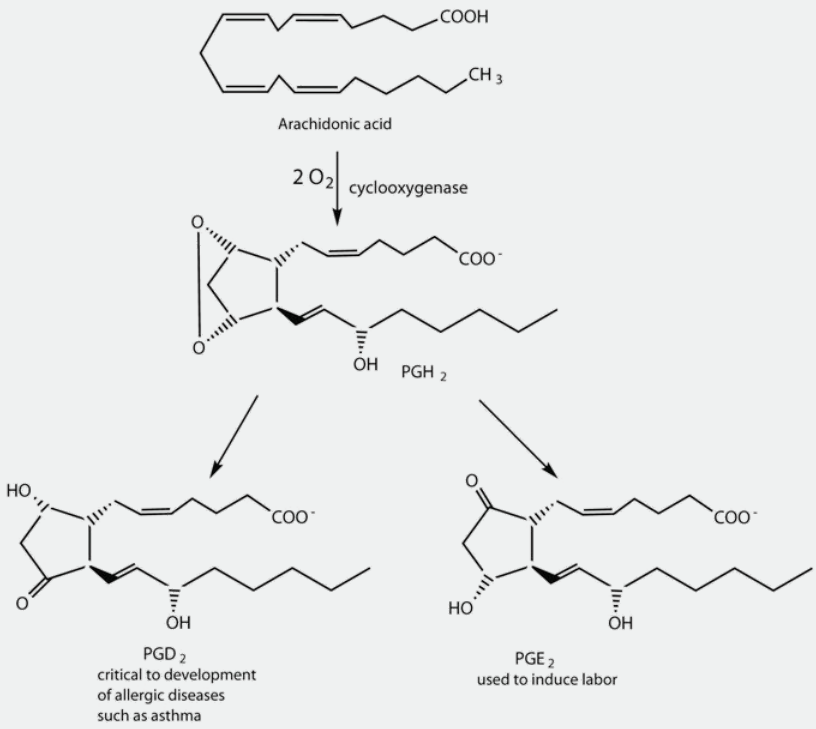


Figure 7.1.2: Conversion of arachidonic acid into prostaglandins.

Their wide range of physiological activity has led to the synthesis of hundreds of prostaglandins and their analogs. Derivatives of PGE_2 are now used in the United States to induce labor. Other prostaglandins have been employed clinically to lower or increase blood pressure, inhibit stomach secretions, relieve nasal congestion, relieve asthma, and prevent the formation of blood clots, which are associated with heart attacks and strokes.

Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure 7.1.3*a*). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure 7.1.3*b*). Such molecules pack closely

together into a crystal lattice, maximizing the strength of dispersion forces and causing fatty acids and the fats derived from them to have relatively high melting points. In contrast, each *cis* carbon-carbon double bond in an unsaturated fatty acid produces a pronounced bend in the molecule, so that these molecules do not stack neatly. As a result, the intermolecular attractions of unsaturated fatty acids (and unsaturated fats) are weaker, causing these substances to have lower melting points. Most are liquids at room temperature.

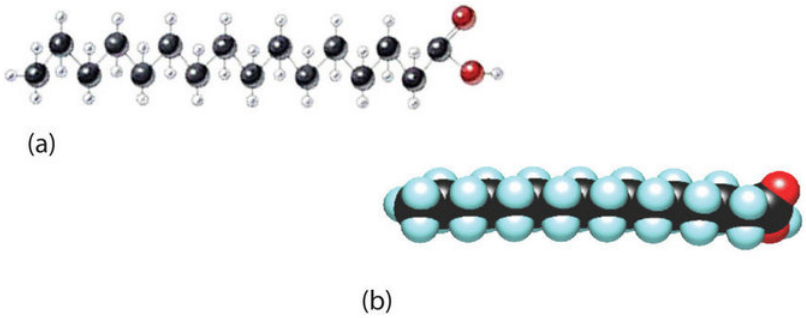


Figure **7.1.3**: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Fatty Acid Numbering Systems

Although fatty acids are long-chained carboxylic acids, they are not always named at such. Instead fatty acids are often named using systems that provide details about the atoms present in the molecule. A **carbon designation** is given to indicate the number of carbon atoms in the fatty acid, number of carbon-carbon
double bonds, and the location of the carbon-carbon double bond(s). There are two systems that provide details on the location of carbon-carbon double bonds: the **delta (Δ) system** and the **omega (ω) system**. The delta system uses the numbering system used in the IUPAC name of carboxylic acids. In this system, carbon 1 is assigned to the carbon of the functional group and the chain is numbered to assign locator numbers to the first carbon in each carbon-carbon double bond present in the molecule. This numbering system is shown as $\Delta^{\#,\#,\cdots}$, where the # symbol is replaced with the locator numbers. The omega system, which is often used in nutrition, begins numbering the carbon chain at the opposite end of the molecule. In this system, carbon 1 is assigned to the carbon farthest from the functional group. Another difference is that the omega system only indicates the location of the first carbon of the first carbon-carbon double bond. This numbering system is shown as ω-#, where the # symbol indicates the position of first double bond only.

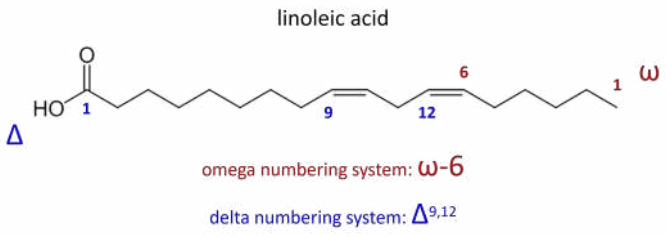


Figure **7.1.4**: Applying the omega (red) and delta (blue) numbering systems to linoleic acid.

With the location of the carbon-carbon double bonds identified, the carbon designation can be determined. The carbon designation is shown as:

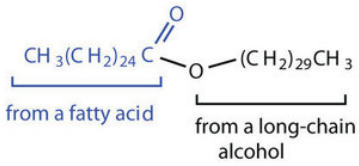
[# of carbon:# of carbon-carbon double bonds], numbering system

The carbon designation of linoleic acid (Figure **7.1.4**) would be shown as [18:2], $\Delta^{9,12}$ or [18:2],ω-6.

Waxes

Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl

cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.



Myricyl cerotate
(found in carnauba wax)

Figure \(\PageIndex{5}\): Structure of a wax.

Example 7.1.1

Classify the following fatty acids and indicate the number of carbon atoms in each molecule.

a. palmitoleic acid
b. myristic acid
c. linoleic acid

Solution

a. monounsaturated; 16 carbon atoms
b. saturated; 14 carbon atoms
c. polyunsaturated; 18 carbon atoms

Exercise 7.1.1

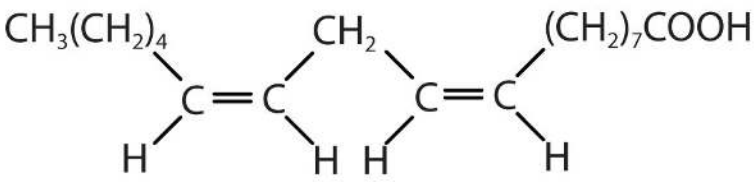
Classify each fatty acid as saturated or unsaturated and indicate the number of carbon atoms in each molecule.

a. stearic acid
b. oleic acid
c. palmitic acid

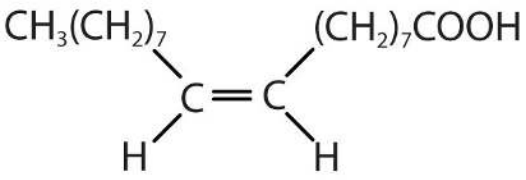
Example 7.1.2

Arrange these fatty acids (all contain 18 carbon atoms) in order of increasing melting point. Justify your arrangement.

a.

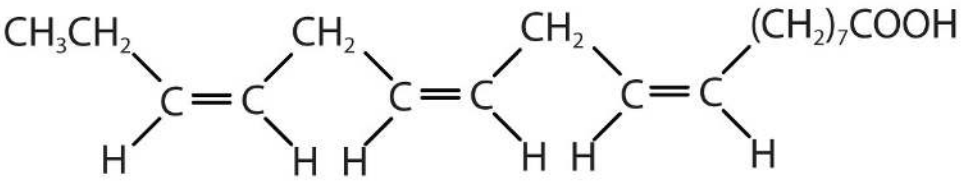


b.



https://chem.libretexts.org/@go/page/342672

c.



Solution

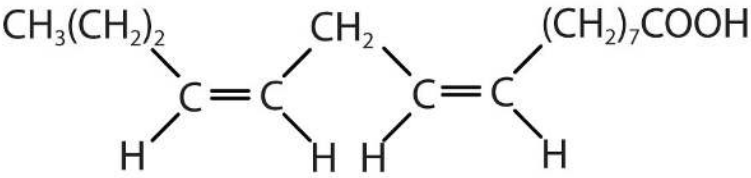
c < a < b; an increase in the number of double bonds will lower the melting point because it is more difficult to closely pack the fatty acids together.

? Exercise 7.1.2

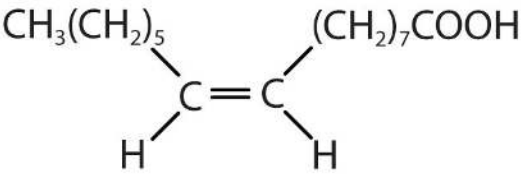
Arrange these fatty acids (all contain 16 carbon atoms) in order of increasing melting point. Justify your arrangement.

a. $CH_3(CH_2)_{14}COOH$

b.



c.



Summary

Fatty acids are carboxylic acids that are the structural components of many lipids. They may be saturated or unsaturated. Most fatty acids are unbranched and contain an even number of carbon atoms. Unsaturated fatty acids have lower melting points than saturated fatty acids containing the same number of carbon atoms. The delta and omega systems can be used in the carbon designation to indicate the location of carbon-carbon double bonds in a fatty acid.

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7.2: Triglycerides

Learning Objectives

- Explain why fats and oils are referred to as triglycerides.
- Explain how the fatty acid composition of the triglycerides determines whether a substance is a fat or oil.
- Describe the importance of key reactions of triglycerides, such as hydrolysis, hydrogenation, and oxidation.

Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

Fats and oils are called **triglycerides** (or ***triacylcylgerols***) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:

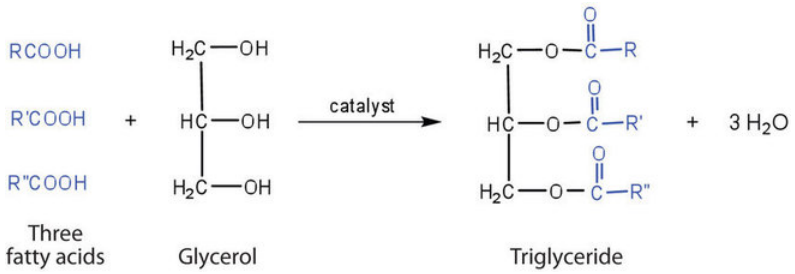


Figure **7.2.1**: Chemical reaction for the formation of a triglyceride.

If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a ***simple triglyceride***. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a ***mixed triglyceride***.

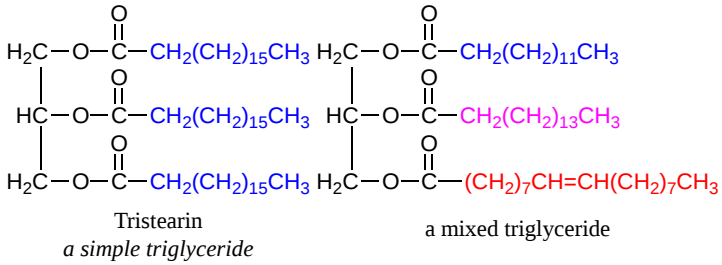


Figure **7.2.2**: Structures of a simple (left) and mixed (right) triglyceride.

A triglyceride is called a **fat** if it is a solid at 25°C; it is called an **oil** if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table **7.2.1** shows the fatty acid compositions of some common fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from as well as on dietetic and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid.

Table **7.2.1**: Average Fatty Acid Composition of Some Common Fats and Oils (%)*

	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Fats							
butter (cow)	3	11	27	12	29	2	1
tallow		3	24	19	43	3	1
lard		2	26	14	44	10	
Oils							
canola oil			4	2	62	22	10
coconut oil†	47	18	9	3	6	2	
corn oil			11	2	28	58	1
olive oil			13	3	71	10	1
peanut oil			11	2	48	32	
soybean oil			11	4	24	54	7

*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

†Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting C_8, C_{10}, and C_{12} saturated fatty acids.

Terms such as *saturated fat* or *unsaturated oil* are often used to describe the fats or oils obtained from foods. Saturated fats contain a high proportion of saturated fatty acids, while unsaturated oils contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

Physical Properties of Fats and Oils

Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.

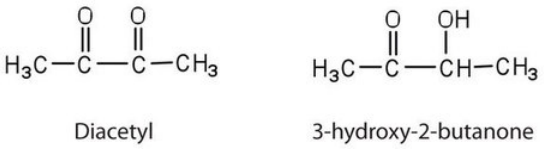


Figure 7.2.3: Compounds responsible for the taste of butter.

Fats and oils are lighter than water, having densities of about 0.8 g/cm^3. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

Chemical Reactions of Fats and Oils

Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):

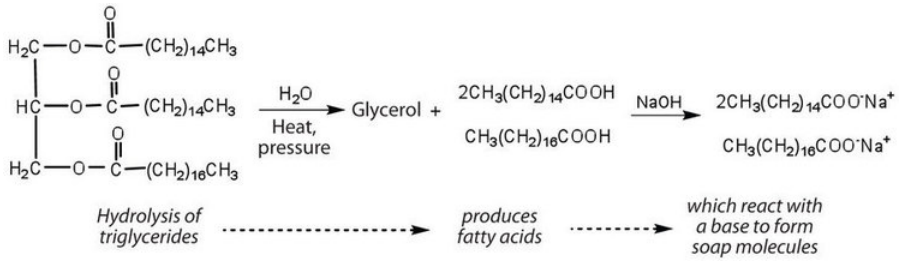
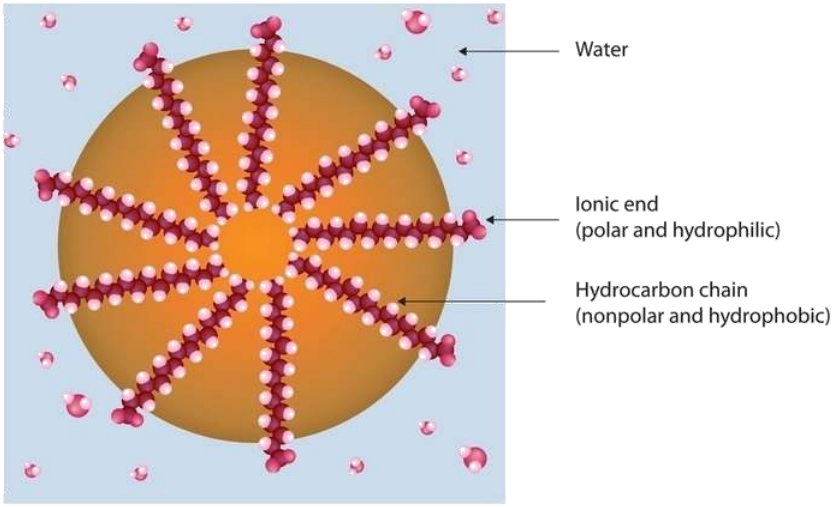


Figure 7.2.4: Chemical reaction of the saponification (base hydrolysis) of a triglyceride.

Looking Closer: Soaps

Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.



Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. The droplets repel each other because of their charged surfaces and do not coalesce. With the oil no longer “gluing” the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.

The double bonds in fats and oils can undergo hydrogenation and also oxidation. The hydrogenation of vegetable oils to produce semisolid fats is an important process in the food industry. Chemically, it is essentially identical to the catalytic hydrogenation reaction described for alkenes.

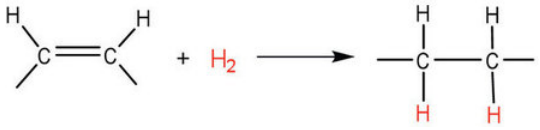


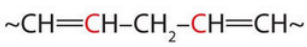
Figure 7.2.5: Chemical reaction of the hydrogenation of an alkene.

In commercial processes, the number of double bonds that are hydrogenated is carefully controlled to produce fats with the desired consistency (soft and pliable). Inexpensive and abundant vegetable oils (canola, corn, soybean) are thus transformed into margarine and cooking fats. In the preparation of margarine, for example, partially hydrogenated oils are mixed with water, salt, and nonfat dry milk, along with flavoring agents, coloring agents, and vitamins A and D, which are added to approximate the look, taste, and nutrition of butter. (Preservatives and antioxidants are also added.) In most commercial peanut butter, the peanut oil has been partially hydrogenated to prevent it from separating out. Consumers could decrease the amount of saturated fat in their diet by using the original unprocessed oils on their foods, but most people would rather spread margarine on their toast than pour oil on it.

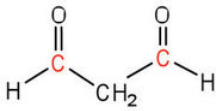
Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* fatty acids mentioned in the opening essay. However, studies have shown that *trans* fatty acids also raise cholesterol levels and increase the incidence of heart disease. *Trans* fatty acids do not have the bend in their structures, which occurs in *cis* fatty acids and thus pack closely together in the same way that the saturated fatty acids do. Consumers are now being advised to use polyunsaturated oils and soft or liquid margarine and reduce their total fat consumption to less than 30% of their total calorie intake each day.

Fats and oils that are in contact with moist air at room temperature eventually undergo oxidation and hydrolysis reactions that cause them to turn rancid, acquiring a characteristic disagreeable odor. One cause of the odor is the release of volatile fatty acids by hydrolysis of the ester bonds. Butter, for example, releases foul-smelling butyric, caprylic, and capric acids. Microorganisms present in the air furnish lipases that catalyze this process. Hydrolytic rancidity can easily be prevented by covering the fat or oil and keeping it in a refrigerator.

Another cause of volatile, odorous compounds is the oxidation of the unsaturated fatty acid components, particularly the readily oxidized structural unit



in polyunsaturated fatty acids, such as linoleic and linolenic acids. One particularly offensive product, formed by the oxidative cleavage of both double bonds in this unit, is a compound called *malonaldehyde*.

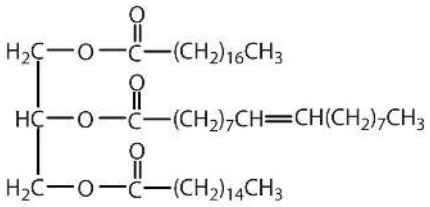


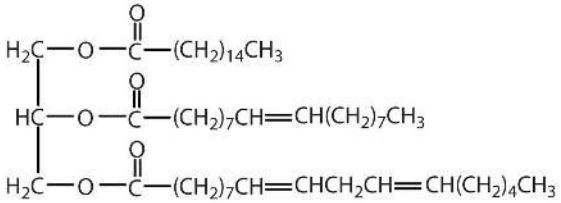
Malonaldehyde

Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better antioxidants, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids.

Example 7.2.1

Which of these triglycerides would you expect to find in higher amounts in oils? In fats? Justify your choice.


(a)


(b)

Solution

The triglyceride labeled as (a) is expected to be present in higher amounts in fats because it is composed of a greater number of saturated fatty acids. The triglyceride labeled as (b) is expected to be present in higher amounts in oils because it is composed of a greater number of unsaturated fatty acids.

Summary

Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol. An increase in the percentage of shorter-chain fatty acids and/or unsaturated fatty acids lowers the melting point of a fat or oil. The hydrolysis of fats and oils in the presence of a base makes soap and is known as saponification. Double bonds present in unsaturated triglycerides can be hydrogenated to convert oils (liquid) into margarine (solid). The oxidation of fatty acids can form compounds with disagreeable odors. This oxidation can be minimized by the addition of antioxidants.

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7.3: Phospholipids

Learning Objectives

- Identify the distinguishing characteristics of membrane lipids.
- Describe membrane components and how they are arranged.

All living cells are surrounded by a cell membrane. Plant cells (Figure **7.3.1***a*) and animal cells (Figure **7.3.1***b*) contain a cell nucleus that is also surrounded by a membrane and holds the genetic information for the cell. Everything between the cell membrane and the nuclear membrane—including intracellular fluids and various subcellular components such as the mitochondria and ribosomes—is called the cytoplasm. The membranes of all cells have a fundamentally similar structure, but membrane function varies tremendously from one organism to another and even from one cell to another within a single organism. This diversity arises mainly from the presence of different proteins and lipids in the membrane.

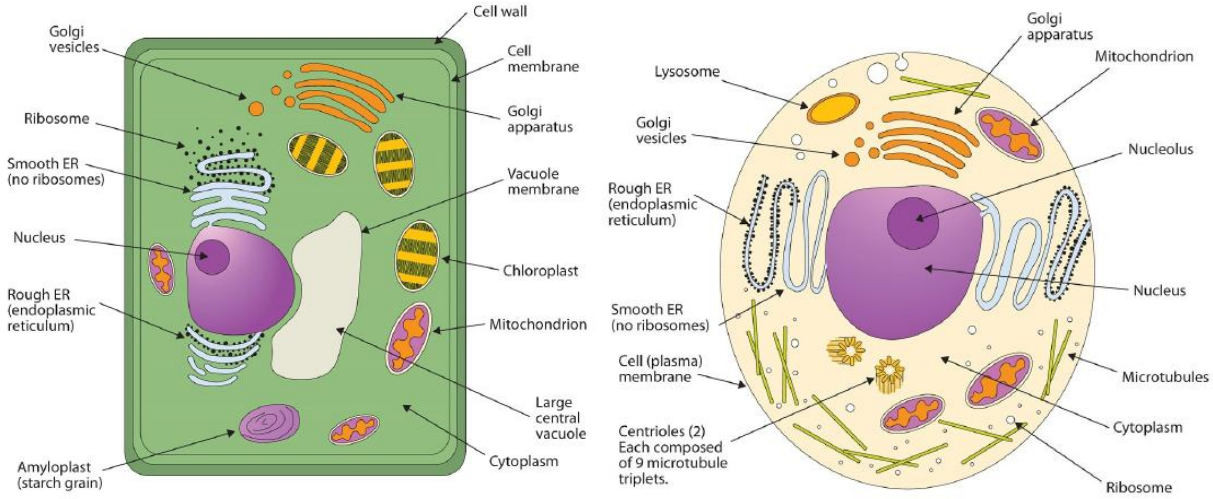


Figure **7.3.1**: (a) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (b) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

The lipids in cell membranes are highly polar but have dual characteristics: part of the lipid is ionic and therefore dissolves in water, whereas the rest has a hydrocarbon structure and therefore dissolves in nonpolar substances. Often, the ionic part is referred to as **hydrophilic**, meaning "water loving," and the nonpolar part as **hydrophobic**, meaning "water fearing" (repelled by water). When allowed to float freely in water, polar lipids spontaneously cluster together in any one of three arrangements: micelles, monolayers, and bilayers (Figure **7.3.2**).

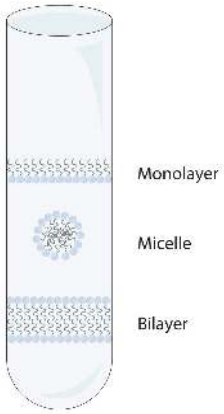


Figure **7.3.2**: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

Micelles are aggregations in which the lipids' hydrocarbon tails—being hydrophobic—are directed toward the center of the assemblage and away from the surrounding water while the hydrophilic heads are directed outward, in contact with the water. Each micelle may contain thousands of lipid molecules. Polar lipids may also form a monolayer, a layer one molecule thick on the surface of the water. The polar heads face into water, and the nonpolar tails stick up into the air. **Bilayers** are double layers of lipids arranged so that the hydrophobic tails are sandwiched between an inner surface and an outer surface consisting of hydrophilic heads. The hydrophilic heads are in contact with water on either side of the bilayer, whereas the tails, sequestered inside the bilayer, are prevented from having contact with the water. Bilayers like this make up every cell membrane (Figure **7.3.3**).

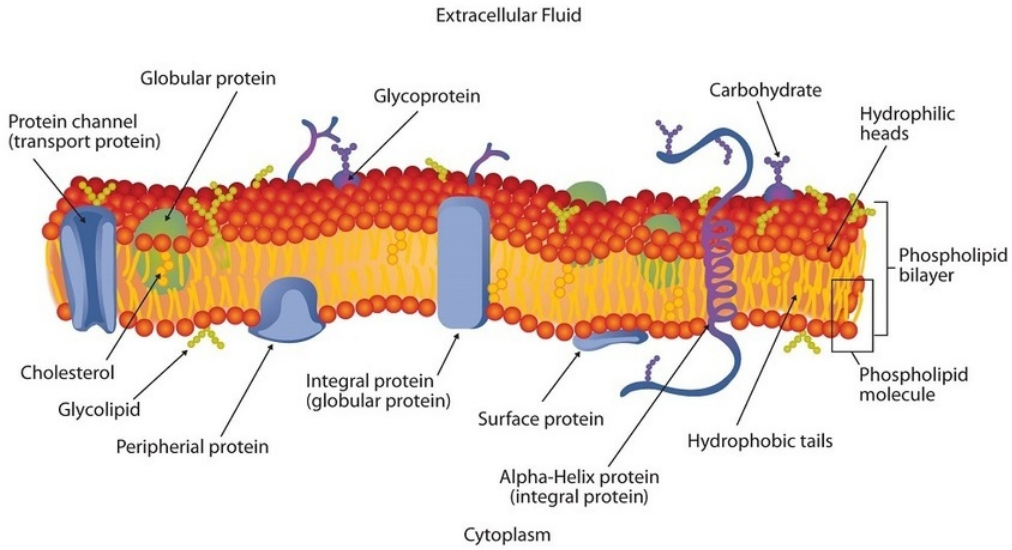


Figure **7.3.3**: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

In the bilayer interior, the hydrophobic tails (that is, the fatty acid portions of lipid molecules) interact by means of dispersion forces. The interactions are weakened by the presence of unsaturated fatty acids. As a result, the membrane components are free to mill about to some extent, and the membrane is described as fluid.

The lipids found in cell membranes can be categorized in various ways. **Phospholipids** are lipids containing phosphorus. **Glycolipids** are sugar-containing lipids. The latter are found exclusively on the outer surface of the cell membrane, acting as distinguishing surface markers for the cell and thus serving in cellular recognition and cell-to-cell communication. Sphingolipids are phospholipids or glycolipids that contain the unsaturated amino alcohol sphingosine rather than glycerol. Diagrammatic structures of representative membrane lipids are presented in Figure **7.3.4**.

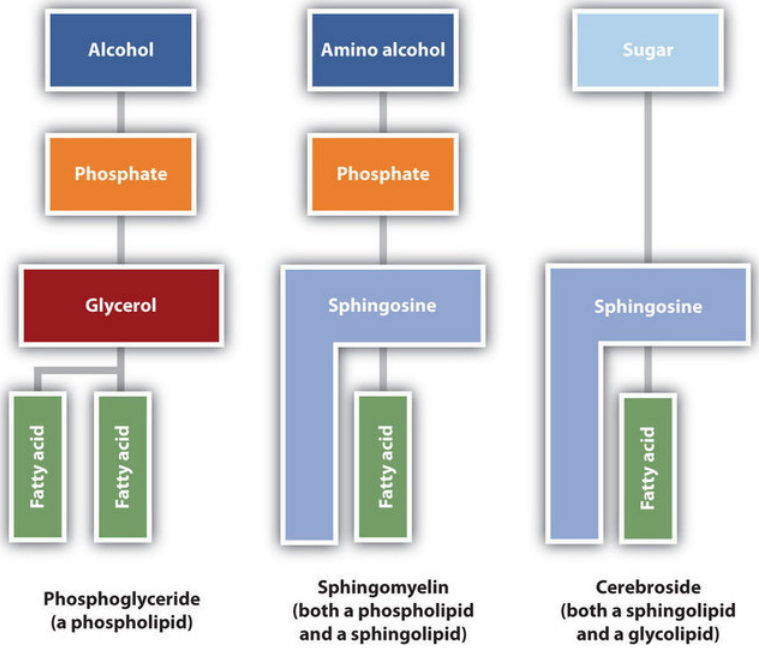


Figure 7.3.4: Component Structures of Some Important Membrane Lipids

Phosphoglycerides (also known as **glycerophospholipids**) are the most abundant phospholipids in cell membranes. They consist of a glycerol unit with fatty acids attached to the first two carbon atoms, while a phosphoric acid unit, esterified with an alcohol molecule (usually an amino alcohol, as in Figure 7.3.5*a*) is attached to the third carbon atom of glycerol (Figure 7.3.5*b*). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (Figure 7.3.5*b*).

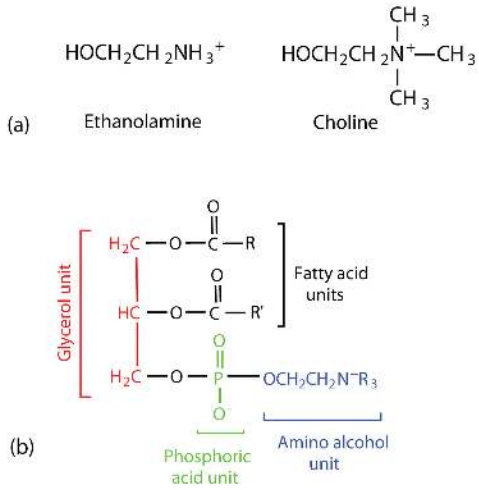
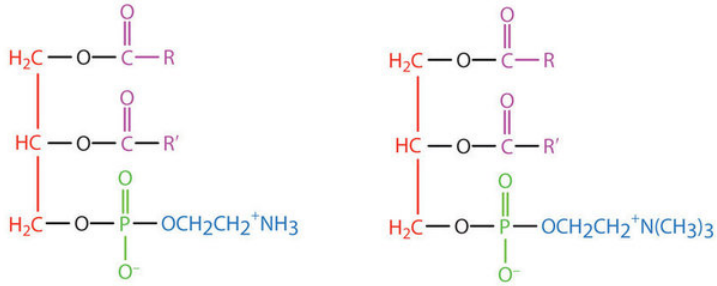


Figure 7.3.5: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

There are two common types of phosphoglycerides. Phosphoglycerides containing ethanolamine as the amino alcohol are called *phosphatidylethanolamines* or *cephalins*. Cephalins are found in brain tissue and nerves and also have a role in blood clotting. Phosphoglycerides containing choline as the amino alcohol unit are called *phosphatidylcholines* or *lecithins*. Lecithins occur in all living organisms. Like cephalins, they are important constituents of nerve and brain tissue. Egg yolks are especially rich in lecithins. Commercial-grade lecithins isolated from soybeans are widely used in foods as emulsifying agents. An emulsifying agent is used to stabilize an emulsion—a dispersion of two liquids that do not normally mix, such as oil and water. Many foods are emulsions. Milk is an emulsion of butterfat in water. The emulsifying agent in milk is a protein called *casein*. Mayonnaise is an emulsion of salad oil in water, stabilized by lecithins present in egg yolk.



Sphingomyelins, the simplest **sphingolipids**, each contain a fatty acid, a phosphoric acid, **sphingosine**, and choline (Figure **7.3.6**). Because they contain phosphoric acid, they are also classified as phospholipids. Sphingomyelins are important constituents of the myelin sheath surrounding the axon of a nerve cell. Multiple sclerosis is one of several diseases resulting from damage to the myelin sheath.

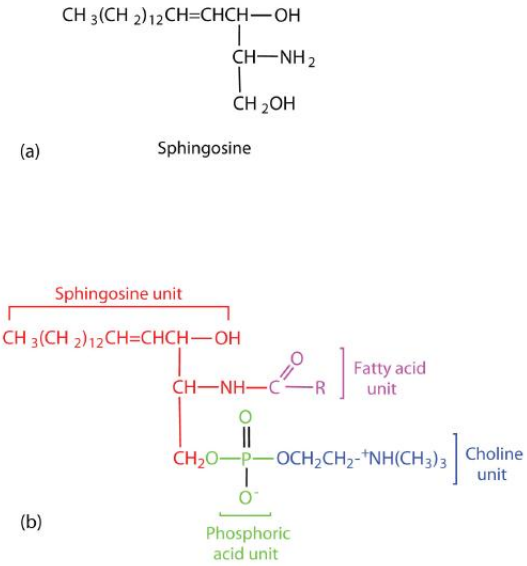


Figure **7.3.6**: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.

Most animal cells contain sphingolipids called **cerebrosides** (Figure **7.3.7**). Cerebrosides are composed of sphingosine, a fatty acid, and galactose or glucose. They therefore resemble sphingomyelins but have a sugar unit in place of the choline phosphate group. Cerebrosides are important constituents of the membranes of nerve and brain cells.

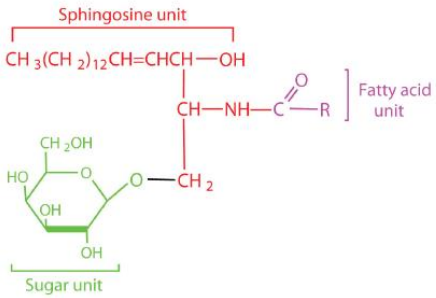


Figure **7.3.7**: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.

The sphingolipids called **gangliosides** are more complex, usually containing a branched chain of three to eight monosaccharides and/or substituted sugars. Because of considerable variation in their sugar components, about 130 varieties of gangliosides have

been identified. Most cell-to-cell recognition and communication processes (e.g., blood group antigens) depend on differences in the sequences of sugars in these compounds. Gangliosides are most prevalent in the outer membranes of nerve cells, although they also occur in smaller quantities in the outer membranes of most other cells. Because cerebrosides and gangliosides contain sugar groups, they are also classified as **glycolipids**.

Membrane Proteins

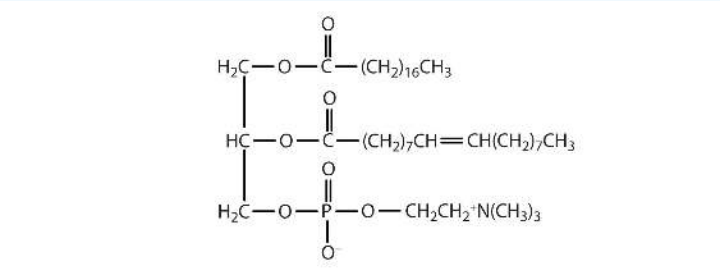
If membranes were composed only of lipids, very few ions or polar molecules could pass through their hydrophobic "sandwich filling" to enter or leave any cell. However, certain charged and polar species do cross the membrane, aided by proteins that move about in the lipid bilayer. The two major classes of proteins in the cell membrane are integral proteins, which span the hydrophobic interior of the bilayer, and peripheral proteins, which are more loosely associated with the surface of the lipid bilayer (Figure **7.3.3**). Peripheral proteins may be attached to integral proteins, to the polar head groups of phospholipids, or to both by hydrogen bonding and electrostatic forces.

Small ions and molecules soluble in water enter and leave the cell by way of channels through the integral proteins. Some proteins, called *carrier proteins*, facilitate the passage of certain molecules, such as hormones and neurotransmitters, by specific interactions between the protein and the molecule being transported.

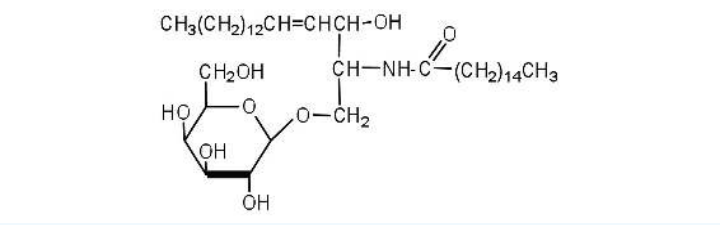
✔ Example 7.3.1

Classify the following as a phospholipid, a glycolipid, and/or a sphingolipid. (Some lipids can be given more than one classification.)

a.



b.



Solution

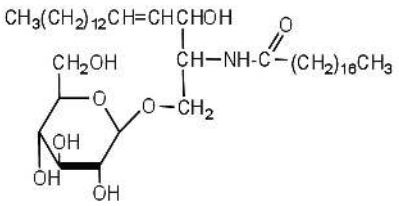
a. phospholipid

b. sphingolipid and glycolipid

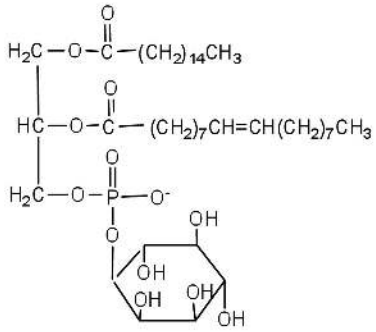
? Exercise 7.3.1

Classify the following as a phospholipid, a glycolipid, and/or a sphingolipid. (Some lipids can be given more than one classification.)

a.



b.



Summary

Lipids are important components of biological membranes. These lipids have dual characteristics: part of the molecule is hydrophilic, and part of the molecule is hydrophobic. Membrane lipids may be classified as phospholipids, glycolipids, and/or sphingolipids. Proteins are another important component of biological membranes. Integral proteins span the lipid bilayer, while peripheral proteins are more loosely associated with the surface of the membrane.

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7.4: Osmosis and Diffusion

Learning Outcomes

- Define osmosis and diffusion.
- Distinguish among hypotonic, hypertonic, and isotonic solutions.
- Describe a semipermeable membrane.
- Predict behavior of blood cells in different solution types.
- Describe flow of solvent molecules across a membrane.
- Identify the polar and nonpolar regions of a cell membrane.
- Explain the components present in a phospholipid.

Fish cells, like all cells, have semipermeable membranes. Eventually, the concentration of "stuff" on either side of them will even out. A fish that lives in salt water will have somewhat salty water inside itself. Put it in freshwater, and the freshwater will, through osmosis, enter the fish, causing its cells to swell, and the fish will die. What will happen to a freshwater fish in the ocean?

Osmosis

Imagine you have a cup that has $100\ \text{mL}$ water, and you add $15\ \text{g}$ of table sugar to the water. The sugar dissolves and the mixture that is now in the cup is made up of a **solute** (the sugar) that is dissolved in the **solvent** (the water). The mixture of a solute in a solvent is called a **solution**.

Imagine now that you have a second cup with $100\ \text{mL}$ of water, and you add $45\ \text{g}$ of table sugar to the water. Just like the first cup, the sugar is the solute, and the water is the solvent. But now you have two mixtures of different solute concentrations. In comparing two solutions of unequal solute concentration, the solution with the higher solute concentration is **hypertonic**, and the solution with the lower solute concentration is **hypotonic**. Solutions of equal solute concentration are **isotonic**. The first sugar solution is hypotonic to the second solution. The second sugar solution is hypertonic to the first.

You now add the two solutions to a beaker that has been divided by a semipermeable membrane, with pores that are too small for the sugar molecules to pass through, but are big enough for the water molecules to pass through. The hypertonic solution is one side of the membrane and the hypotonic solution on the other. The hypertonic solution has a lower water concentration than the hypotonic solution, so a concentration gradient of water now exists across the membrane. Water molecules will move from the side of higher water concentration to the side of lower concentration until both solutions are isotonic. At this point, **equilibrium** is reached.

Red blood cells behave the same way (Figure 7.4.1). When red blood cells are in a hypertonic (higher concentration) solution, water flows out of the cell faster than it comes in. This results in **crenation** (shrinking/shriveling) of the blood cell. On the other extreme, a red blood cell that is hypotonic (lower concentration outside the cell) will result in more water flowing into the cell than out. This results in swelling of the cell and potential **hemolysis** (swelling/bursting) of the cell. In an isotonic solution, the flow of water in and out of the cell is happening at the same rate.

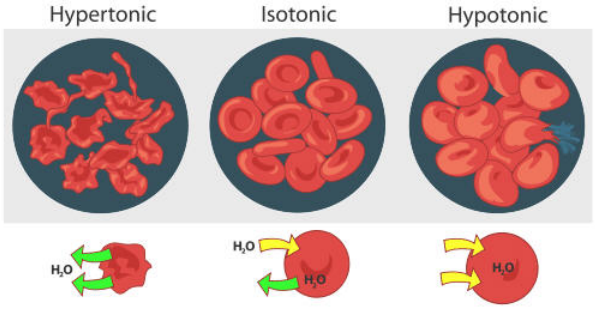


Figure 7.4.1: Red blood cells in hypertonic, isotonic, and hypotonic solutions.

Osmosis is the diffusion of water molecules across a semipermeable membrane from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water). Water moves into and out of cells by osmosis.

- If a cell is in a hypertonic solution, the solution has a lower water concentration than the cell cytosol, and water moves out of the cell until both solutions are isotonic.
- Cells placed in a hypotonic solution will take in water across their membranes until both the external solution and the cytosol are isotonic.

A red blood cell will swell and undergo hemolysis (burst) when placed in a hypotonic solution. When placed in a hypertonic solution, a red blood cell will lose water and undergo *crenation* (shrivel). Animal cells tend to do best in an isotonic environment, where the flow of water in and out of the cell is occurring at equal rates.

Diffusion

Passive transport is a way that small molecules or ions move across the cell membrane without input of energy by the cell. The three main kinds of passive transport are diffusion (or simple diffusion), osmosis, and facilitated diffusion. Simple diffusion and osmosis do not involve transport proteins. **Facilitated diffusion** requires the assistance of proteins.

Diffusion is the movement of molecules from an area of high concentration of the molecules to an area with a lower concentration. For cell transport, diffusion is the movement of small molecules across the cell membrane. The difference in the concentrations of the molecules in the two areas is called the **concentration gradient**. The kinetic energy of the molecules results in random motion, causing diffusion. In simple diffusion, this process proceeds without the aid of a transport protein. It is the random motion of the molecules that causes them to move from an area of high concentration to an area with a lower concentration.

Diffusion will continue until the concentration gradient has been eliminated. Since diffusion moves materials from an area of higher concentration to the lower, it is described as moving solutes "down the concentration gradient". The end result is an equal concentration, or **equilibrium**, of molecules on both sides of the membrane. At equilibrium, movement of molecules does not stop. At equilibrium, there is equal movement of materials in both directions.

Not everything can make it into your cells. Your cells have a plasma membrane that helps to guard your cells from unwanted intruders.

The Plasma Membrane and Cytosol

If the outside environment of a cell is water-based, and the inside of the cell is also mostly water, something has to make sure the cell stays intact in this environment. What would happen if a cell dissolved in water, like sugar does? Obviously, the cell could not survive in such an environment. So something must protect the cell and allow it to survive in its water-based environment. All cells have a barrier around them that separates them from the environment and from other cells. This barrier is called the **plasma membrane**, or cell membrane.

The Plasma Membrane

The plasma membrane (Figure **7.4.2**) is made of a double layer of special lipids, known as **phospholipids**. The phospholipid is a lipid molecule with a hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails. Because of the hydrophilic and hydrophobic nature of the phospholipid, the molecule must be arranged in a specific pattern as only certain parts of the molecule can physically be in contact with water. Remember that there is water outside the cell, and the **cytoplasm** inside the cell is mostly water as well. So the phospholipids are arranged in a double layer (a bilayer) to keep the cell separate from its environment. Lipids do not mix with water (recall that oil is a lipid), so the phospholipid bilayer of the cell membrane acts as a barrier, keeping water out of the cell, and keeping the cytoplasm inside the cell. The cell membrane allows the cell to stay structurally intact in its water-based environment.

The function of the plasma membrane is to control what goes in and out of the cell. Some molecules can go through the cell membrane to enter and leave the cell, but some cannot. The cell is therefore not completely permeable. "Permeable" means that anything can cross a barrier. An open door is completely permeable to anything that wants to enter or exit through the door. The plasma membrane is **semipermeable**, meaning that some things can enter the cell, and some things cannot.

Molecules that cannot easily pass through the bilayer include ions and small hydrophilic molecules, such as glucose, and macromolecules, including proteins and RNA. Examples of molecules that can easily diffuse across the plasma membrane include carbon dioxide and oxygen gas. These molecules diffuse freely in and out of the cell, along their concentration gradient. Though water is a polar molecule, it can also diffuse through the plasma membrane.

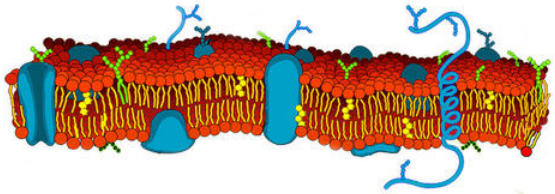


Figure 7.4.2: Plasma membranes are primarily made up of phospholipids (orange). The hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails are shown. The phospholipids form a bilayer (two layers). The middle of the bilayer is an area without water. There can be water on either side of the bilayer. There are many proteins throughout the membrane.

Cytosol

The inside of all cells also contain a jelly-like substance called **cytosol**. Cytosol is composed of water and other molecules, including **enzymes**, which are proteins that speed up the cell's chemical reactions. Everything in the cell sits in the cytosol, like fruit in a Jell-o mold. The term cytoplasm refers to the cytosol and all of the organelles, the specialized compartments of the cell. The cytoplasm does not include the nucleus. As a prokaryotic cell does not have a nucleus, the DNA is in the cytoplasm.

✔ Example 7.4.1

Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

a. Which one has a higher concentration?
b. Which way will water molecules flow?
c. Which volume will increase?
d. Which volume will decrease?
e. What will happen to the concentration of solution A?
f. What will happen to the concentration of solution B?

Solution

a. Solution B
b. A → → B
c. Solution B
d. Solution A
e. increase
f. decrease

? Exercise 7.4.1

Two solutions are separated by a semipermeable membrane. Solution A contains 20.0 g of NaCl in 75.0 mL of water and solution B contains 25.0 g of NaCl in 100.0 mL of water.

a. Which one has a higher concentration?
b. Which way will water molecules flow?
c. Which volume will increase?
d. Which volume will decrease?
e. What will happen to the concentration of solution A?
f. What will happen to the concentration of solution B?

Supplemental Resources

- The Plasma Membrane: www.youtube.com/watch?v=moPJkCbKjBs

Key Takeaways

- Water moves into and out of cells by osmosis.
- Water (solvent) moves from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water).

Contributors

-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

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7.5: Steroids

Learning Objectives

- Recognize the structural features of lipids.

One major class of lipids is the **steroids**, which have structures totally different from the other classes of lipids. The main feature of steroids is the steroid nucleus, a fused ring system of three cyclohexanes and one cyclopentane (Figure 7.5.1). There are a variety of functional groups that may be attached. The main feature, as in all lipids, is the large number of carbon and hydrogen which make steroids non-polar.

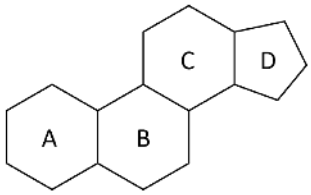


Figure 7.5.1: Structure of the steroid nucleus, which is present in all steroids.

Steroids include such well known compounds as cholesterol, sex hormones, birth control pills, cortisone, and anabolic steroids.

Cholesterol

The best known and most abundant steroid in the body is **cholesterol**. Cholesterol is formed in brain tissue, nerve tissue, and the blood stream. It is the major compound found in gallstones and bile salts.

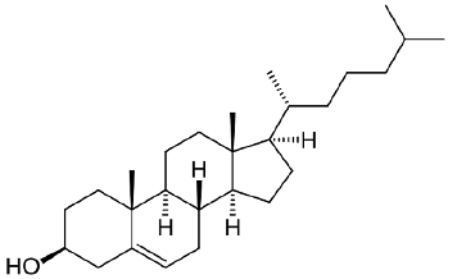


Figure 7.5.2: Structure of cholesterol.

Cholesterol also contributes to the formation of deposits on the inner walls of blood vessels. These deposits harden and obstruct the flow of blood. This condition, known as atherosclerosis, results in various heart diseases, strokes, and high blood pressure.

Structures of Sex Hormones

Sex hormones are also steroids. The primary male hormone, testosterone, is responsible for the development of secondary sex characteristics. Two female sex hormones, progesterone and estrogen (or estradiol) control the ovulation cycle. Notice that the male and female hormones have only slight differences in structures, but yet have very different physiological effects.

Testosterone promotes the normal development of male genital organs ans is synthesized from cholesterol in the testes. It also promotes secondary male sexual characteristics such as deep voice, facial and body hair. Estrogen, along with progesterone regulates changes occurring in the uterus and ovaries known as the menstrual cycle. For more details see Birth Control. Estrogen is synthesized from testosterone by making the first ring aromatic which results in mole double bonds, the loss of a methyl group and formation of an alcohol group.

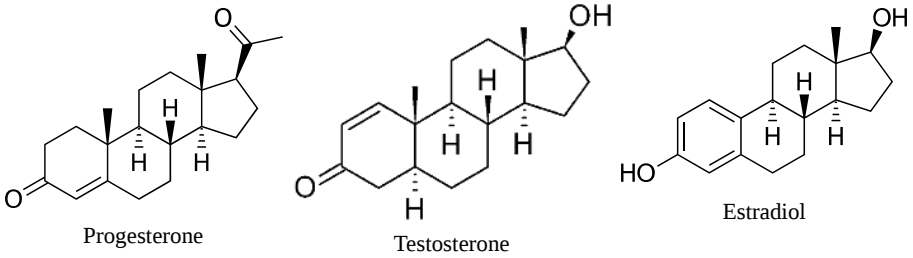


Figure 7.5.3: Structures of sex hormones.

Adrenocorticoid Hormones

The adrenocorticoid hormones are products of the adrenal glands ("adrenal" means adjacent to the renal (kidney)). The most important mineralocrticoid is **aldosterone**, which regulates the reabsorption of sodium and chloride ions in the kidney tubules and increases the loss of potassium ions. Aldosterone is secreted when blood sodium ion levels are too low to cause the kidney to retain sodium ions. If sodium levels are elevated, aldosterone is not secreted, so that some sodium will be lost in the urine. Aldosterone also controls swelling in the tissues.

Cortisol, the most important glucocortinoid, has the function of increasing glucose and glycogen concentrations in the body. These reactions are completed in the liver by taking fatty acids from lipid storage cells and amino acids from body proteins to make glucose and glycogen.

In addition, cortisol and its ketone derivative, **cortisone**, have the ability to inflammatory effects. Cortisone or similar synthetic derivatives such as prednisolone are used to treat inflammatory diseases, rheumatoid arthritis, and bronchial asthma. There are many side effects with the use of cortisone drugs, so there use must be monitored carefully.

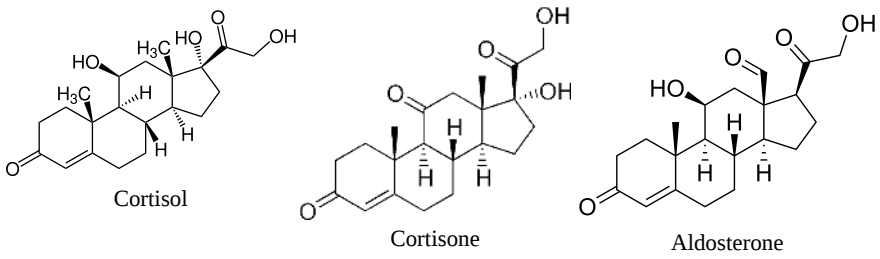


Figure 7.5.4: Structures of adrenocorticoid hormones.

Contributors

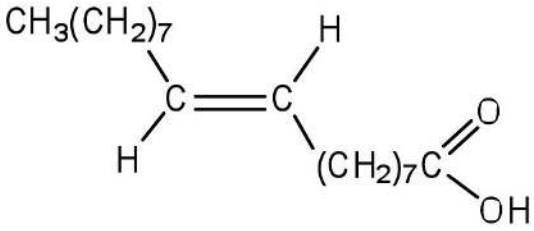
- Charles Ophardt, Professor Emeritus, Elmhurst College; Virtual Chembook

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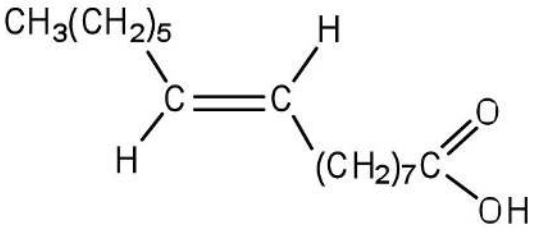
7.E: Lipids (Exercises)

Additional Exercises

1. The melting point of elaidic acid is 52°C.
   a. What trend is observed when comparing the melting points of elaidic acid, oleic acid, and stearic acid? Explain.
   b. Would you expect the melting point of palmitelaidic acid to be lower or higher than that of elaidic acid? Explain.

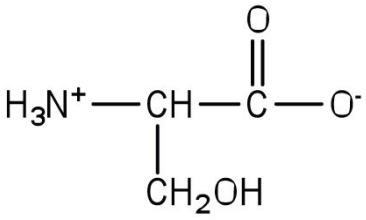


Elaidic acid



Palmitelaidic acid

2. Examine the labels on two brands of margarine and two brands of shortening and list the oils used in the various brands.
3. Draw a typical lecithin molecule that incorporates glycerol, palmitic acid, oleic acid, phosphoric acid, and choline. Circle all the ester bonds.
4. In cerebrosides, is the linkage between the fatty acid and sphingosine an amide bond or an ester bond? Justify your answer.
5. Serine is an amino acid that has the following structure. Draw the structure for a phosphatidylserine that contains a palmitic acid and a palmitoleic acid unit.

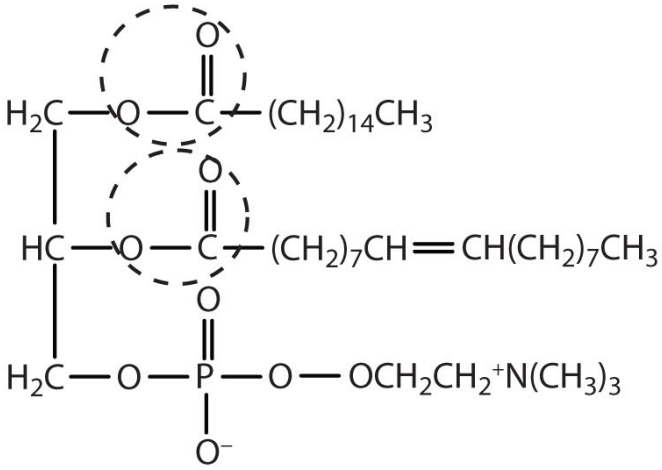


6. Explain whether each compound would be expected to diffuse through the lipid bilayer of a cell membrane.
   a. potassium chloride
   b. $CH_3CH_2CH_2CH_2CH_2CH_3$
   c. fructose
7. Identify the role of each steroid hormone in the body.
   a. progesterone
   b. aldosterone
   c. testosterone
   d. cortisol
8. How does the structure of cholic acid differ from that of cholesterol? Which compound would you expect to be more polar? Why?
9. a. What fatty acid is the precursor for the prostaglandins?
   b. Identify three biological effects of prostaglandins.
10. Why is it important to determine the ratio of LDLs to HDLs, rather than just the concentration of serum cholesterol?

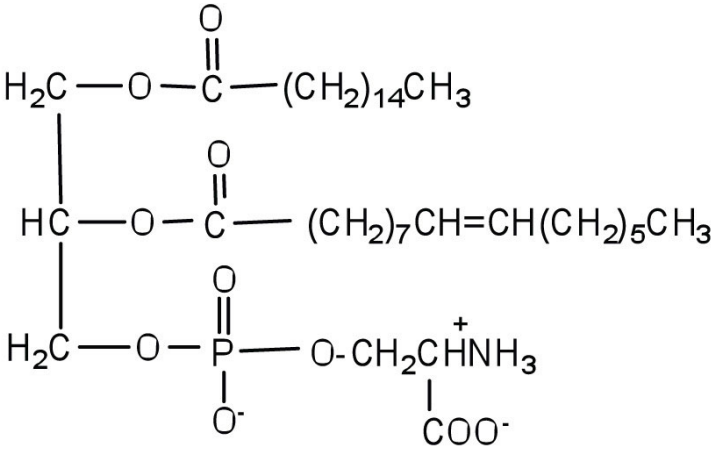
Answers

1. a. Stearic acid has the highest melting point, followed by elaidic acid, and then oleic acid with the lowest melting point. Elaidic acid is a *trans* fatty acid, and the carbon chains can pack together almost as tightly as those of the saturated stearic acid. Oleic acid is a *cis* fatty acid, and the bend in the hydrocarbon chain keeps these carbon chains from packing as closely together; fewer interactions lead to a much lower melting point.
   b. The melting point of palmitelaidic acid should be lower than that of elaidic acid because it has a shorter carbon chain (16, as compared to 18 for elaidic acid). The shorter the carbon chain, the lower the melting point due to a decrease in intermolecular interactions.

3.



5.



7. a. regulates the menstrual cycle and maintains pregnancy
   b. regulates salt metabolism by stimulating the kidneys to retain sodium and excrete potassium
   c. stimulates and maintains male sex characteristics
   d. stimulates the conversion of proteins to carbohydrates

9. a. arachidonic acid
   b. induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response

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7.S: Lipids (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Lipids, found in the body tissues of all organisms, are compounds that are more soluble in organic solvents than in water. Many of them contain **fatty acids**, which are carboxylic acids that generally contain an even number of 4–20 carbon atoms in an unbranched chain. **Saturated fatty acids** have no carbon-to-carbon double bonds. **Monounsaturated fatty acids** have a single carbon-to-carbon double bond, while **polyunsaturated fatty acids** have more than one carbon-to-carbon double bond. Linoleic and linolenic acid are known as **essential fatty acids** because the human body cannot synthesize these polyunsaturated fatty acids. The lipids known as **fats** and **oils** are triacylglycerols, more commonly called **triglycerides**—esters composed of three fatty acids joined to the trihydroxy alcohol glycerol. Fats are triglycerides that are solid at room temperature, and oils are triglycerides that are liquid at room temperature. Fats are found mainly in animals, and oils found mainly in plants. *Saturated triglycerides* are those containing a higher proportion of saturated fatty acid chains (fewer carbon-to-carbon double bonds); *unsaturated triglycerides* contain a higher proportion of unsaturated fatty acid chains.

Saponification is the hydrolysis of a triglyceride in a basic solution to form glycerol and three carboxylate anions or soap molecules. Other important reactions are the hydrogenation and oxidation of double bonds in unsaturated fats and oils.

Phospholipids are lipids containing phosphorus. In **phosphoglycerides**, the phosphorus is joined to an amino alcohol unit. Some phosphoglycerides, like lecithins, are used to stabilize an **emulsion**—a dispersion of two liquids that do not normally mix, such as oil and water. **Sphingolipids** are lipids for which the precursor is the amino alcohol sphingosine, rather than glycerol. A **glycolipid** has a sugar substituted at one of the OH groups of either glycerol or sphingosine. All are highly polar lipids found in cell membranes.

Polar lipids have dual characteristics: one part of the molecule is ionic and dissolves in water; the rest has a hydrocarbon structure and dissolves in nonpolar substances. Often, the ionic part is referred to as **hydrophilic** (literally, “water loving”) and the nonpolar part as **hydrophobic** (“water fearing”). When placed in water, polar lipids disperse into any one of three arrangements: *micelles*, *monolayers*, and *bilayers*. **Micelles** are aggregations of molecules in which the hydrocarbon tails of the lipids, being hydrophobic, are directed inward (away from the surrounding water), and the hydrophilic heads that are directed outward into the water. **Bilayers** are double layers arranged so that the hydrophobic tails are sandwiched between the two layers of hydrophilic heads, which remain in contact with the water.

Every living cell is enclosed by a *cell membrane* composed of a lipid bilayer. In animal cells, the bilayer consists mainly of phospholipids, glycolipids, and the steroid cholesterol. Embedded in the bilayer are **integral proteins**, and **peripheral proteins** are loosely associated with the surface of the bilayer. Everything between the cell membrane and the membrane of the cell nucleus is called the **cytoplasm**.

Most lipids can be saponified, but some, such as **steroids**, cannot be saponified. The steroid **cholesterol** is found in animal cells but never in plant cells. It is a main component of all cell membranes and a precursor for hormones, vitamin D, and bile salts. Bile salts are the most important constituents of **bile**, which is a yellowish-green liquid secreted by the gallbladder into the small intestine and is needed for the proper digestion of lipids.

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CHAPTER OVERVIEW

8: Proteins

Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells. We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins. We end the chapter with a discussion of enzymes—the proteins that act as catalysts in the body.

8.1: Amino Acids
8.2: Reactions of Amino Acids
8.3: Peptides
8.4: Proteins
8.5: Enzymes - Biological Catalysts
8.6: Enzyme Activity
8.7: Enzyme Inhibition
8.8: Proteins (Summary)
8.9: E- Proteins (Exercises)

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8.1: Amino Acids

Learning Objectives

- To recognize amino acids and classify them based on the characteristics of their side chains.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 **amino acids**. The term “amino” indicates the presence of an amino group ($–NH_2$), while “acid” indicates that a carboxylic acid group (–COOH). The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid.

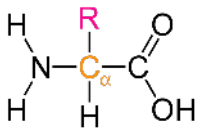


Figure 8.1.1: General structure of an alpha amino acid. Benjah-bmm27, Public domain, via Wikimedia Commons

Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as **essential amino acids**. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a **zwitterion**.

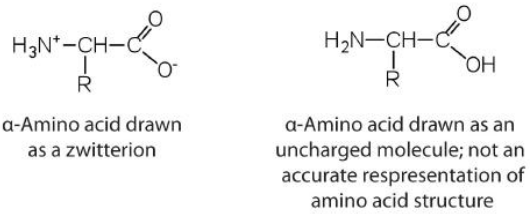
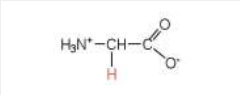
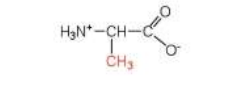
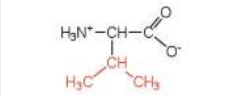
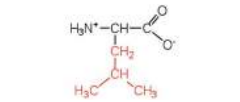
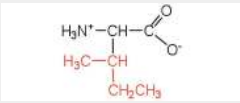
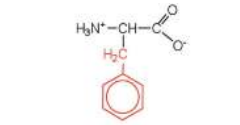
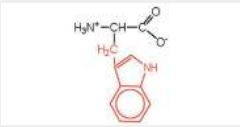
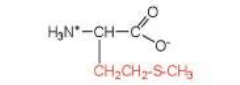
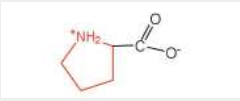
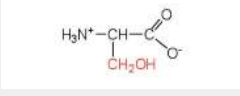
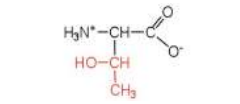
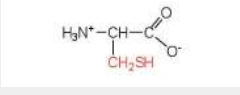


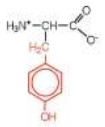
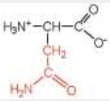
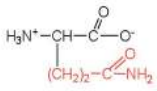
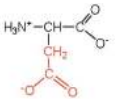
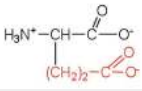
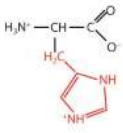
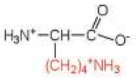
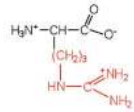
Figure 8.1.2: Structures of a zwitterion (left) and generic (right) alpha amino acid.

Classification

In addition to the amino and carboxyl groups, amino acids have a **side chain or R group** attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the 20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table 8.1.1.

Table 8.1.1: Common Amino Acids Found in Proteins

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				
glycine	gly (G)		75	the only amino acid lacking a chiral carbon
alanine	ala (A)		89	—
valine	val (V)		117	a branched-chain amino acid
leucine	leu (L)		131	a branched-chain amino acid
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.

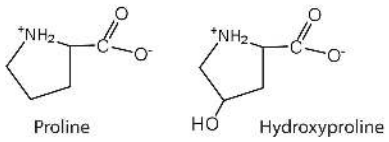


Figure 8.1.3: Structures of proline and hydroxyproline.

Configuration

Notice in Table **8.1.1** that glycine is the only amino acid whose α-carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as the reference compound for the assignment of absolute configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, an amino group takes the place of the OH group on the chiral carbon of the L-glyceraldehyde and a carboxylic acid replaces the aldehyde. Modern stereochemistry assignments using the Cahn-Ingold-Prelog priority rules used ubiquitously in chemistry show that all of the naturally occurring chiral amino acids are S except Cys which is R.

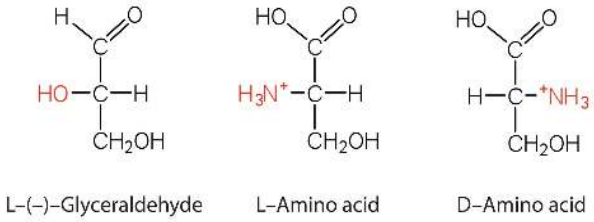


Figure **8.1.4**: Configuration of amino acid enantiomers.

We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of **L-amino acids**. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

✔ Example 8.1.1

Identify an amino acid whose side chain contains a(n)

a. amide functional group.
b. aromatic ring.
c. carboxyl group.

Solution

a. asparagine or glutamine
b. phenylalanine, tryptophan, or tyrosine
c. aspartate/aspartic acid or glutamate/glutamic acid

? Exercise 8.1.1

Identify an amino acid whose side chain contains a(n)

a. OH group
b. branched chain
c. amino group

Summary

Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

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8.2: Reactions of Amino Acids

Learning Objectives

- To explain how an amino acid can act as both an acid and a base.

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen (H^+) ion, and the amino acid becomes positively charged. If base is added, ion removal of the H^+ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid (H^+) or base (OH^-) from solution.

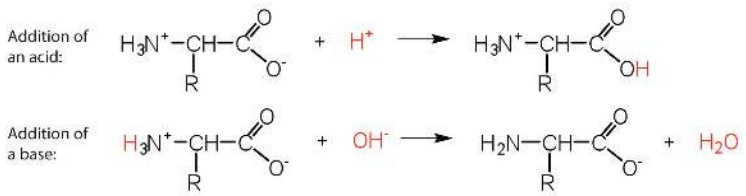


Figure 8.2.1: Reaction schemes representing the additional of acid (top) and base (bottom) to a solution containing a zwitterion.

Example 8.2.1

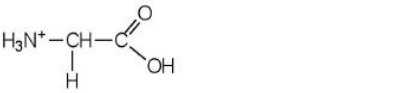
a. Draw the structure for the anion formed when glycine (at neutral pH) reacts with a base.
b. Draw the structure for the cation formed when glycine (at neutral pH) reacts with an acid.

Solution

a. The base removes H^+ from the protonated amine group.



b. The acid adds H^+ to the carboxylate group.



Exercise 8.2.1

a. Draw the structure for the cation formed when valine (at neutral pH) reacts with an acid.
b. Draw the structure for the anion formed when valine (at neutral pH) reacts with a base.

The particular pH at which a given amino acid exists in solution as a zwitterion is called the **isoelectric point (pI)**. At its pI, the positive and negative charges on the amino acid balance, and the molecule as a whole is electrically neutral. The amino acids whose side chains are always neutral have isoelectric points ranging from 5.0 to 6.5. The basic amino acids (which have positively charged side chains at neutral pH) have relatively high examples. Acidic amino acids (which have negatively charged side chains at neutral pH) have quite low examples (Table 8.2.1).

Table 8.2.1: ExampIes of Some Representative Amino Acids

Amino Acid	Classification	pI
alanine	nonpolar	6.0
valine	nonpolar	6.0
serine	polar, uncharged	5.7
threonine	polar, uncharged	6.5
arginine	positively charged (basic)	10.8
histidine	positively charged (basic)	7.6
lysine	positively charged (basic)	9.8
aspartic acid	negatively charged (acidic)	3.0
glutamic acid	negatively charged (acidic)	3.2

Amino acids undergo reactions characteristic of carboxylic acids and amines. The reactivity of these functional groups is particularly important in linking amino acids together to form peptides and proteins, as you will see later in this chapter. Simple chemical tests that are used to detect amino acids take advantage of the reactivity of these functional groups. An example is the ninhydrin test in which the amine functional group of α-amino acids reacts with ninhydrin to form purple-colored compounds. Ninhydrin is used to detect fingerprints because it reacts with amino acids from the proteins in skin cells transferred to the surface by the individual leaving the fingerprint.

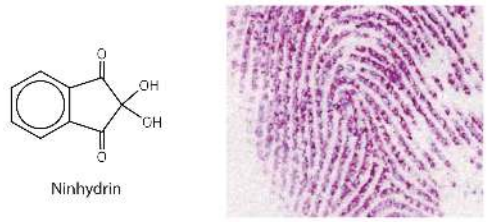
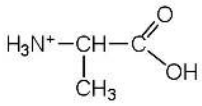


Figure **8.2.2**: Structure of ninhydrin (left) and an observation of ninhydrin reacting with skin cells to leave a fingerprint (right).

✔ Example 8.2.1

Draw the structure for the cation formed when alanine (at neutral pH) reacts with an acid.

Solution



? Exercise 8.2.1

Draw the structure for the anion formed when alanine (at neutral pH) reacts with a base.

✔ Example 8.2.2

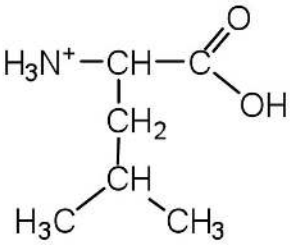
Draw the structure of leucine and determine the charge on the molecule in a(n)

a. acidic solution (pH = 1).
b. neutral solution (pH = 7).

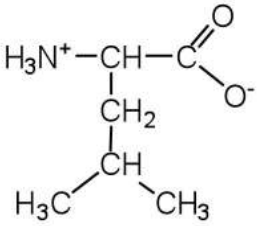
c. a basic solution (pH = 11)

Solution

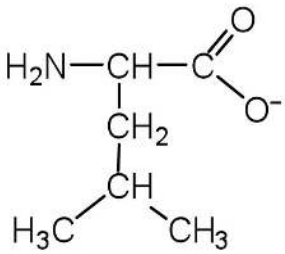
a.



b.



c.



? Exercise 8.2.2

Draw the structure of isoleucine and determine the charge on the molecule in a(n)

a. acidic solution (pH = 1).
b. neutral solution (pH = 7).
c. basic solution (pH = 11).

Summary

Amino acids can act as both an acid and a base due to the presence of the amino and carboxyl functional groups. The pH at which a given amino acid exists in solution as a zwitterion is called the *isoelectric point* (pI).

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8.3: Peptides

Learning Objectives

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia (or an amine) and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage:

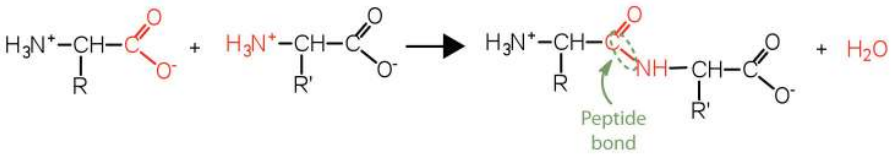
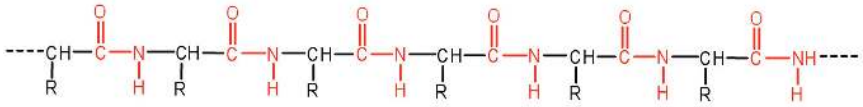


Figure 8.3.1: Reaction scheme of the formation of an amide linkage between amino acids.

An amide bond joining two amino acid units is called a **peptide bond**. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.



A chain consisting of only two amino acid units is called a **dipeptide**; a chain consisting of three is a **tripeptide**. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the N-terminal end) on the left and the amino acid with a free carboxyl group (the C-terminal end) to the right.

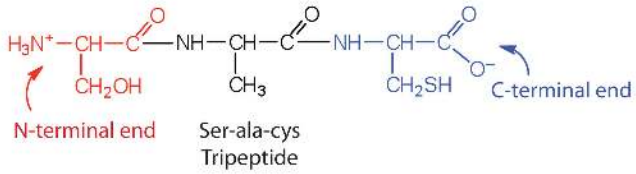


Figure 8.3.2: Structure of a tripeptide formed with serine, alanine, and cysteine.

The general term **peptide** refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called **proteins or polypeptides**. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

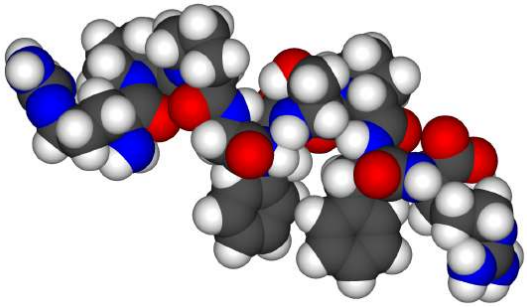


Figure 8.3.3: Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The **order**, or **sequence**, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure **8.3.3**) produced in the blood that has the following amino acid sequence:

arg-pro-pro-gly-phe-ser-pro-phe-arg

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

arg-phe-pro-ser-phe-gly-pro-pro-arg

the peptide resulting from this synthesis shows none of the activity of bradykinin.

Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of "incorrect" amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That "minor" error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

Example 8.3.1

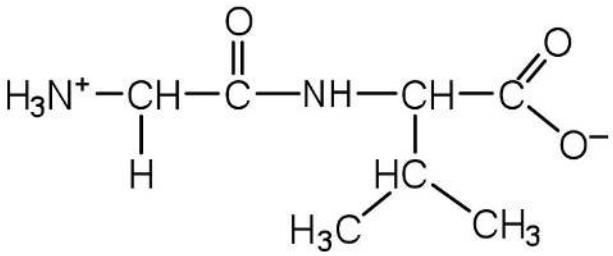
Draw the structure for each peptide.

a. gly-val

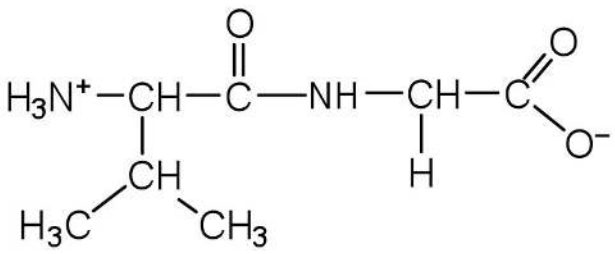
b. val-gly

Solution

a.



b.



c.
d.

Exercise 8.3.1

Draw the structure for each peptide.

a. thr-leu
b. leu-thr

Example 8.3.2

Identify the C- and N-terminal amino acids for the peptide lys-val-phe-gly-arg-cys.

Solution

C-terminal amino acid: cysteine (cys or C)
N-terminal amino acid: lysine (lys or K)

Exercise 8.3.2

Identify the C- and N-terminal amino acids for the peptide asp-arg-val-tyr-ile-his-pro-phe.

Summary

The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together. Additional amino acids can be added on through the formation of addition peptide (amide) bonds. A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).

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8.4: Proteins

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain what happens when proteins are denatured.
- Identify how a protein can be denatured.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These **fibrous proteins** are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the **primary structure**, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure 8.4.1.

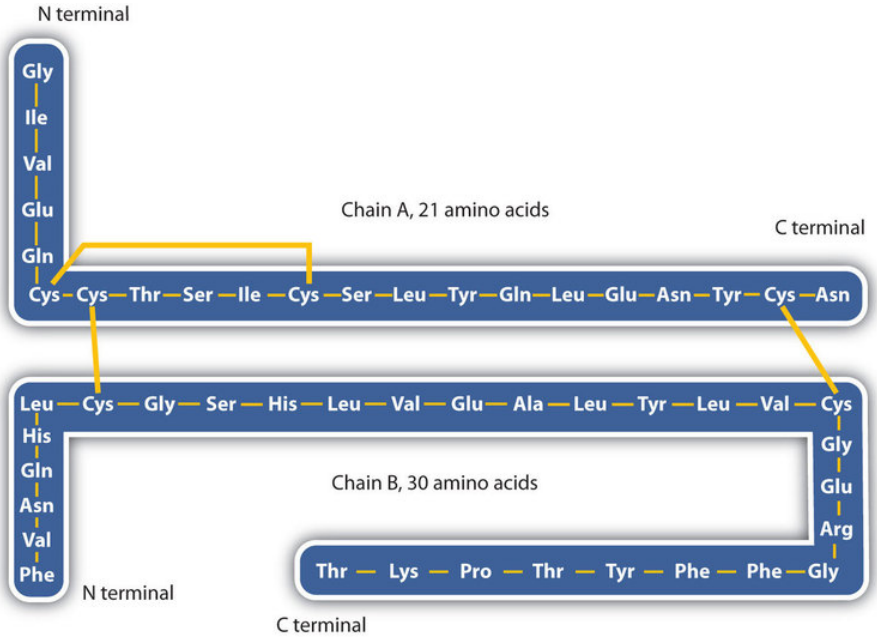


Figure 8.4.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term **secondary structure** refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed **α-helix**. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure 8.4.2). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

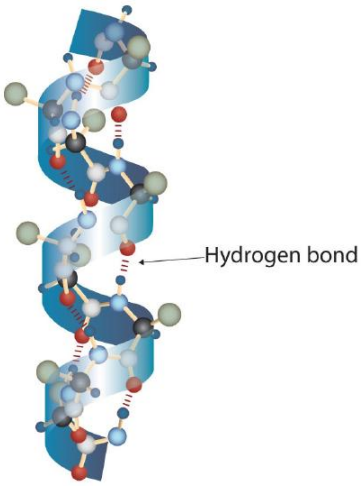


Figure 8.4.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the **β-pleated sheet conformation**, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—

and are connected by *interchain* hydrogen bonding (Figure 8.4.3). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

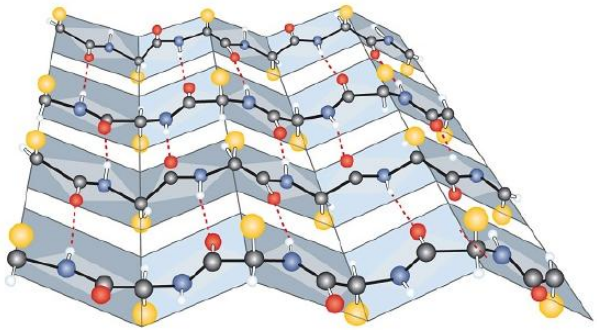


Figure 8.4.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure 8.4.4 shows a depiction of the three-dimensional structure of insulin.

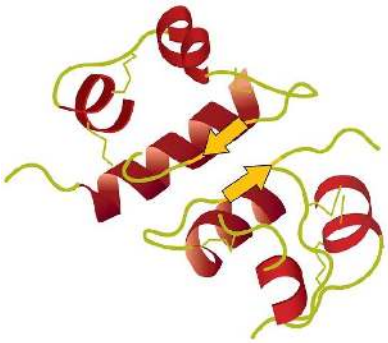
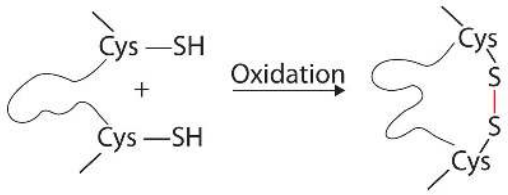


Figure 8.4.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins.

1. **Ionic bonding** (also called **salt bridges**). Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (Figure 8.4.5*a*).
2. **Hydrogen bonding**. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (Figure 8.4.5*b*).
3. **Disulfide linkages**. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (Figure 8.4.5*c*). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 8.4.1) and have a strong stabilizing effect on the tertiary structure.



4. **Dispersion forces**. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (Figure 8.4.5*d*). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

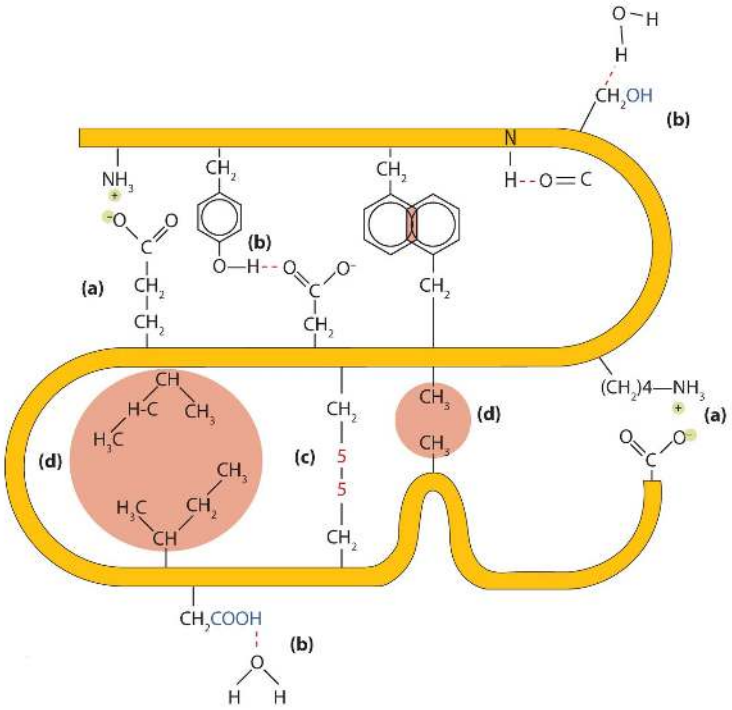


Figure 8.4.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a ***subunit***. The arrangement of multiple subunits represents a fourth level of structure, the **quaternary structure** of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 8.4.6). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 8.4.7.

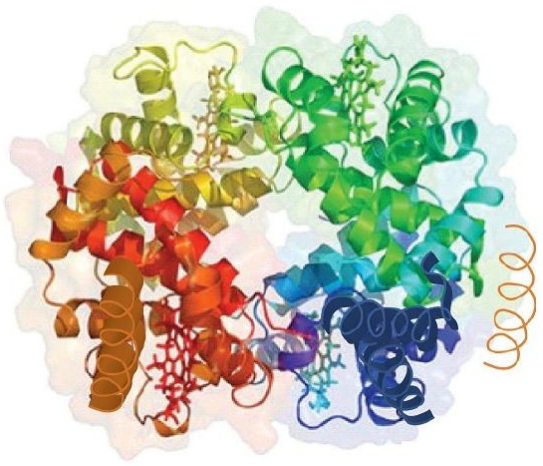


Figure 8.4.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

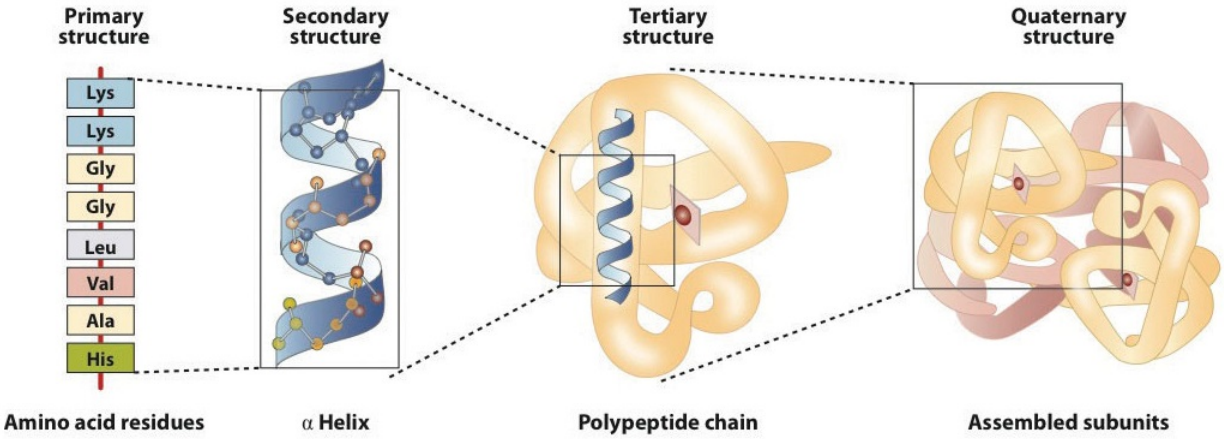


Figure 8.4.7: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. **Denaturation** is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 8.4.8).

Figure 8.4.1: Protein Denaturation Methods

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure 8.4.8). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

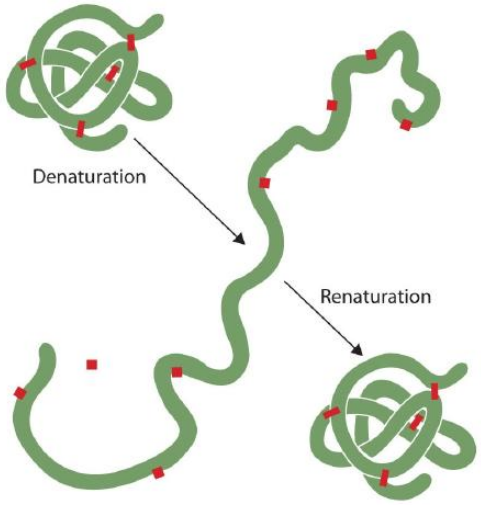


Figure 8.4.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

✔ Example 8.4.1

A protein has a tertiary structure formed by interactions between the side chains of the following pairs of amino acids. For each pair, identify the strongest type of interaction between these amino acids.

a. aspartic acid and lysine
b. phenylalanine and alanine
c. serine and lysine
d. two cysteines

Solution

a. ionic bonding
b. dispersion forces
c. dispersion forces
d. disulfide linkage

? Exercise 8.4.1

A protein has a tertiary structure formed by interactions between the side chains of the following pairs of amino acids. For each pair, identify the strongest type of interaction between these amino acids.

a. valine and isoleucine
b. asparagine and serine
c. glutamic acid and arginine
d. tryptophan and methionine

Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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8.5: Enzymes - Biological Catalysts

Learning Outcomes

- Explain the role of an enzyme in the body.
- Define active site and substrate.
- Describe the lock and key vs. induced-fit model of enzymes.
- Provide the characteristics of a cofactor and a coenzyme.

All living cells carry out a great variety of chemical reactions essential for maintenance of life. Chemical reactions in living cells are different from chemical reactions in most other systems in that they are much faster and are highly ordered and regulated. The source of these differences is that the chemistry of living things is carried out by proteins functioning as specific biological catalysts, called **enzymes**. Enzymes accelerate and regulate biochemical processes allowing reactions to occur in the milliseconds necessary to maintain life.

The first enzyme to be isolated was discovered in 1926 by American chemist James Sumner, who crystallized the protein. The enzyme was urease, which catalyzes the hydrolytic decomposition of urea, a component of urine, into ammonia and carbon dioxide.

$$\mathrm{H_2NCON_2}\,(aq) + \mathrm{H_2O}\,(l) \overset{\text{urease}}{\rightarrow} 2\mathrm{NH_3}\,(g) + \mathrm{CO_2}\,(g) \tag{8.5.1}$$

His discovery was ridiculed at first because nobody believed that enzymes would behave the same way that other chemicals did. Sumner was eventually proven right and won the Nobel Prize in Chemistry in 1946.

Enzyme-Catalyzed Reactions

Most chemical reactions within organisms would be impossible under the conditions in cells. For example, the body temperature of most organisms is too low for reactions to occur quickly enough to carry out life processes. Reactants may also be present in such low concentrations that it is unlikely they will meet and collide. Therefore, the rate of most biochemical reactions must be increased by a catalyst. A **catalyst** is a chemical that speeds up chemical reactions. In organisms, catalysts are called **enzymes**. Essentially, enzymes are **biological catalysts**.

Like other catalysts, enzymes are not reactants in the reactions they control. They help the reactants interact but are not used up in the reactions. Instead, they may be used over and over again. Unlike other catalysts, enzymes are usually highly specific for particular chemical reactions. They generally catalyze only one or a few types of reactions.

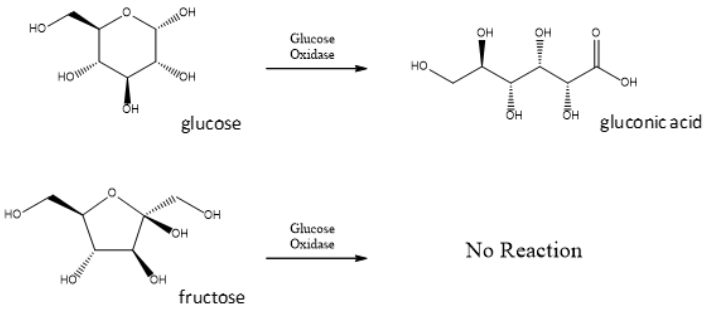


Figure 8.5.1: Enzymes catalyze specific reactions.

Enzymes are extremely efficient in speeding up reactions. They can catalyze up to several million reactions per second. As a result, the difference in rates of biochemical reactions with and without enzymes may be enormous. A typical biochemical reaction might take hours or even days to occur under normal cellular conditions without an enzyme, but less than a second with an enzyme.

The first step in an enzyme-catalyzed reaction is that the **substrate** binds to a specific part of the enzyme molecule. A substrate is the molecule(s) on which the enzyme acts. The binding of the substrate is dictated by the shape of each molecule. Side chains on the enzyme interact with the substrate in a specific way, resulting in the making and breaking of bonds. The **active site** is the specific part of an enzyme where the substrate binds. An enzyme folds in such a way that it typically has one active site, usually a

pocket or crevice formed by the folding pattern of the protein. Because the active site of an enzyme has such a unique shape, only one particular substrate is capable of binding to that enzyme. This **substrate specificity** means that each enzyme catalyzes only one chemical reaction with only one substrate. Once the **enzyme-substrate (ES) complex** is formed, the reaction occurs and the substrate is transformed into products. Finally, the product molecule(s) are released from the active site. Note that the enzyme is left unaffected by the reaction and is now capable of catalyzing the reaction of another substrate molecule.

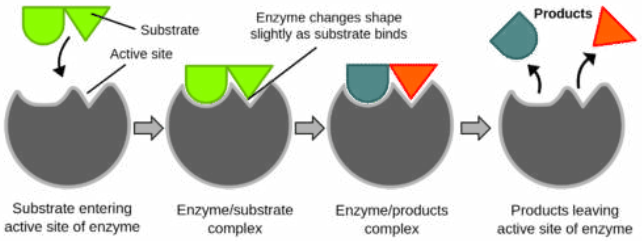


Figure 8.5.2: The sequence of steps for a substrate binding to an enzyme in its active site, reacting, then being released as products.

For many enzymes, the active site follows a **lock and key** (Figure 8.5.3*A*) model where the substrate fits exactly into the active site. The enzyme and substrate must be a perfect match so the enzyme only functions as a catalyst for one reaction. Other enzymes have an **induced fit** (Figure 8.5.3*B*) model. In an induced fit model, the active site can make minor adjustments to accommodate the substrate. This results in an enzyme that is capable of interacting with a small group of similar substrates. Look at the shape of the active site compared to the shape of the substrate in B of the figure below. The active site adjusts to accommodate the substrate.

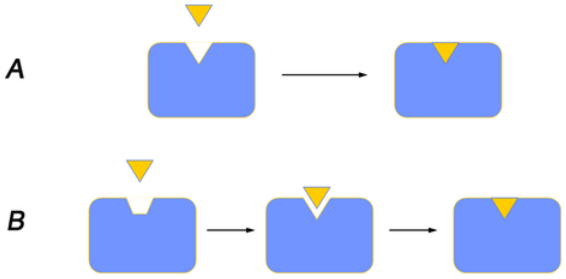


Figure 8.5.3: (A) Lock and key enzyme model and (B) induced fit enzyme model.

Cofactors and Coenzymes

Some enzymes require the presence of another substrate as a "helper" molecule in order to function properly. **Cofactors** and **coenzymes** serve in this role. Cofactors are inorganic species and coenzymes are small organic molecules. Many vitamins, such as B vitamins, are coenzymes. Some metal ions which function as cofactors for various enzymes include zinc, magnesium, potassium, and iron.

Classes of Enzymes

Enzymes are named consisting of the root of the name of its substrate(s) with the *-ase* suffix and classified by the types of reaction they catalyze.

Table 8.5.1: Classes of Enzymes

Class	Type of Reaction Catalyzed	Examples
oxidoreductases	oxidation-reduction reactions	Dehydrogenases catalyze oxidation-reduction reactions involving hydrogen and reductases catalyze reactions in which a substrate is reduced.
transferases	transfer reactions of groups, such as methyl, amino, and acetyl	Transaminases catalyze the transfer of amino group, and kinases catalyze the transfer of a phosphate group.
hydrolases	hydrolysis reactions	Lipases catalyze the hydrolysis of lipids, and proteases catalyze the hydrolysis of proteins
lyases	reactions in which groups are removed without hydrolysis or addition of groups to a double bond	Decarboxylases catalyze the removal of carboxyl groups.
isomerases	reactions in which a compound is converted to its isomer	Isomerases may catalyze the conversion of an aldose to a ketose, and mutases catalyze reactions in which a functional group is transferred from one atom in a substrate to another.
ligases	reactions in which new bonds are formed between carbon and another atom; energy is required	Synthetases catalyze reactions in which two smaller molecules are linked to form a larger one.

✔ Example 8.5.1

Identify the substrate catalyzed by each enzyme.

a. lactase
b. cellulase
c. peptidase

Solution

a. lactose
b. cellulose
c. peptides

? Exercise 8.5.2

Identify the substrate catalyzed by each enzyme.

a. lipase
b. amylase
c. maltase

✔ Example 8.5.2

Identify each type of enzyme.

a. decarboxylase

b. protease

c. transaminase

Solution

a. lyase
b. hydrolase
c. transferase

? Exercise 8.5.2

Identify each type of enzyme.

a. dehydrogenase
b. isomerase
c. lipase

Summary

An enzyme is a biological catalyst, a substance that increases the rate of a chemical reaction without being changed or consumed in the reaction. A systematic process is used to name and classify enzymes. A substrate binds to a specific region on an enzyme known as the active site, where the substrate can be converted to product. The substrate binds to the enzyme primarily through hydrogen bonding and other electrostatic interactions. The induced-fit model says that an enzyme can undergo a conformational change when binding a substrate. Enzymes exhibit varying degrees of substrate specificity.

Supplemental Resources

- Enzymes: https://youtu.be/E90D4BmaVJM

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8.6: Enzyme Activity

Learning Outcomes

- Describe how substrate concentration, pH, and temperature affect enzyme activity.
- Interpret graphs of reaction rate vs. reaction conditions.

The most important property of enzymes is the ability to increase the rates of reactions occurring in living organisms. Determining how fast an enzymatic reaction occurs is a measure of **enzyme (or catalytic) activity**. Because most enzymes are proteins, their activity is affected by factors that disrupt protein structure, as well as by factors that affect catalysts in general. These factors include concentration, pH of the surroundings, and temperature.

Concentration

As with most reactions, the concentration of the reactant(s) affects the reaction rate. This is also true in enzyme concentration. When either substrate or enzyme concentration is low, the rate of the reaction will be slower than where there are higher concentrations. The two species must interact for a reaction to occur and higher concentrations of one or both will result in more effective interactions between the two.

Concentration of Substrate

In the presence of a given amount of enzyme, the rate of an enzymatic reaction increases as the substrate concentration increases until a limiting rate is reached, after which further increase in the substrate concentration produces no significant change in the reaction rate (Figure 8.6.1*a*). At this point, so much substrate is present that essentially all of the enzyme active sites have substrate bound to them. In other words, the enzyme molecules are **saturated** with substrate. The excess substrate molecules cannot react until the substrate already bound to the enzymes has reacted and been released (or been released without reacting). When the enzyme becomes saturated with substrate, it would operate at **steady state**, the condition in which an enzyme is operating at maximum activity.

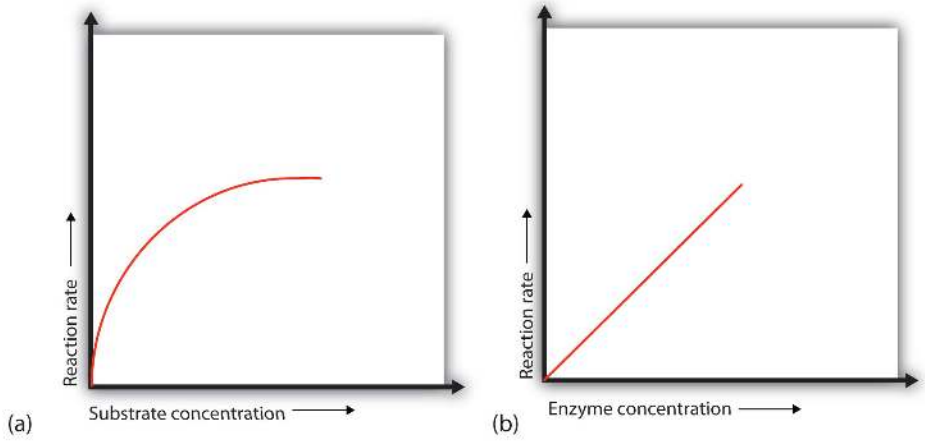


Figure 8.6.1: Concentration versus Reaction Rate. (a) This graph shows the effect of substrate concentration on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph shows the effect of enzyme concentration on the reaction rate at a constant level of substrate.

Let's consider an analogy. Ten taxis (enzyme molecules) are waiting at a taxi stand to take people (substrate) on a 10-minute trip to a concert hall, one passenger at a time. If only 5 people are present at the stand, the rate of their arrival at the concert hall is 5 arrivals in 10 minutes. If the number of people at the stand is increased to 10, the rate increases to 10 arrivals in 10 minutes. With 20 people at the stand, the rate would still be 10 arrivals in 10 minutes. The taxis have been "saturated." If the taxis could carry 2 or 3 passengers each, the same principle would apply. The rate would simply be higher (20 or 30 people in 10 minutes) before it leveled off.

Concentration of Enzyme

When the concentration of the enzyme is significantly lower than the concentration of the substrate (as when the number of taxis is far lower than the number of waiting passengers), the rate of an enzyme-catalyzed reaction is directly dependent on the enzyme concentration (Figure 8.6.1*b*). This is true for any catalyst; the reaction rate increases as the concentration of the catalyst is increased.

pH

Some enzymes work best at acidic pHs, while others work best in neutral environments. For example, digestive enzymes secreted in the acidic environment (low pH) of the stomach help break down proteins into smaller molecules. The main digestive enzyme in the stomach is **pepsin**, which works best at a pH of about 1.5. These enzymes would not work optimally at other pH levels. Trypsin is another enzyme in the digestive system, which breaks protein chains in food into smaller particles. **Trypsin** works in the small intestine, which is not an acidic environment, and has an optimum pH is about 8.

Different reactions and different enzymes will achieve their maximum rate at certain pH values. An enzyme is most active at its **optimum pH**, which is the pH where it maintains the native tertiary structure. As shown in Figure 8.6.2, the enzyme achieves a maximum reaction rate at a pH of 4. Notice that the reaction will continue at lower and higher pH values because the enzyme will still function at other pH values but will not be as effective. At very high or very low pH values, denaturation will occur because an enzyme is just a protein with a specific function.

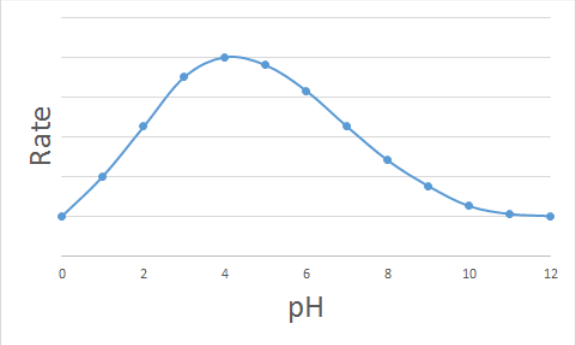


Figure 8.6.2: Relationship between rate and pH.

Temperature

As with pH, reactions also have an **optimum temperature** where the enzyme functions most effectively. It will still function at higher and lower temperatures, but the rate will be less. For many biological reactions, the optimum temperature is at physiological conditions which is around **37°C** which is normal body temperature. Many enzymes lose function at lower and higher temperatures. At higher temperatures, an enzyme's shape deteriorates. Only when the temperature comes back to normal does the enzyme regain its shape and normal activity unless the temperature was so high that it caused irreversible damage.

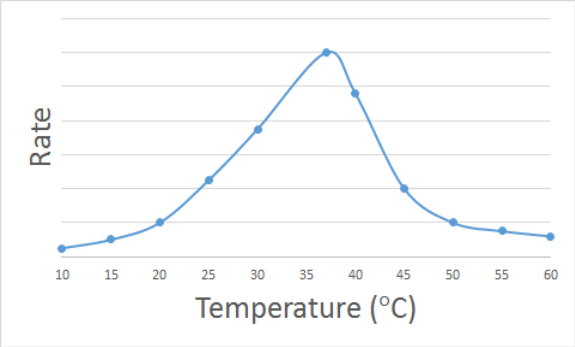


Figure 8.6.3: Relationship between temperature and rate.

Example 8.6.1

An enzyme has an optimum pH of 7.4. What is most likely to happen to the activity of the enzyme if the pH drops to 6.3? Explain.

Solution

The activity will decrease; a pH of 6.3 is more acidic than 7.4, and one or more key groups in the active site may bind a hydrogen ion, changing the charge on that group.

Exercise 8.6.1

An enzyme has an optimum pH of 7.2. What is most likely to happen to the activity of the enzyme if the pH increases to 8.5? Explain.

Summary

Initially, an increase in substrate concentration leads to an increase in the rate of an enzyme-catalyzed reaction. As the enzyme molecules become saturated with substrate, this increase in reaction rate levels off. The rate of an enzyme-catalyzed reaction increases with an increase in the concentration of an enzyme. At low temperatures, an increase in temperature increases the rate of an enzyme-catalyzed reaction. At higher temperatures, the protein is denatured, and the rate of the reaction dramatically decreases. An enzyme has an optimum pH range in which it exhibits maximum activity.

Supplemental Resources

- Enzymes: https://youtu.be/E90D4BmaVJM

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8.7: Enzyme Inhibition

Learning Outcomes

- Define allosteric site.
- Distinguish between reversible and irreversible inhibitors.
- Distinguish between competitive and noncompetitive inhibitors.
- Define feedback inhibition.

In addition to concentration, pH, and, temperature; the presence of **inhibitors** will also affect enzyme activity. Inhibitors are compounds that cause enzymes to lose activity, either by slowing or stopping the chemical reaction. Some inhibitors cause temporary loss of activity, while others cause permanent loss of activity.

Reversible Inhibitors

A **reversible inhibitor** is one that will cause a temporary loss of enzymatic activity. This substance forms a non-covalent interaction with the enzyme. Reversible inhibitors can be competitive of noncompetitive.

A **competitive inhibitor** is any compound that bears a structural resemblance to a particular substrate and thus competes with that substrate for binding at the active site of an enzyme. The inhibitor is not acted on by the enzyme but does prevent the substrate from approaching the active site.

The degree to which a competitive inhibitor interferes with an enzyme's activity depends on the relative concentrations of the substrate and the inhibitor. If the inhibitor is present in relatively large quantities, it will initially block most of the active sites. But because the binding is reversible, some substrate molecules will eventually bind to the active site and be converted to product. Increasing the substrate concentration promotes displacement of the inhibitor from the active site. Competitive inhibition can be completely reversed by adding substrate so that it reaches a much higher concentration than that of the inhibitor.

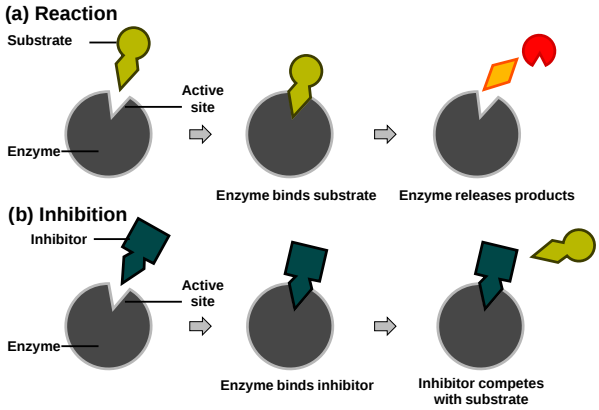


Figure 8.7.1: A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.

A **noncompetitive inhibitor** attaches at an **allosteric site**, which is any site on the enzyme that is not the active site. The attachment of the non-competitive inhibitor to the allosteric site results in a shift in three-dimensional structure that alters the shape of the active site so that the substrate will no longer fit in the active site properly (Figure 8.7.2). A noncompetitive inhibitor can combine with either the free enzyme or the enzyme-substrate complex because its binding site on the enzyme is distinct from the active site. Because the inhibitor does not structurally resemble the substrate, the addition of excess substrate does *not* reverse the inhibitory effect.

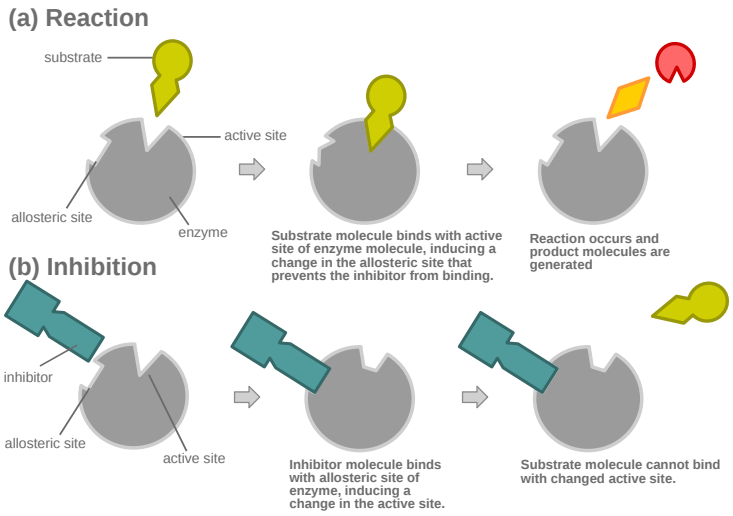


Figure **8.7.2**: A noncompetitive inhibitor binding at the allosteric site.

Feedback inhibition is a normal biochemical process that makes use of noncompetitive inhibitors to control some enzymatic activity. In this process, the final product inhibits the enzyme that catalyzes the first step in a series of reactions. Feedback inhibition is used to regulate the synthesis of many amino acids. For example, bacteria synthesize isoleucine from threonine in a series of five enzyme-catalyzed steps. As the concentration of isoleucine increases, some of it binds as a noncompetitive inhibitor to the first enzyme of the series (threonine deaminase), thus bringing about a decrease in the amount of isoleucine being formed (Figure **8.7.3**).

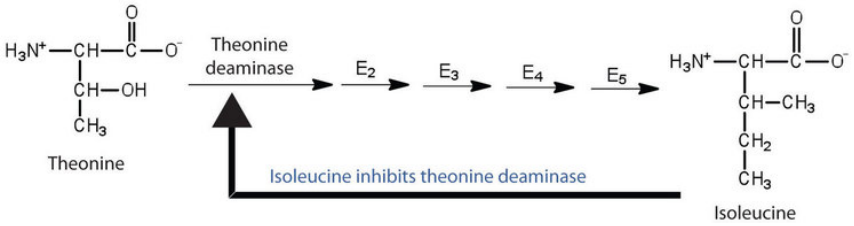


Figure **8.7.3**: Feedback Inhibition of Threonine Deaminase by Isoleucine. Threonine deaminase is the first enzyme in the conversion of threonine to isoleucine. Isoleucine inhibits threonine deaminase through feedback inhibition.

Irreversible Inhibitors

An **irreversible inhibitor** is one that will cause a permanent loss of enzymatic activity. An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. The inhibitor-enzyme bond is so strong that the inhibition cannot be reversed by the addition of excess substrate. The nerve gases, especially Diisopropyl fluorophosphate (DIFP), irreversibly inhibit biological systems by forming an enzyme-inhibitor complex with a specific OH group of serine situated at the active sites of certain enzymes. The peptidases trypsin and chymotrypsin contain serine groups at the active site and are inhibited by DIFP.

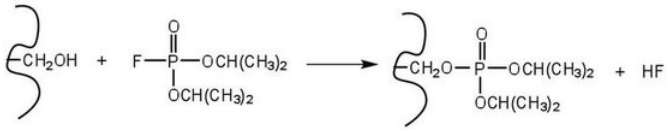


Figure **8.7.4**: An irreversible inhibitor forming a covalent bond.

Example 8.7.1

What are the characteristics of an irreversible inhibitor?

Solution

It inactivates an enzyme by bonding covalently to a particular group at the active site.

? Exercise 8.7.1

In what ways does a competitive inhibitor differ from a noncompetitive inhibitor?

Summary

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. A reversible inhibitor inactivates an enzyme through noncovalent, reversible interactions. A competitive inhibitor competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site.

Supplemental Resources

- Enzymes: https://youtu.be/E90D4BmaVJM

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8.8: Proteins (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

A **protein** is a large biological polymer synthesized from **amino acids**, which are carboxylic acids containing an α-amino group. Proteins have a variety of important roles in living organisms, yet they are made from the same 20 L-amino acids. About half of these amino acids, the **essential amino acids**, cannot be synthesized by the human body and must be obtained from the diet. In the solid state and in neutral solutions, amino acids exist as **zwitterions**, species that are charged but electrically neutral. In this form, they behave much like inorganic salts. Each amino acid belongs to one of four classes depending on the characteristics of its R group or amino acid side chain: nonpolar, polar but neutral, positively charged, and negatively charged. Depending on the conditions, amino acids can act as either acids or bases, which means that proteins act as buffers. The pH at which an amino acid exists as the zwitterion is called the **isoelectric point (pI)**.

The amino acids in a protein are linked together by **peptide bonds**. Protein chains containing 10 or fewer amino acids are usually referred to as **peptides**, with a prefix such as di- or tri- indicating the number of amino acids. Chains containing more than 50 amino acid units are referred to as *proteins* or **polypeptides**. Proteins are classified globular or fibrous, depending on their structure and resulting solubility in water. **Globular proteins** are nearly spherical and are soluble in water; **fibrous proteins** have elongated or fibrous structures and are not soluble in water.

Protein molecules can have as many as four levels of structure. The **primary structure** is the sequence of amino acids in the chain. The **secondary structure** is the arrangement of adjacent atoms in the peptide chain; the most common arrangements are α-helices or β-pleated sheets. The **tertiary structure** is the overall three-dimensional shape of the molecule that results from the way the chain bends and folds in on itself. Proteins that consist of more than one chain have **quaternary structure**, which is the way the multiple chains are packed together.

Four types of intramolecular and intermolecular forces contribute to secondary, tertiary, and quaternary structure: (1) **hydrogen bonding** between an oxygen or a nitrogen atom and a hydrogen atom bound to an oxygen atom or a nitrogen atom, either on the same chain or on a neighboring chain; (2) **ionic bonding (or salt bridges)** between one positively charged side chain and one negatively charged side chain; (3) **disulfide linkages** between cysteine units; and (4) **dispersion forces** between nonpolar side chains.

Because of their complexity, protein molecules are delicate and easy to disrupt. A *denatured* protein is one whose conformation has been changed, in a process called **denaturation**, so that it can no longer do its physiological job. A variety of conditions, such as heat, ultraviolet radiation, the addition of organic compounds, or changes in pH can denature a protein.

An **enzyme** is an organic catalyst produced by a living cell. Enzymes are such powerful catalysts that the reactions they promote occur rapidly at body temperature. Without the help of enzymes, these reactions would require high temperatures and long reaction times.

The molecule or molecules on which an enzyme acts are called its **substrates**. An enzyme has an **active site** where its substrate or substrates bind to form an enzyme-substrate complex. The reaction occurs, and product is released:

$$E + S \rightarrow E\text{–}S \rightarrow E + P \tag{8.8.1}$$

The original **lock-and-key model** of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer **induced-fit model** describes the enzyme active site as changing its conformation after binding to the substrate.

Most enzymes have maximal activity in a narrow pH range centered on an **optimum pH**. In this pH range, the enzyme is correctly folded, and catalytic groups in the active site have the correct charge (positive, negative, or neutral). For most enzymes, the optimum pH is between 6 and 8.

Substances that interfere with enzyme function are called inhibitors. An **irreversible inhibitor** inactivates enzymes by forming covalent bonds to the enzyme, while a **reversible inhibitor** inactivates an enzyme by a weaker, noncovalent interaction that is easier to disrupt. A **competitive inhibitor** is a reversible inhibitor that is structurally similar to the substrate and binds to the active

site. When the inhibitor is bound, the substrate is blocked from the active site and no reaction occurs. Because the binding of such an inhibitor is reversible, a high substrate concentration will overcome the inhibition because it increases the likelihood of the substrate binding. A **noncompetitive inhibitor** binds reversibly at a site distinct from the active site. Thus, it can bind to either the enzyme or the enzyme-substrate complex. The inhibitor changes the conformation of the active site so that the enzyme cannot function properly. Noncompetitive inhibitors are important in **feedback inhibition**, in which the amount of product produced by a series of reactions is carefully controlled. The final product in a series of reactions acts as a noncompetitive inhibitor of the initial enzyme.

Simple enzymes consist entirely of one or more amino acid chains. Complex enzymes are composed of one or more amino acid chains joined to **cofactors**—inorganic ions or organic **coenzymes**. **Vitamins** are organic compounds that are essential in very small amounts for the maintenance of normal metabolism and generally cannot be synthesized at adequate levels by the body. Vitamins are divided into two broad categories: *fat-soluble* vitamins and *water-soluble* vitamins. Many of the water-soluble vitamins are used for the synthesis of coenzymes.

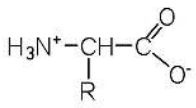
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8.9: E- Proteins (Exercises)

18.1: Properties of Amino Acids

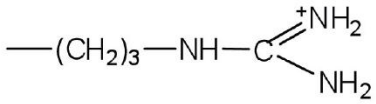
Concept Review Exercises

1. What is the general structure of an α-amino acid?
2. Identify the amino acid that fits each description.
   a. also known as aspartate
   b. almost as strong a base as sodium hydroxide
   c. does not have a chiral carbon
3. 

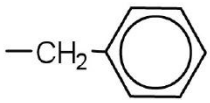
4. a. aspartic acid
   b. arginine
   c. glycine
5. Write the side chain of each amino acid.
   a. serine
   b. arginine
   c. phenylalanine
6. Write the side chain of each amino acid.
   a. aspartic acid
   b. methionine
   c. valine
7. Draw the structure for each amino acid.
   a. alanine
   b. cysteine
   c. histidine
8. Draw the structure for each amino acid.
   a. threonine
   b. glutamic acid
   c. leucine
9. Identify an amino acid whose side chain contains a(n)
   a. amide functional group.
   b. aromatic ring.
   c. carboxyl group.
10. Identify an amino acid whose side chain contains a(n)
    a. OH group
    b. branched chain
    c. amino group

1. a. CH_2OH^-

b.

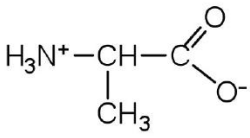


c.

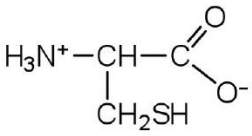


2.

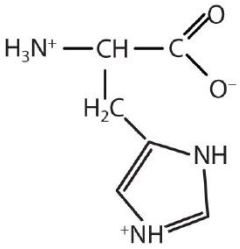
3. a.



b.



c.



4.

5. a. asparagine or glutamine
   b. phenylalanine, tyrosine, or tryptophan
   c. aspartic acid or glutamic acid

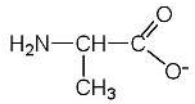
18.2: Reactions of Amino Acids

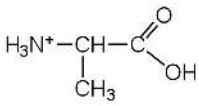
Concept Review Exercises

1. Define each term.
   a. zwitterion
   b. isoelectric point
2. Draw the structure for the anion formed when alanine (at neutral pH) reacts with a base.
3. Draw the structure for the cation formed when alanine (at neutral pH) reacts with an acid.

Answers

1. a. an electrically neutral compound that contains both negatively and positively charged groups
   b. the pH at which a given amino acid exists in solution as a zwitterion

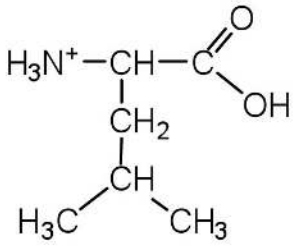
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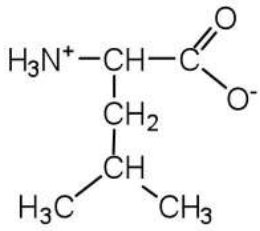
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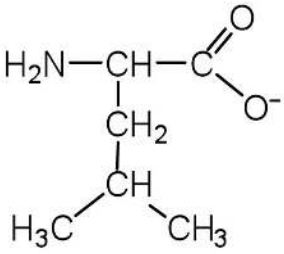
Exercises

1. Draw the structure of leucine and determine the charge on the molecule in a(n)
   a. acidic solution (pH = 1).
   b. neutral solution (pH = 7).
   c. a basic solution (pH = 11)
2. Draw the structure of isoleucine and determine the charge on the molecule in a(n)
   a. acidic solution (pH = 1).
   b. neutral solution (pH = 7).
   c. basic solution (pH = 11).

Answer

1. a. 

   b. 

   c. 

18.3: Peptides

Concept Review Exercises

1. Distinguish between the N-terminal amino acid and the C-terminal amino acid of a peptide or protein.
2. Describe the difference between an amino acid and a peptide.
3. Amino acid units in a protein are connected by peptide bonds. What is another name for the functional group linking the amino acids?

Answers

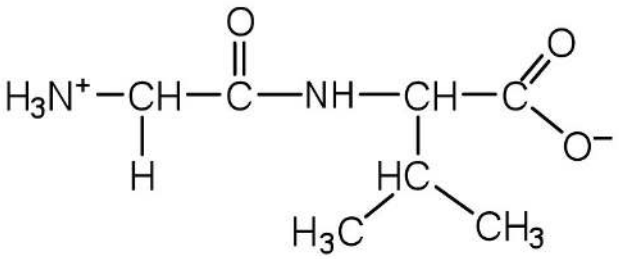
1. The N-terminal end is the end of a peptide or protein whose amino group is free (not involved in the formation of a peptide bond), while the C-terminal end has a free carboxyl group.
2. A peptide is composed of two or more amino acids. Amino acids are the building blocks of peptides.
3. amide bond

Exercises

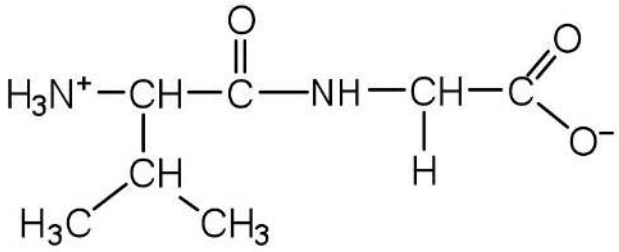
1. Draw the structure for each peptide.
   a. gly-val
   b. val-gly
2. Draw the structure for cys-val-ala.
3. Identify the C- and N-terminal amino acids for the peptide lys-val-phe-gly-arg-cys.
4. Identify the C- and N-terminal amino acids for the peptide asp-arg-val-tyr-ile-his-pro-phe.

Answers

1. a.



   b.



3. C-terminal amino acid: cys; N-terminal amino acid: lys

18.4: Proteins

Concept Review Exercises

1. What is the predominant attractive force that stabilizes the formation of secondary structure in proteins?
2. Distinguish between the tertiary and quaternary levels of protein structure.
3. Briefly describe four ways in which a protein could be denatured.

Answers

1. hydrogen bonding
2. Tertiary structure refers to the unique three-dimensional shape of a single polypeptide chain, while quaternary structure describes the interaction between multiple polypeptide chains for proteins that have more than one polypeptide chain.
3. (1) heat a protein above 50°C or expose it to UV radiation; (2) add organic solvents, such as ethyl alcohol, to a protein solution; (3) add salts of heavy metal ions, such as mercury, silver, or lead; and (4) add alkaloid reagents such as tannic acid

Exercises

1. Classify each protein as fibrous or globular.
   a. albumin
   b. myosin
   c. fibroin
2. Classify each protein as fibrous or globular.
   a. hemoglobin
   b. keratin
   c. myoglobin
3. What name is given to the predominant secondary structure found in silk?
4. What name is given to the predominant secondary structure found in wool protein?
5. A protein has a tertiary structure formed by interactions between the side chains of the following pairs of amino acids. For each pair, identify the strongest type of interaction between these amino acids.
   a. aspartic acid and lysine
   b. phenylalanine and alanine
   c. serine and lysine
   d. two cysteines
6. A protein has a tertiary structure formed by interactions between the side chains of the following pairs of amino acids. For each pair, identify the strongest type of interaction between these amino acids.
   a. valine and isoleucine
   b. asparagine and serine
   c. glutamic acid and arginine
   d. tryptophan and methionine
7. What level(s) of protein structure is(are) ordinarily disrupted in denaturation? What level(s) is(are) not?
8. Which class of proteins is more easily denatured—fibrous or globular?

Answers

1. a. globular
   b. fibrous
   c. fibrous
3. β-pleated sheet
5. a. ionic bonding
   b. dispersion forces
   c. dispersion forces
   d. disulfide linkage
7. Protein denaturation disrupts the secondary, tertiary, and quaternary levels of structure. Only primary structure is unaffected by denaturation.

18.5: Enzymes

Concept Review Exercise

In the small intestine, sucrose is hydrolyzed to form glucose and fructose in a reaction catalyzed by sucrase.

1. Identify the substrate in this reaction.
2. Name the enzyme.

Answers

1. sucrose
2. sucrase

Exercises

1. Identify the substrate catalyzed by each enzyme.
    a. lactase
    b. cellulase
    c. peptidase
2. Identify the substrate catalyzed by each enzyme.
    a. lipase
    b. amylase
    c. maltase
3. Identify each type of enzyme.
    a. decarboxylase
    b. protease
    c. transaminase
4. Identify each type of enzyme.
    a. dehydrogenase
    b. isomerase
    c. lipase

Answers

1. a. lactose
    b. cellulose
    c. peptides
3. a. lyase
    b. hydrolase
    c. transferase

18.6: Enzyme Action

Concept Review Exercises

1. Distinguish between the lock-and-key model and induced-fit model of enzyme action.
2. Which enzyme has greater specificity—urease or carboxypeptidase? Explain.

Answers

1. The lock-and-key model portrays an enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site. The induced fit model portrays the enzyme structure as more flexible and is complementary to the substrate only after the substrate is bound.
2. Urease has the greater specificity because it can bind only to a single substrate. Carboxypeptidase, on the other hand, can catalyze the removal of nearly any amino acid from the carboxyl end of a peptide or protein.

Exercises

1. What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?
   a. COOH
   b. NH_3^+
   c. OH
   d. $CH(CH_3)_2$
2. What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?
   a. SH
   b. NH_2
   c. C_6H_5
   d. COO^-
3. For each functional group in Exercise 1, suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you identified.
4. For each functional group in Exercise 2, suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you identified.

Answers

1. a. hydrogen bonding
   b. ionic bonding
   c. hydrogen bonding
   d. dispersion forces
3. a. The amino acid has a polar side chain capable of engaging in hydrogen bonding; serine (answers will vary).
   b. The amino acid has a negatively charged side chain; aspartic acid (answers will vary).
   c. The amino acid has a polar side chain capable of engaging in hydrogen bonding; asparagine (answers will vary).
   d. The amino acid has a nonpolar side chain; isoleucine (answers will vary).

18.7: Enzyme Activity

Concept Review Exercises

1. The concentration of substrate X is low. What happens to the rate of the enzyme-catalyzed reaction if the concentration of X is doubled?
2. What effect does an increase in the enzyme concentration have on the rate of an enzyme-catalyzed reaction?

Answers

1. If the concentration of the substrate is low, increasing its concentration will increase the rate of the reaction.
2. An increase in the amount of enzyme will increase the rate of the reaction (provided sufficient substrate is present).

Exercises

1. In non-enzyme-catalyzed reactions, the reaction rate increases as the concentration of reactant is increased. In an enzyme-catalyzed reaction, the reaction rate initially increases as the substrate concentration is increased but then begins to level off, so that the increase in reaction rate becomes less and less as the substrate concentration increases. Explain this difference.
2. Why do enzymes become inactive at very high temperatures?
3. An enzyme has an optimum pH of 7.4. What is most likely to happen to the activity of the enzyme if the pH drops to 6.3? Explain.
4. An enzyme has an optimum pH of 7.2. What is most likely to happen to the activity of the enzyme if the pH increases to 8.5? Explain.

Answers

1. In an enzyme-catalyzed reaction, the substrate binds to the enzyme to form an enzyme-substrate complex. If more substrate is present than enzyme, all of the enzyme binding sites will have substrate bound, and further increases in substrate concentration cannot increase the rate.
3. The activity will decrease; a pH of 6.3 is more acidic than 7.4, and one or more key groups in the active site may bind a hydrogen ion, changing the charge on that group.

18.8: Enzyme Inhibition

Concept Review Exercises

1. What is the difference between a cofactor and a coenzyme?
2. How are vitamins related to coenzymes?

Answers

1. A coenzyme is one type of cofactor. Coenzymes are organic molecules required by some enzymes for activity. A cofactor can be either a coenzyme or an inorganic ion.
2. Coenzymes are synthesized from vitamins.

Exercises

1. Identify each vitamin as water soluble or fat soluble.
   a. vitamin D
   b. vitamin C
   c. vitamin B_{12}
2. Identify each vitamin as water soluble or fat soluble.
   a. niacin
   b. cholecalciferol
   c. biotin
3. What vitamin is needed to form each coenzyme?
   a. pyridoxal phosphate
   b. flavin adenine dinucleotide
   c. coenzyme A
   d. nicotinamide adenine dinucleotide
4. What coenzyme is formed from each vitamin?
   a. niacin
   b. thiamine
   c. cyanocobalamin
   d. pantothenic acid

5. What is the function of each vitamin or coenzyme?
   a. flavin adenine dinucleotide
   b. vitamin A
   c. biotin
6. What is the function of each vitamin or coenzyme?
   a. vitamin K
   b. pyridoxal phosphate
   c. tetrahydrofolate

Answers

1. a. fat soluble
   b. water soluble
   c. water soluble
3. a. vitamin B_6 or pyridoxine
   b. vitamin B_2 or riboflavin
   c. pantothenic acid
   d. vitamin B_3 or niacin
5. a. needed by enzymes that catalyze oxidation-reduction reactions in which two hydrogen atoms are transferred
   b. needed for the formation of vision pigments
   c. needed by enzymes that catalyze carboxylation reactions

18.9: Enzyme Cofactors and Vitamins

Concept Review Exercises

1. What are the characteristics of an irreversible inhibitor?
2. In what ways does a competitive inhibitor differ from a noncompetitive inhibitor?

Answers

1. It inactivates an enzyme by bonding covalently to a particular group at the active site.
2. A competitive inhibitor structurally resembles the substrate for a given enzyme and competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site and can bind to either the free enzyme or the enzyme-substrate complex.

Exercises

1. What amino acid is present in the active site of all enzymes that are irreversibly inhibited by nerve gases such as DIFP?
2. Oxaloacetate (OOCCH2COCOO) inhibits succinate dehydrogenase. Would you expect oxaloacetate to be a competitive or noncompetitive inhibitor? Explain.

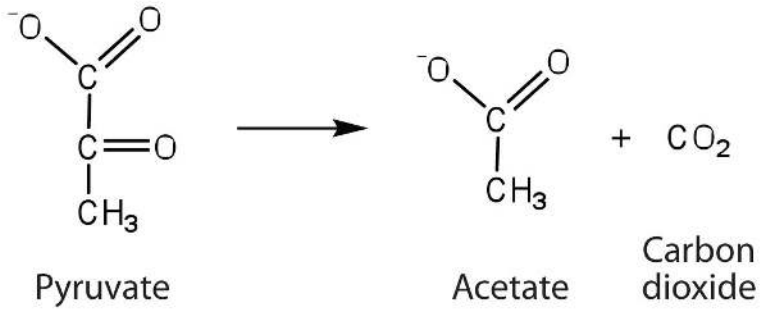
Answer

1. serine

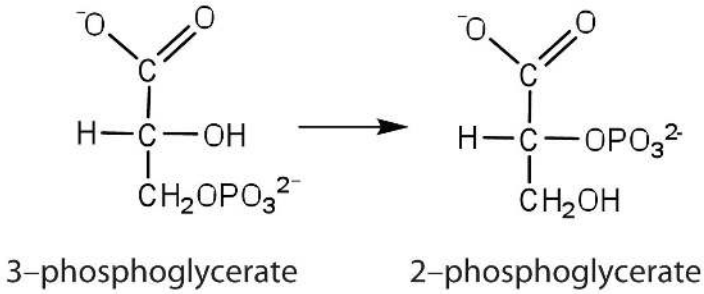
Additional Exercises

1. Draw the structure of the amino acid γ-aminobutyric acid (GABA). Would you expect to find GABA in the amino acid sequence of a protein? Explain.
2. Draw the structure of the amino acid homocysteine (R group = CH_2CH_2SH). Would you expect to find homocysteine in the amino acid sequence of a protein? Justify your answer.
3. Write equations to show how leucine can act as a buffer (that is, how it can neutralize added acid or base).

4. Write equations to show how isoleucine can act as a buffer (that is, how it can neutralize added acid or base).
5. Glutathione (γ-glutamylcysteinylglycine) is a tripeptide found in all cells of higher animals. It contains glutamic acid joined in an unusual peptide linkage involving the carboxyl group of the R group (known as γ-carboxyl group), rather than the usual carboxyl group (the α-carboxyl group). Draw the structure of glutathione.
6. Draw the structure of the pentapeptide whose sequence is arg-his-gly-leu-asp. Identify which of the amino acids have R groups that can donate or gain hydrogen ions.
7. Bradykinin is a peptide hormone composed of nine amino acids that lowers blood pressure. Its primary structure is arg-pro-pro-gly-phe-ser-pro-phe-arg. Would you expect bradykinin to be positively charged, negatively charged, or neutral at a pH of 6.0? Justify your answer.
8. One of the neurotransmitters involved in pain sensation is a peptide called substance P, which is composed of 11 amino acids and is released by nerve-cell terminals in response to pain. Its primary structure is arg-pro-lys-pro-gln-gln-phe-phe-gly-leu-met. Would you expect this peptide to be positively charged, negatively charged, or neutral at a pH of 6.0? Justify your answer.
9. Carbohydrates are incorporated into *glycoproteins*. Would you expect the incorporation of sugar units to increase or decrease the solubility of a protein? Justify your answer.
10. Some proteins have phosphate groups attached through an ester linkage to the OH groups of serine, threonine, or tyrosine residues to form *phosphoproteins*. Would you expect the incorporation of a phosphate group to increase or decrease the solubility of a protein? Justify your answer.
11. Refer to Table 18.5 and determine how each enzyme would be classified.
    a. the enzyme that catalyzes the conversion of ethanol to acetaldehyde
    b. the enzyme that catalyzes the breakdown of glucose 6-phosphate to glucose and inorganic phosphate ion (water is also a reactant in this reaction)
12. Refer to Table 18.5 and determine how each enzyme would be classified.
    a. the enzyme that catalyzes the removal of a carboxyl group from pyruvate to form acetate

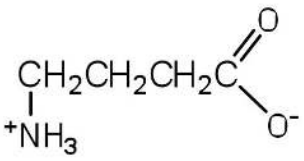


    b. the enzyme that catalyzes the rearrangement of 3-phosphoglycerate to form 2-phosphoglycerate



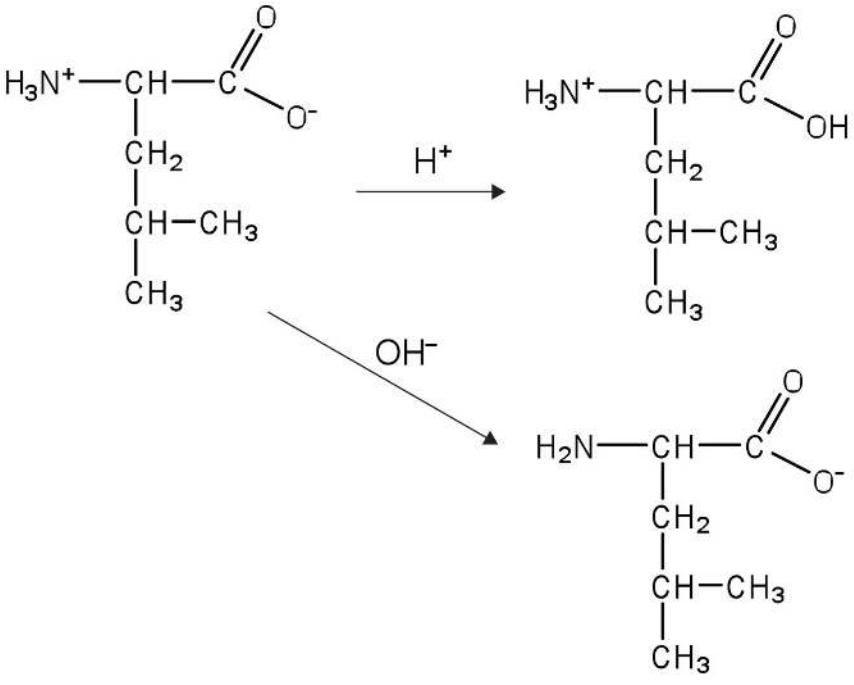
13. The enzyme lysozyme has an aspartic acid residue in the active site. In acidic solution, the enzyme is inactive, but activity increases as the pH rises to around 6. Explain why.
14. The enzyme lysozyme has a glutamic acid residue in the active site. At neutral pH (6–7), the enzyme is active, but activity decreases as the pH rises. Explain why.
15. The activity of a purified enzyme is measured at a substrate concentration of 1.0 μM and found to convert 49 μmol of substrate to product in 1 min. The activity is measured at 2.0 μM substrate and found to convert 98 μmol of substrate to product/minute.
    a. When the substrate concentration is 100 μM, how much substrate would you predict is converted to product in 1 min? What if the substrate concentration were increased to 1,000 μM (1.0 mM)?
    b. The activities actually measured are 676 μmol product formed/minute at a substrate concentration of 100 μM and 698 μmol product formed/minute at 1,000 μM (1.0 mM) substrate. Is there any discrepancy between these values and those you predicted in Exercise 15a? Explain.
16. A patient has a fever of 39°C. Would you expect the activity of enzymes in the body to increase or decrease relative to their activity at normal body temperature (37°C)?
17. Using your knowledge of factors that influence enzyme activity, describe what happens when milk is pasteurized.

Answers



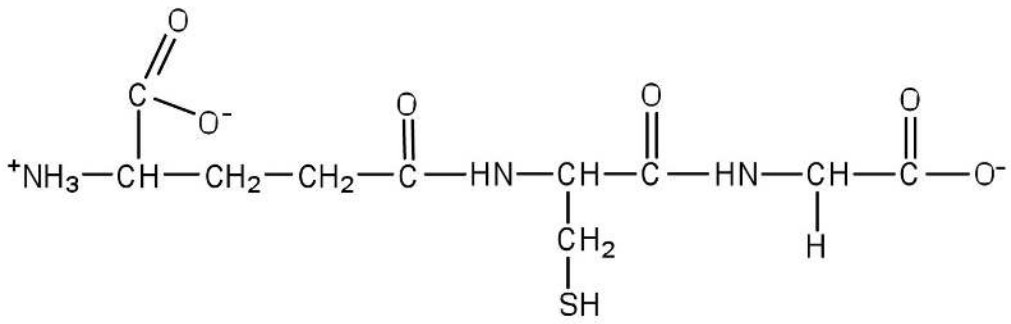
1.

This amino acid would not be found in proteins because it is not an α-amino acid.



3.

5.



7. Bradykinin would be positively charged; all of the amino acids, except for arginine, have R groups that do not become either positively or negatively charged. The two arginines are R groups that are positively charged at neutral pH, so the peptide would have an overall positive charge.

9. Carbohydrates have many OH groups attached, which can engage in hydrogen bonding with water, which increases the solubility of the proteins.

11.

a. oxidoreductase
b. hydrolase

13. The enzyme is active when the carboxyl group in the R group of aspartic acid does not have the hydrogen attached (forming COO^-); the hydrogen is removed when the pH of the solution is around pH 6 or higher.

15.

a. at 100 µM, you would predict that the rate would increase 100 times to 4,900 µmol of substrate to product in 1 min; at 1.0 mM, you would predict an increase to 49,000 µmol of substrate to product in 1 min.
b. There is a great discrepancy between the predicted rates and actual rates; this occurs because the enzyme becomes saturated with substrate, preventing a further increase in the rate of the reaction (the reaction is no longer linear with respect to substrate concentration because it is at very low concentrations).

17. When milk is pasteurized, it is heated to high temperatures. These high temperatures denature the proteins in bacteria, so they cannot carry out needed functions to grow and multiply.

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CHAPTER OVERVIEW

9: Nucleic Acids

The blueprint for the reproduction and the maintenance of each organism is found in the nuclei of its cells, concentrated in elongated, threadlike structures called chromosomes. These complex structures, consisting of DNA and proteins, contain the basic units of heredity, called genes. The number of chromosomes (and genes) varies with each species. Human body cells have 23 pairs of chromosomes having 20,000–40,000 different genes.

Sperm and egg cells contain only a single copy of each chromosome; that is, they contain only one member of each chromosome pair. Thus, in sexual reproduction, the entire complement of chromosomes is achieved only when an egg and sperm combine. A new individual receives half its hereditary material from each parent. Calling the unit of heredity a “gene” merely gives it a name. But what really are genes and how is the information they contain expressed? One definition of a gene is that it is a segment of DNA that constitutes the code for a specific polypeptide. If genes are segments of DNA, we need to learn more about the structure and physiological function of DNA. We begin by looking at the small molecules needed to form DNA and RNA (ribonucleic acid)—the nucleotides.

9.1: Nucleotides
9.2: Nucleic Acid Structure
9.3: DNA Replication and Transcription
9.4: RNA Translation and Protein Synthesis
9.5: Mutations and Genetic Diseases
9.6: Viruses
9.E: Nucleic Acids (Exercises)
9.S: Nucleic Acids (Summary)

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9.1: Nucleotides

Learning Objectives

- Identify the components of nucleosides and nucleotides.
- Identify structural differences between the nitrogenous bases.
- To identify the different molecules that combine to form nucleotides.
- Differentiate between the components in DNA and RNA.
- Demonstrate naming nucleosides and nucleotides.

Nucleic acids are molecules that store and replicate information for cellular growth and reproduction. The two types of nucleic acids are **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. The repeating, or monomer, units that are linked together to form nucleic acids are known as **nucleotides**.

Structural Components of Nucleotides

The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar} \tag{9.1.1}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a **ribonucleotide**, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a **deoxyribonucleotide**, and the nucleic acid is DNA.

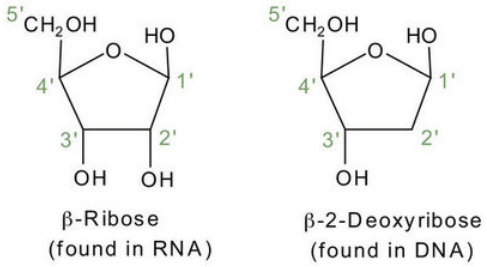


Figure **9.1.1**: Structures of pentose sugar found in nucleic acids: ribose (left) and 2-deoxyribose (right).

The nitrogenous bases found in nucleotides are classified as **pyrimidines** or **purines**. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure **9.1.2**).

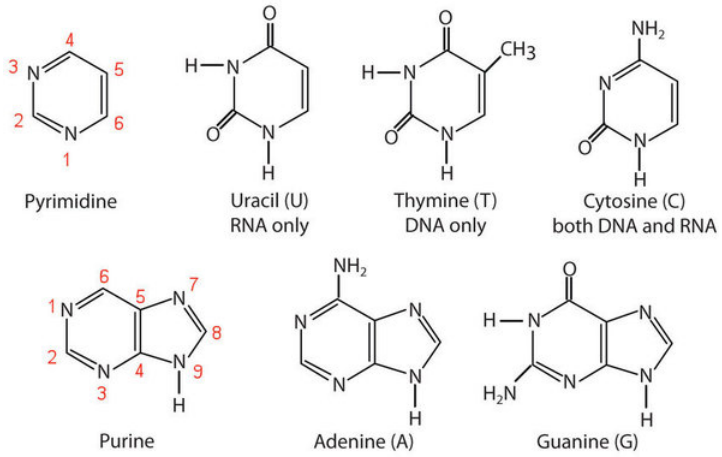


Figure 9.1.2: The Nitrogenous Bases Found in DNA and RNA

The formation of a **glycosidic bond** between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table **9.1.1** summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

Table 9.1.1: Composition of Nucleotides in DNA and RNA

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

Nucleosides

A **nucleoside** is produced during the condensation reaction between the pentose and nitrogenous base.

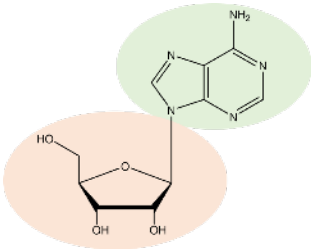


Figure 9.1.3: Structure of a nucleoside formed with the pentose sugar (shaded orange) and adenine base (shaded green).

Nucleosides are named according to the identity of the nitrogenous base, by changing the ending of the name. If the base is a purine, the -ine ending is replaced *-osine*. If the base is a pyrimidine, the -ine or -il ending is replaced with *-idine*. If the nucleotide represents a deoxyribonucleotide, the word deoxy- is added to the front of the name. Using these guidelines, the name of the nucleoside shown in Figure **9.1.3** is deteremined to be adenosine.

Naming Nucleotides

Nucleotides are named by adding monophosphate (sometimes shown as 5'-monophosphate) to the end of the name of the corresponding nucleoside. In addition to the full name, abbreviations can be used to indicate the composition of the nucleotide. If deoxyribose is present, a lower case d is used. The names (full and abbreviated) and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure **9.1.4**.

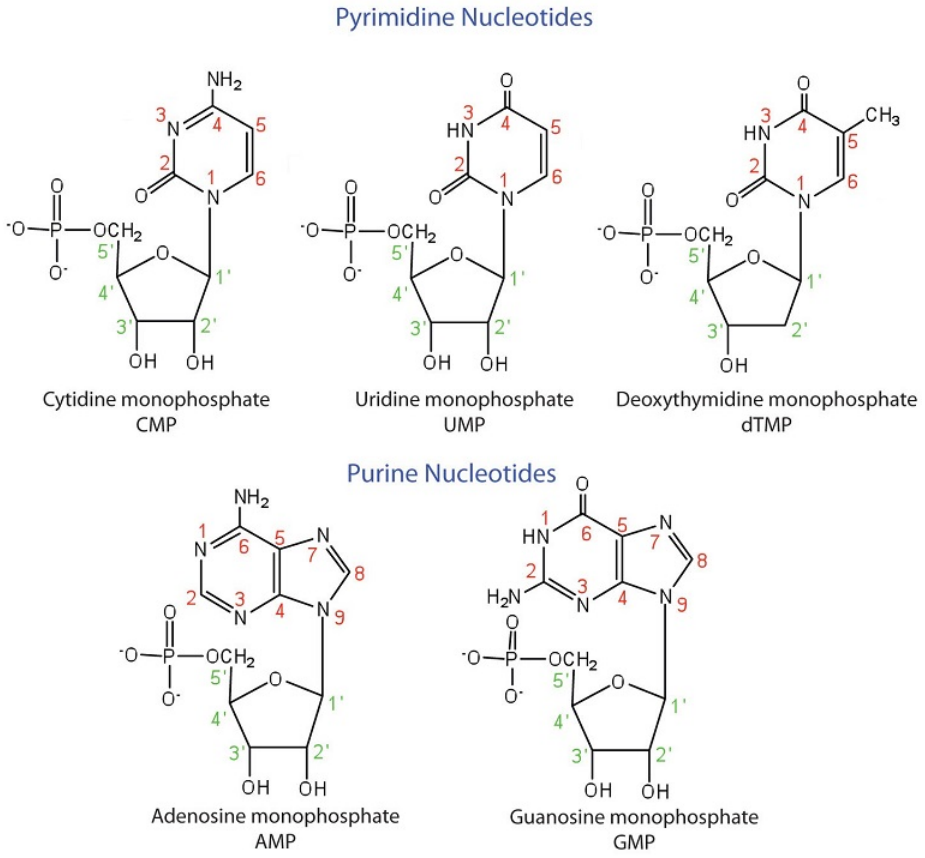


Figure **9.1.4**: The Pyrimidine and Purine Nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure **9.1.5**, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD^+), and coenzyme A, contain adenine nucleotides as structural components.

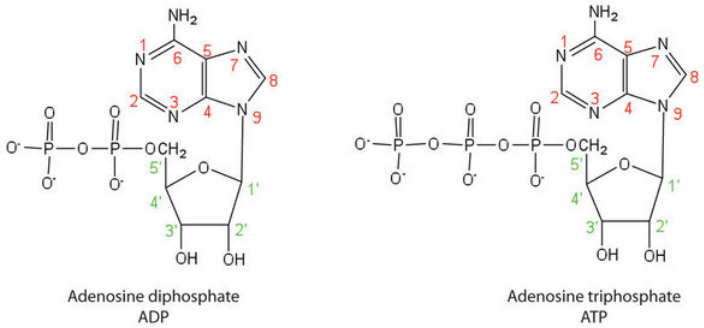


Figure **9.1.5**: Structures of Two Important Adenine-Containing Nucleotides

Example 9.1.1

Classify each compound as a pentose sugar, a purine, or a pyrimidine. Indicate whether it can exist in DNA, RNA, or both.

a. adenine
b. guanine
c. deoxyribose

Solution

a. purine, it can exist in both DNA and RNA
b. purine, it can exist in both DNA and RNA
c. pentose sugar, it can only exist in DNA

Exercise 9.1.1

Classify each compound as a pentose sugar, a purine, or a pyrimidine. Indicate whether it can exist in DNA, RNA, or both.

a. thymine
b. ribose
c. cytosine

Summary

Nucleosides are composed of a pentose sugar (ribose or deoxyribose) and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Nucleosides containing a purine base end with *osine* and those containing a pyrimidine end with *idine*. If the deoxyribose sugar is present, *deoxy* is added to the front of the name.

Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose. Nucleotides are named by adding monophosphate to the end of the nucleoside name.

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9.2: Nucleic Acid Structure

Learning Objectives

- Identify the two types of nucleic acids and the function of each type.
- Describe how nucleotides are linked together to form nucleic acids.
- Describe the secondary structure of DNA and the importance of complementary base pairing.

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. **Deoxyribonucleic acid (DNA)** is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. **Ribonucleic acid (RNA)** is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure **9.2.1**). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> *Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.*

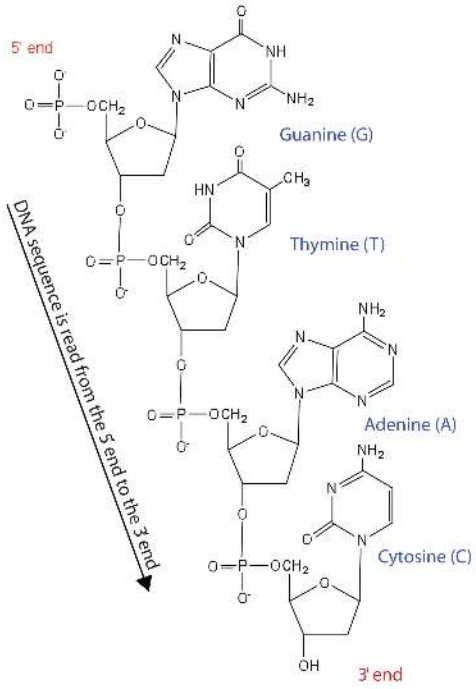


Figure **9.2.1** Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2′, and uracil would replace thymine.

Like proteins, nucleic acids have a **primary structure** that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases, shown in Figure **9.2.1**) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are

deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure **9.2.1** would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the **secondary structure** of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running **antiparallel** to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a **double helix**—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure **9.2.2**).

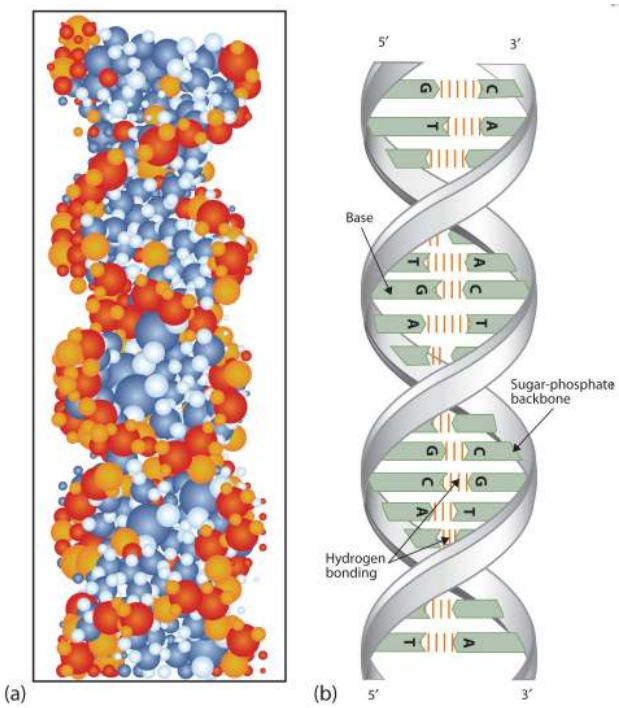


Figure **9.2.2** DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the **pairing of complementary bases**. Figure **9.2.3** shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

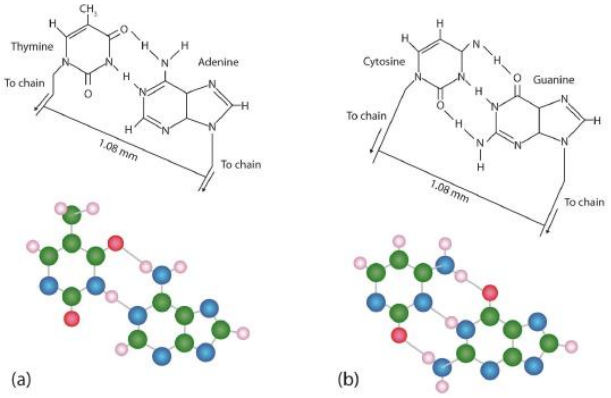


Figure **9.2.3** Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure **9.2.4**. If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure **9.2.3** is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

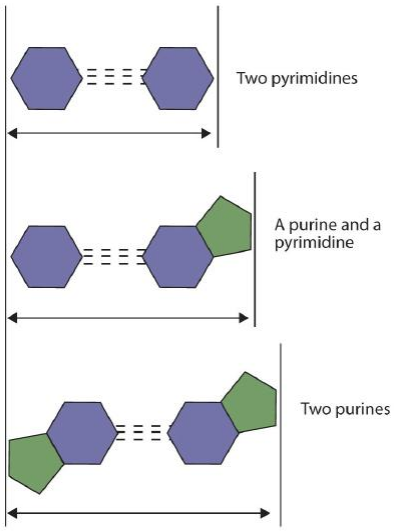
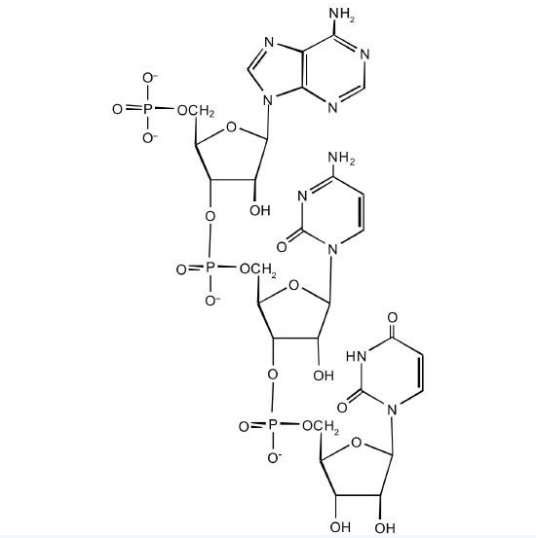


Figure **9.2.4** Difference in Widths of Possible Base Pairs

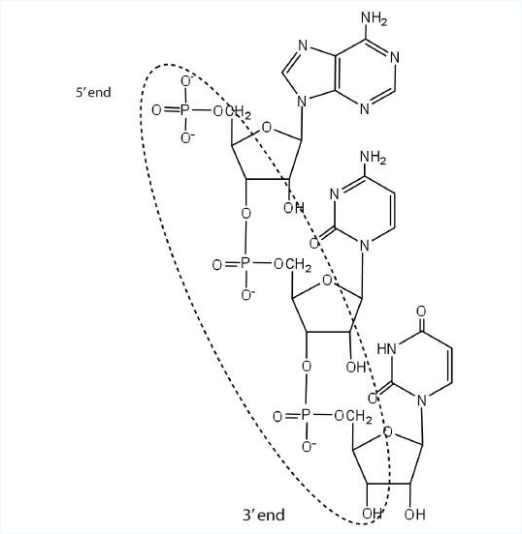
Example 9.2.1

For this short nucleic acid segment,

a. identify the 5′ end and the 3′ end of the molecule.
b. circle the atoms that comprise the backbone of the nucleic acid chain.
c. write the nucleotide sequence of this RNA segment.



Solution

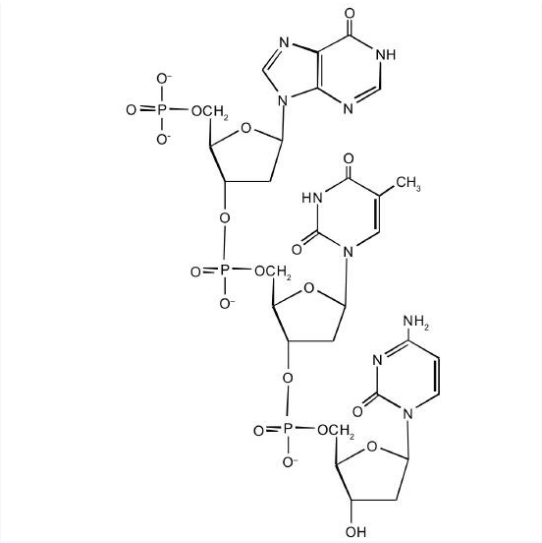


c. ACU

? Exercise 9.2.1

For this short nucleic acid segment,

a. identify the 5′ end and the 3′ end of the molecule.
b. circle the atoms that comprise the backbone of the nucleic acid chain.
c. write the nucleotide sequence of this DNA segment.



Example 9.2.2

Which nitrogenous base in DNA pairs with each nitrogenous base?

a. cytosine
b. adenine
c. guanine
d. thymine

Solution

a. guanine
b. thymine
c. cytosine
d. adenine

Exercise 9.2.2

Which nitrogenous base in RNA pairs with each nitrogenous base?

a. cytosine
b. adenine
c. guanine
d. thymine

Summary

- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleotides are joined together to form nucleic acids through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.

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9.3: DNA Replication and Transcription

Learning Objectives

- Describe how a new copy of DNA is synthesized.
- Describe how RNA is synthesized from DNA.
- Identify the different types of RNA and the function of each type of RNA.

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) ***replication***, in which new copies of DNA are made; (2) ***transcription***, in which a segment of DNA is used to produce RNA; and (3) ***translation***, in which the information in RNA is translated into a protein sequence.

Replication

New cells are continuously forming in the body through the process of cell division. For this to happen, the DNA in a dividing cell must be copied in a process known as **replication**. The complementary base pairing of the double helix provides a ready model for how genetic replication occurs. If the two chains of the double helix are pulled apart, disrupting the hydrogen bonding between base pairs, each chain can act as a *template*, or pattern, for the synthesis of a new complementary DNA chain.

The nucleus contains all the necessary enzymes, proteins, and nucleotides required for this synthesis. A short segment of DNA is "unzipped," so that the two strands in the segment are separated to serve as templates for new DNA. DNA polymerase, an enzyme, recognizes each base in a template strand and matches it to the complementary base in a free nucleotide. The enzyme then catalyzes the formation of an ester bond between the 5′ phosphate group of the nucleotide and the 3′ OH end of the new, growing DNA chain. In this way, each strand of the original DNA molecule is used to produce a duplicate of its former partner (Figure **9.3.1**). Whatever information was encoded in the original DNA double helix is now contained in each replicate helix. When the cell divides, each daughter cell gets one of these replicates and thus all of the information that was originally possessed by the parent cell.

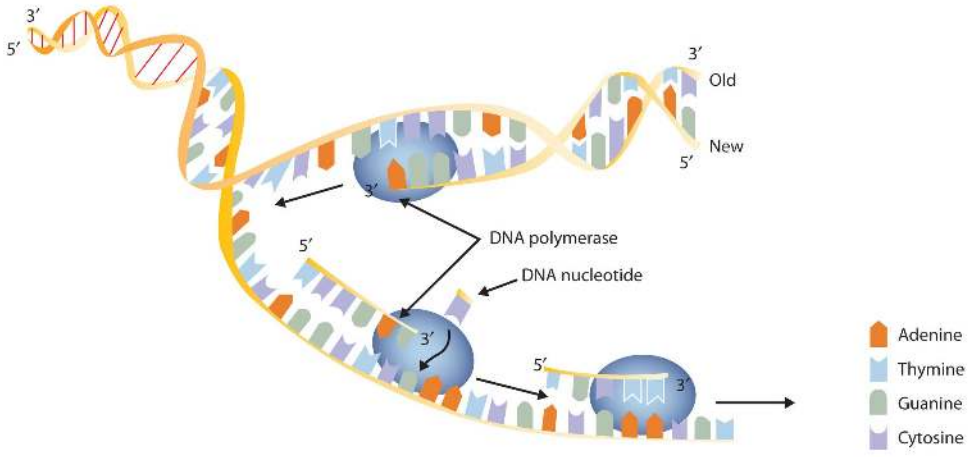


Figure **9.3.1**: A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called *semiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

Example 9.3.1

A segment of one strand from a DNA molecule has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Solution

Knowing that the two strands are antiparallel and that T base pairs with A, while C base pairs with G, the sequence of the complementary strand will be 3′-AGGTACTCAACT-5′ (can also be written as TCAACTCATGGA).

? Exercise 9.3.1

A segment of one strand from a DNA molecule has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

What do we mean when we say information is encoded in the DNA molecule? An organism's DNA can be compared to a book containing directions for assembling a model airplane or for knitting a sweater. Letters of the alphabet are arranged into words, and these words direct the individual to perform certain operations with specific materials. If all the directions are followed correctly, a model airplane or sweater is produced.

In DNA, the particular sequences of nucleotides along the chains encode the directions for building an organism. Just as *saw* means one thing in English and *was* means another, the sequence of bases CGT means one thing, and TGC means something different. Although there are only four letters—the four nucleotides—in the genetic code of DNA, their sequencing along the DNA strands can vary so widely that information storage is essentially unlimited.

Transcription

For the hereditary information in DNA to be useful, it must be "expressed," that is, used to direct the growth and functioning of an organism. The first step in the processes that constitute DNA expression is the synthesis of RNA, by a template mechanism that is in many ways analogous to DNA replication. Because the RNA that is synthesized is a complementary copy of information contained in DNA, RNA synthesis is referred to as **transcription**. There are three key differences between replication and transcription:

1. RNA molecules are much shorter than DNA molecules; only a portion of one DNA strand is copied or transcribed to make an RNA molecule.
2. RNA is built from ribonucleotides rather than deoxyribonucleotides.
3. The newly synthesized RNA strand does not remain associated with the DNA sequence it was transcribed from.

The DNA sequence that is transcribed to make RNA is called the ***template strand***, while the complementary sequence on the other DNA strand is called the ***coding* or *informational strand***. To initiate RNA synthesis, the two DNA strands unwind at specific sites along the DNA molecule. Ribonucleotides are attracted to the uncoiling region of the DNA molecule, beginning at the 3′ end of the template strand, according to the rules of base pairing. Thymine in DNA calls for adenine in RNA, cytosine specifies guanine, guanine calls for cytosine, and adenine requires uracil. RNA polymerase—an enzyme—binds the complementary ribonucleotide and catalyzes the formation of the ester linkage between ribonucleotides, a reaction very similar to that catalyzed by DNA polymerase (Figure **9.3.2**). Synthesis of the RNA strand takes place in the 5′ to 3′ direction, antiparallel to the template strand. Only a short segment of the RNA molecule is hydrogen-bonded to the template strand at any time during transcription. When transcription is completed, the RNA is released, and the DNA helix reforms. The nucleotide sequence of the RNA strand formed during transcription is identical to that of the corresponding coding strand of the DNA, except that U replaces T.

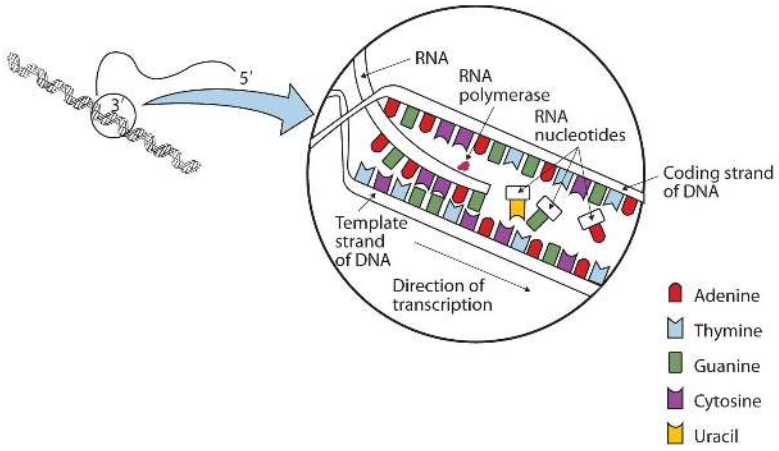


Figure 9.3.2: A Schematic Diagram of RNA Transcription from a DNA Template. The representation of RNA polymerase is proportionately much smaller than the actual molecule, which encompasses about 50 nucleotides at a time.

Example 9.3.2

A portion of the template strand of a gene has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the RNA that is formed from this template?

Solution

Four things must be remembered in answering this question: (1) the DNA strand and the RNA strand being synthesized are antiparallel; (2) RNA is synthesized in a 5′ to 3′ direction, so transcription begins at the 3′ end of the template strand; (3) ribonucleotides are used in place of deoxyribonucleotides; and (4) thymine (T) base pairs with adenine (A), A base pairs with uracil (U; in RNA), and cytosine (C) base pairs with guanine (G). The sequence is determined to be 3′-AGGUACUCAACU-5′ (can also be written as 5′-UCAACUCAUGGA-3′).

Exercise 9.3.2

A portion of the template strand of a gene has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the RNA that is formed from this template?

Three types of RNA are formed during transcription: ***messenger RNA* (mRNA)**, ***ribosomal RNA* (rRNA)**, and ***transfer RNA* (tRNA)**. These three types of RNA differ in function, size, and percentage of the total cell RNA (Table 9.3.1). mRNA makes up only a small percent of the total amount of RNA within the cell, primarily because each molecule of mRNA exists for a relatively short time; it is continuously being degraded and resynthesized. The molecular dimensions of the mRNA molecule vary according to the amount of genetic information a given molecule contains. After transcription, which takes place in the nucleus, the mRNA passes into the cytoplasm, carrying the genetic message from DNA to the ribosomes, the sites of protein synthesis. Elsewhere, we shall see how mRNA directly determines the sequence of amino acids during protein synthesis.

Table 9.3.1: Properties of Cellular RNA in Escherichia coli

Type	Function	Approximate Number of Nucleotides	Percentage of Total Cell RNA
mRNA	codes for proteins	100–6,000	~3
rRNA	component of ribosomes	120–2900	83
tRNA	adapter molecule that brings the amino acid to the ribosome	75–90	14

Ribosomes are cellular substructures where proteins are synthesized. They contain about 65% rRNA and 35% protein, held together by numerous noncovalent interactions, such as hydrogen bonding, in an overall structure consisting of two globular particles of unequal size.

Molecules of tRNA, which bring amino acids (one at a time) to the ribosomes for the construction of proteins, differ from one another in the kinds of amino acid each is specifically designed to carry. A set of three nucleotides, known as a codon, on the mRNA determines which kind of tRNA will add its amino acid to the growing chain. Each of the 20 amino acids found in proteins has at least one corresponding kind of tRNA, and most amino acids have more than one.

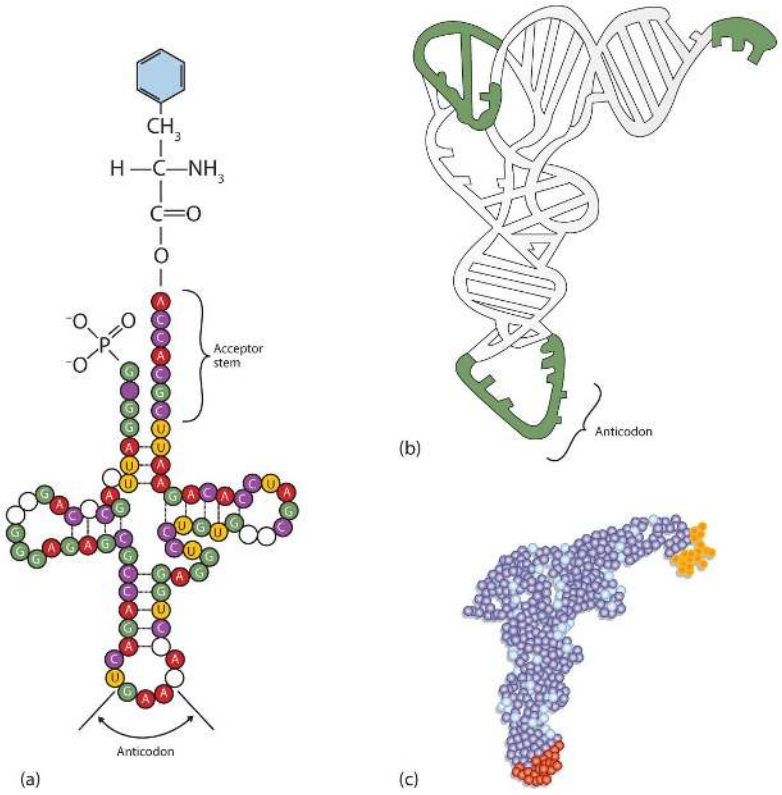


Figure **9.3.3**: Transfer RNA. (a) In the two-dimensional structure of a yeast tRNA molecule for phenylalanine, the amino acid binds to the acceptor stem located at the 3′ end of the tRNA primary sequence. (The nucleotides that are not specifically identified here are slightly altered analogs of the four common ribonucleotides A, U, C, and G.) (b) In the three-dimensional structure of yeast phenylalanine tRNA, note that the anticodon loop is at the bottom and the acceptor stem is at the top right. (c) This shows a space-filling model of the tRNA.

The two-dimensional structure of a tRNA molecule has three distinctive loops, reminiscent of a cloverleaf (Figure **9.3.3**). On one loop is a sequence of three nucleotides that varies for each kind of tRNA. This triplet, called the anticodon, is complementary to and pairs with the codon on the mRNA. At the opposite end of the molecule is the acceptor stem, where the amino acid is attached.

Example 9.3.3

A portion of the coding strand for a given gene has the sequence 5′-ATGAGCGACTTTGCGGGATTA-3′.

a. What is the sequence of complementary template strand?

b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?

Solution

a. 3′-TACTCGCTGAAACGCCCTAAT-5′

b. 5′-AUGAGCGACUUUGCGGGAUUA-3′

? Exercise 9.3.3

A portion of the coding strand for a given gene has the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′.

a. What is the sequence of complementary template strand?
b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?

Summary

- In DNA replication, each strand of the original DNA serves as a template for the synthesis of a complementary strand.
- DNA polymerase is the primary enzyme needed for replication.
- In transcription, a segment of DNA serves as a template for the synthesis of an RNA sequence.
- RNA polymerase is the primary enzyme needed for transcription.
- Three types of RNA are formed during transcription: mRNA, rRNA, and tRNA.

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9.4: RNA Translation and Protein Synthesis

Learning Objectives

- Describe the characteristics of the genetic code.
- Describe how a protein is synthesized from mRNA.

One of the definitions of a gene is as follows: a segment of deoxyribonucleic acid (DNA) carrying the code for a specific polypeptide. Each molecule of messenger RNA (mRNA) is a transcribed copy of a gene that is used by a cell for synthesizing a polypeptide chain. If a protein contains two or more different polypeptide chains, each chain is coded by a different gene. We turn now to the question of how the sequence of nucleotides in a molecule of ribonucleic acid (RNA) is translated into an amino acid sequence.

How can a molecule containing just 4 different nucleotides specify the sequence of the 20 amino acids that occur in proteins? If each nucleotide coded for 1 amino acid, then obviously the nucleic acids could code for only 4 amino acids. What if amino acids were coded for by groups of 2 nucleotides? There are 4^2, or 16, different combinations of 2 nucleotides (AA, AU, AC, AG, UU, and so on). Such a code is more extensive but still not adequate to code for 20 amino acids. However, if the nucleotides are arranged in groups of 3, the number of different possible combinations is 4^3, or 64. Here we have a code that is extensive enough to direct the synthesis of the primary structure of a protein molecule.



***Video**: NDSU Virtual Cell Animations project animation "Translation". For more information, see http://vcell.ndsu.nodak.edu/animations*

The **genetic code** can therefore be described as the identification of each group of three nucleotides and its particular amino acid. The sequence of these triplet groups in the mRNA dictates the sequence of the amino acids in the protein. Each individual three-nucleotide coding unit, as we have seen, is called a **codon**.

Protein synthesis is accomplished by orderly interactions between mRNA and the other ribonucleic acids (transfer RNA [tRNA] and ribosomal RNA [rRNA]), the ribosome, and more than 100 enzymes. The mRNA formed in the nucleus during transcription is transported across the nuclear membrane into the cytoplasm to the ribosomes—carrying with it the genetic instructions. The process in which the information encoded in the mRNA is used to direct the sequencing of amino acids and thus ultimately to synthesize a protein is referred to as **translation**.

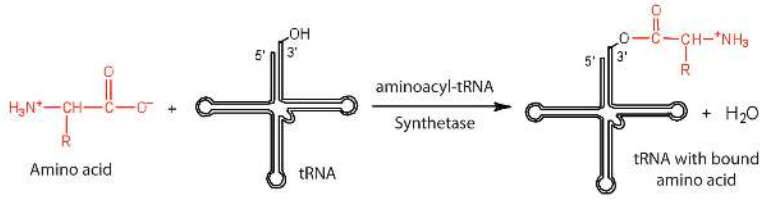


Figure 9.4.1: Binding of an Amino Acid to Its tRNA

Before an amino acid can be incorporated into a polypeptide chain, it must be attached to its unique tRNA. This crucial process requires an enzyme known as aminoacyl-tRNA synthetase (Figure 9.4.1). There is a specific aminoacyl-tRNA synthetase for each amino acid. This high degree of specificity is vital to the incorporation of the correct amino acid into a protein. After the amino acid molecule has been bound to its tRNA carrier, protein synthesis can take place. The tRNA, which contains an **anticodon** located at end of the molecule that is complementary to the codon on the mRNA, transfers the mRNA sequence into an amino acid. Figure 9.4.2 depicts a schematic stepwise representation of this all-important process.

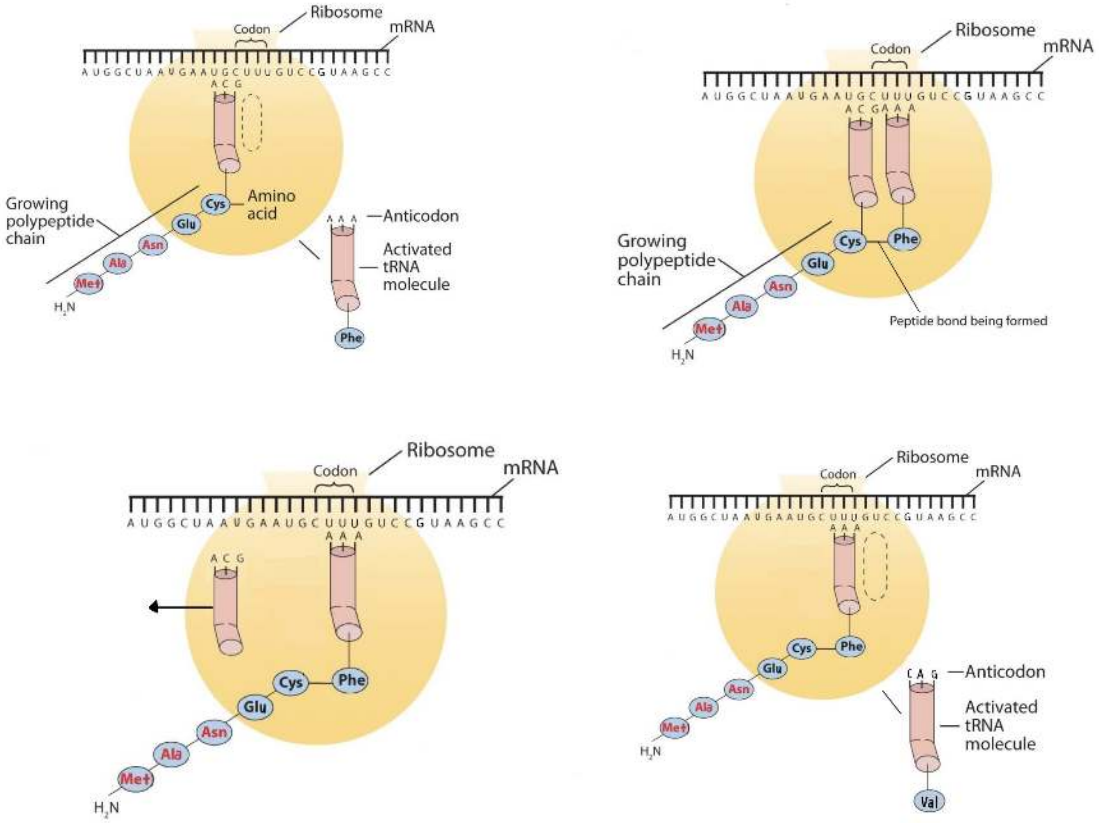


Figure 9.4.2: The Elongation Steps in Protein Synthesis

Early experimenters were faced with the task of determining which of the 64 possible codons stood for each of the 20 amino acids. The cracking of the genetic code was the joint accomplishment of several well-known geneticists—notably Har Khorana, Marshall Nirenberg, Philip Leder, and Severo Ochoa—from 1961 to 1964. The genetic dictionary they compiled, summarized in Figure 9.4.3, shows that 61 codons code for amino acids, and 3 codons serve as signals for the termination of polypeptide synthesis (much like the period at the end of a sentence). Notice that only methionine (AUG) and tryptophan (UGG) have single codons. All other amino acids have two or more codons.

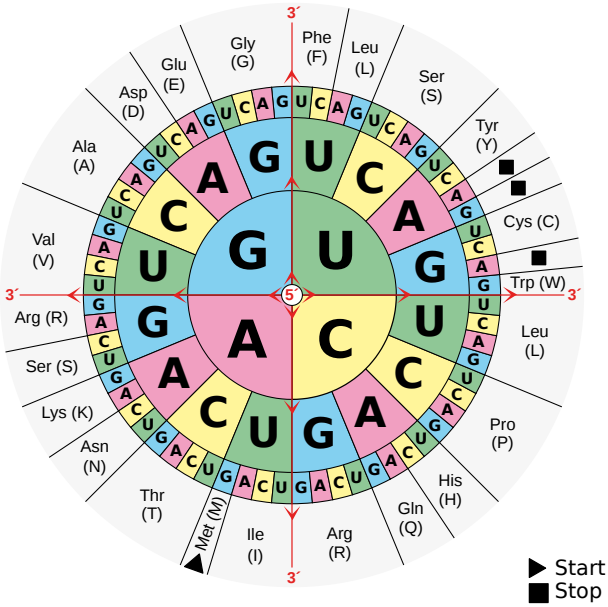


Figure **9.4.3**: The Genetic Code. Scott Henry Maxwell, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons

Example 9.4.1

A portion of an mRNA molecule has the sequence 5′-AUGCCACGAGUUGAC-3′. What amino acid sequence does this code for?

Solution

Use Figure **9.4.3** to determine what amino acid each set of three nucleotides (codon) codes for. Remember that the sequence is read starting from the 5′ end and that a protein is synthesized starting with the N-terminal amino acid. The sequence 5′-AUGCCACGAGUUGAC-3′ codes for met-pro-arg-val-asp.

Exercise 9.4.1

A portion of an RNA molecule has the sequence 5′-AUGCUGAAUUGCGUAGGA-3′. What amino acid sequence does this code for?

Further experimentation threw much light on the nature of the genetic code, as follows:

1. The code is virtually universal; animal, plant, and bacterial cells use the same codons to specify each amino acid (with a few exceptions).
2. The code is “degenerate”; in all but two cases (methionine and tryptophan), more than one triplet codes for a given amino acid.
3. The first two bases of each codon are most significant; the third base often varies. This suggests that a change in the third base by a mutation may still permit the correct incorporation of a given amino acid into a protein. The third base is sometimes called the “wobble” base.
4. The code is continuous and nonoverlapping; there are *no* nucleotides between codons, and adjacent codons do not overlap.
5. The three termination codons are read by special proteins called release factors, which signal the end of the translation process.
6. The codon AUG codes for methionine and is also the initiation codon. Thus methionine is the first amino acid in each newly synthesized polypeptide. This first amino acid is usually removed enzymatically before the polypeptide chain is completed; the vast majority of polypeptides do not begin with methionine.

Example 9.4.1

Write the anticodon on tRNA that would pair with each mRNA codon.

a. 5′-UUU-3′
b. 5′-CAU-3′
c. 5′-AGC-3′
d. 5′-CCG-3′

Solution

a. 3′-AAA-5′
b. 3′-GUA-5′
c. 3′-UCG-5′
d. 3′-GGC-5′

Exercise 9.4.1

Write the codon on mRNA that would pair with each tRNA anticodon.

a. 5′-UUG-3′
b. 5′-GAA-3′
c. 5′-UCC-3′
d. 5′-CAC-3′

Summary

In translation, the information in mRNA directs the order of amino acids in protein synthesis. A set of three nucleotides (codon) codes for a specific amino acid.

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9.5: Mutations and Genetic Diseases

Learning Objectives

- To describe the causes of genetic mutations and how they lead to genetic diseases.

We have seen that the sequence of nucleotides in a cell's deoxyribonucleic acid (DNA) is what ultimately determines the sequence of amino acids in proteins made by the cell and thus is critical for the proper functioning of the cell. On rare occasions, however, the nucleotide sequence in DNA may be modified either spontaneously (by errors during replication, occurring approximately once for every 10 billion nucleotides) or from exposure to heat, radiation, or certain chemicals. Any chemical or physical change that alters the nucleotide sequence in DNA is called a mutation. When a mutation occurs in an egg or sperm cell that then produces a living organism, it will be inherited by all the offspring of that organism.

Common types of mutations include **substitution** (a different nucleotide is substituted), **insertion** (the addition of a new nucleotide), and **deletion** (the loss of a nucleotide). These changes within DNA are called point mutations because only one nucleotide is substituted, added, or deleted (Figure 9.5.1). Because an insertion or deletion results in a **frame-shift** that changes the reading of subsequent codons and, therefore, alters the entire amino acid sequence that follows the mutation, insertions and deletions are usually more harmful than a substitution in which only a single amino acid is altered.

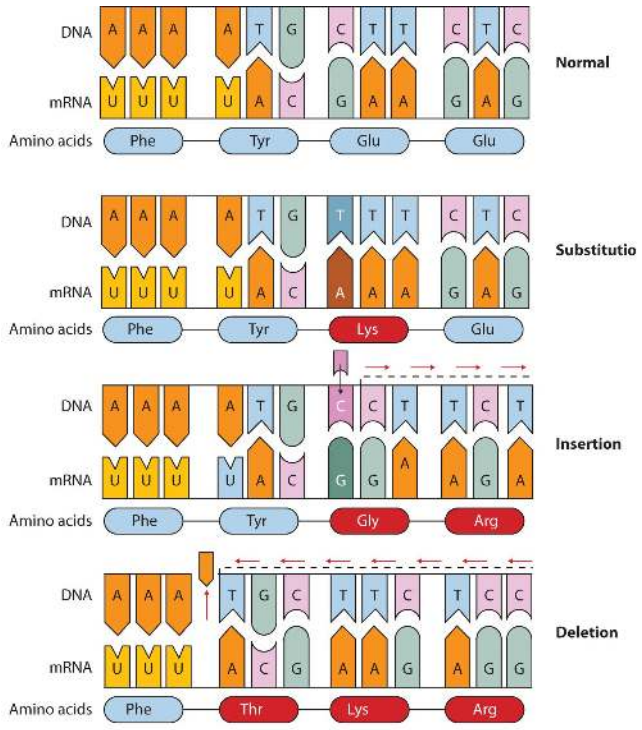


Figure 9.5.1: Three Types of Point Mutations

The chemical or physical agents that cause mutations are called **mutagens**. Examples of physical mutagens are ultraviolet (UV) and gamma radiation. Radiation exerts its mutagenic effect either directly or by creating free radicals that in turn have mutagenic effects. Radiation and free radicals can lead to the formation of bonds between nitrogenous bases in DNA. For example, exposure to UV light can result in the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer (Figure 9.5.2). If not repaired, the dimer prevents the formation of the double helix at the point where it occurs. The genetic disease *xeroderma pigmentosum* is caused by a lack of the enzyme that cuts out the thymine dimers in damaged DNA. Individuals affected by this condition are abnormally sensitive to light and are more prone to skin cancer than normal individuals.

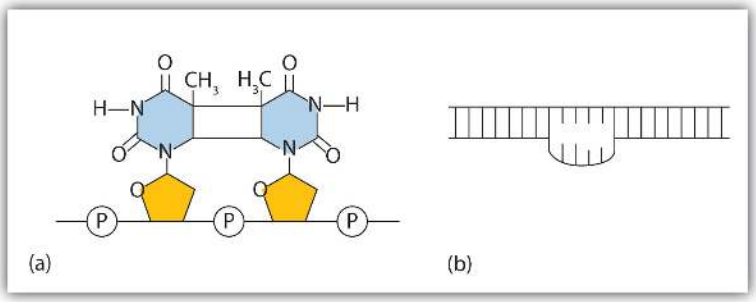


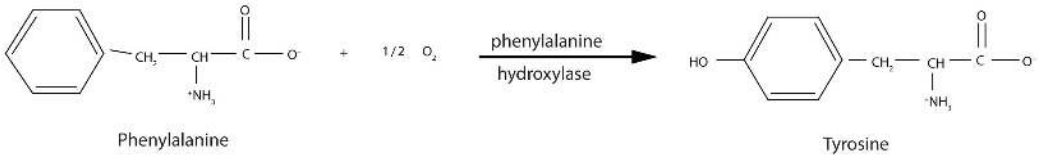
Figure **9.5.2**: An Example of Radiation Damage to DNA. (a) The thymine dimer is formed by the action of UV light. (b) When a defect in the double strand is produced by the thymine dimer, this defect temporarily stops DNA replication, but the dimer can be removed, and the region can be repaired by an enzyme repair system.

Sometimes gene mutations are beneficial, but most of them are detrimental. For example, if a point mutation occurs at a crucial position in a DNA sequence, the affected protein will lack biological activity, perhaps resulting in the death of a cell. In such cases the altered DNA sequence is lost and will not be copied into daughter cells. Nonlethal mutations in an egg or sperm cell may lead to metabolic abnormalities or hereditary diseases. Such diseases are called *inborn errors of metabolism* or genetic diseases. A partial listing of genetic diseases is presented in Figure **9.5.1**, and two specific diseases are discussed in the following sections. In most cases, the defective gene results in a failure to synthesize a particular enzyme.

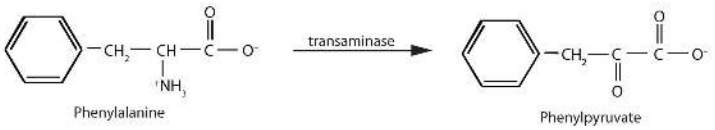
Figure **9.5.1**: Some Representative Genetic Diseases in Humans and the Protein or Enzyme Responsible

Disease	Responsible Protein or Enzyme
alkaptonuria	homogentisic acid oxidase
galactosemia	galactose 1-phosphate uridyl transferase, galactokinase, or UDP galactose epimerase
Gaucher disease	glucocerebrosidase
gout and Lesch-Nyhan syndrome	hypoxanthine-guanine phosphoribosyl transferase
hemophilia	antihemophilic factor (factor VIII) or Christmas factor (factor IX)
homocystinuria	cystathionine synthetase
maple syrup urine disease	branched chain α-keto acid dehydrogenase complex
McArdle syndrome	muscle phosphorylase
Niemann-Pick disease	sphingomyelinase
phenylketonuria (PKU)	phenylalanine hydroxylase
sickle cell anemia	hemoglobin
Tay-Sachs disease	hexosaminidase A
tyrosinemia	fumarylacetoacetate hydrolase or tyrosine aminotransferase
von Gierke disease	glucose 6-phosphatase
Wilson disease	Wilson disease protein

PKU results from the absence of the enzyme phenylalanine hydroxylase. Without this enzyme, a person cannot convert phenylalanine to tyrosine, which is the precursor of the neurotransmitters dopamine and norepinephrine as well as the skin pigment melanin.



When this reaction cannot occur, phenylalanine accumulates and is then converted to higher than normal quantities of phenylpyruvate. The disease acquired its name from the high levels of phenylpyruvate (a phenyl ketone) in urine. Excessive amounts of phenylpyruvate impair normal brain development, which causes severe mental retardation.



PKU may be diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites. Medical authorities recommend testing every newborn's blood for phenylalanine within 24 h to 3 weeks after birth. If the condition is detected, mental retardation can be prevented by immediately placing the infant on a diet containing little or no phenylalanine. Because phenylalanine is plentiful in naturally produced proteins, the low-phenylalanine diet depends on a synthetic protein substitute plus very small measured amounts of naturally produced foods. Before dietary treatment was introduced in the early 1960s, severe mental retardation was a common outcome for children with PKU. Prior to the 1960s, 85% of patients with PKU had an intelligence quotient (IQ) less than 40, and 37% had IQ scores below 10. Since the introduction of dietary treatments, however, over 95% of children with PKU have developed normal or near-normal intelligence. The incidence of PKU in newborns is about 1 in 12,000 in North America.

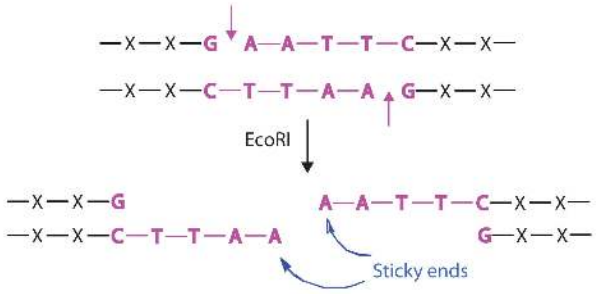
> *Every state in the United States has mandated that screening for PKU be provided to all newborns.*

Several genetic diseases are collectively categorized as *lipid-storage diseases*. Lipids are constantly being synthesized and broken down in the body, so if the enzymes that catalyze lipid degradation are missing, the lipids tend to accumulate and cause a variety of medical problems. When a genetic mutation occurs in the gene for the enzyme hexosaminidase A, for example, gangliosides cannot be degraded but accumulate in brain tissue, causing the ganglion cells of the brain to become greatly enlarged and nonfunctional. This genetic disease, known as *Tay-Sachs disease*, leads to a regression in development, dementia, paralysis, and blindness, with death usually occurring before the age of three. There is currently no treatment, but Tay-Sachs disease can be diagnosed in a fetus by assaying the amniotic fluid (amniocentesis) for hexosaminidase A. A blood test can identify Tay-Sachs carriers—people who inherit a defective gene from only one rather than both parents—because they produce only half the normal amount of hexosaminidase A, although they do not exhibit symptoms of the disease.

Looking Closer: Recombinant DNA Technology

More than 3,000 human diseases have been shown to have a genetic component, caused or in some way modulated by the person's genetic composition. Moreover, in the last decade or so, researchers have succeeded in identifying many of the genes and even mutations that are responsible for specific genetic diseases. Now scientists have found ways of identifying and isolating genes that have specific biological functions and placing those genes in another organism, such as a bacterium, which can be easily grown in culture. With these techniques, known as ***recombinant DNA technology***, the ability to cure many serious genetic diseases appears to be within our grasp.

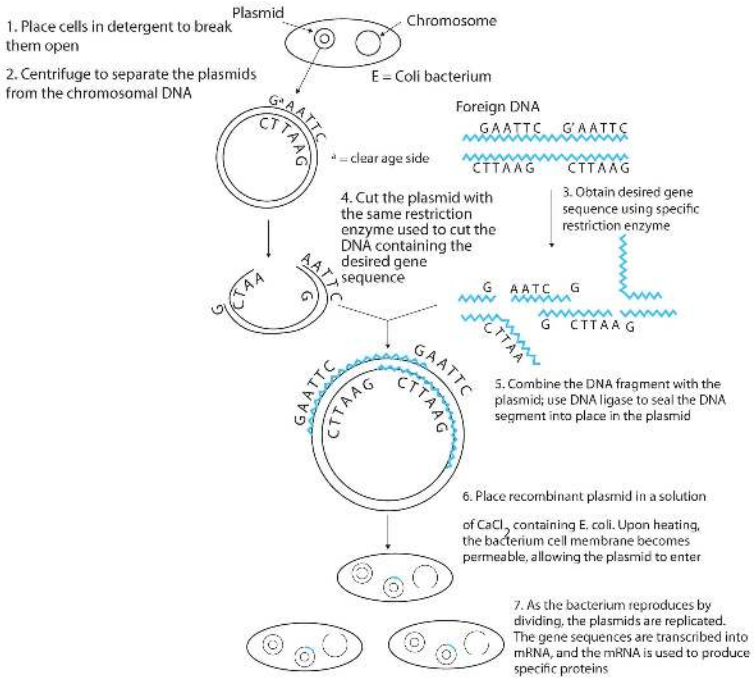
Isolating the specific gene or genes that cause a particular genetic disease is a monumental task. One reason for the difficulty is the enormous amount of a cell's DNA, only a minute portion of which contains the gene sequence. Thus, the first task is to obtain smaller pieces of DNA that can be more easily handled. Fortunately, researchers are able to use *restriction enzymes* (also known as restriction endonucleases), discovered in 1970, which are enzymes that cut DNA at specific, known nucleotide sequences, yielding DNA fragments of shorter length. For example, the restriction enzyme *EcoRI* recognizes the nucleotide sequence shown here and cuts both DNA strands as indicated:



Once a DNA strand has been fragmented, it must be cloned; that is, multiple identical copies of each DNA fragment are produced to make sure there are sufficient amounts of each to detect and manipulate in the laboratory. Cloning is accomplished by inserting the individual DNA fragments into phages (bacterial viruses) that can enter bacterial cells and be replicated. When a bacterial cell infected by the modified phage is placed in an appropriate culture medium, it forms a colony of cells, all containing copies of the original DNA fragment. This technique is used to produce many bacterial colonies, each containing a different DNA fragment. The result is a *DNA library*, a collection of bacterial colonies that together contain the entire genome of a particular organism.

The next task is to screen the DNA library to determine which bacterial colony (or colonies) has incorporated the DNA fragment containing the desired gene. A short piece of DNA, known as a ***hybridization probe***, which has a nucleotide sequence complementary to a known sequence in the gene, is synthesized, and a radioactive phosphate group is added to it as a "tag." You might be wondering how researchers are able to prepare such a probe if the gene has not yet been isolated. One way is to use a segment of the desired gene isolated from another organism. An alternative method depends on knowing all or part of the amino acid sequence of the protein produced by the gene of interest: the amino acid sequence is used to produce an approximate genetic code for the gene, and this nucleotide sequence is then produced synthetically. (The amino acid sequence used is carefully chosen to include, if possible, many amino acids such as methionine and tryptophan, which have only a single codon each.)

After a probe identifies a colony containing the desired gene, the DNA fragment is clipped out, again using restriction enzymes, and spliced into another replicating entity, usually a plasmid. ***Plasmids*** are tiny mini-chromosomes found in many bacteria, such as *Escherichia coli* (*E. coli*). A recombined plasmid would then be inserted into the host organism (usually the bacterium *E. coli*), where it would go to work to produce the desired protein.



Proponents of recombinant DNA research are excited about its great potential benefits. An example is the production of human growth hormone, which is used to treat children who fail to grow properly. Formerly, human growth hormone was available only in tiny amounts obtained from cadavers. Now it is readily available through recombinant DNA technology. Another gene that has been cloned is the gene for epidermal growth factor, which stimulates the growth of skin cells and can be used to speed the healing of burns and other skin wounds. Recombinant techniques are also a powerful research tool, providing enormous aid to scientists as they map and sequence genes and determine the functions of different segments of an organism's DNA.

In addition to advancements in the ongoing treatment of genetic diseases, recombinant DNA technology may actually lead to cures. When appropriate genes are successfully inserted into *E. coli*, the bacteria can become miniature pharmaceutical factories, producing great quantities of insulin for people with diabetes, clotting factor for people with hemophilia, missing enzymes, hormones, vitamins, antibodies, vaccines, and so on. Recent accomplishments include the production in *E. coli* of recombinant DNA molecules containing synthetic genes for tissue plasminogen activator, a clot-dissolving enzyme that can rescue heart attack victims, as well as the production of vaccines against hepatitis B (humans) and hoof-and-mouth disease (cattle).

Scientists have used other bacteria besides *E. coli* in gene-splicing experiments and also yeast and fungi. Plant molecular biologists use a bacterial plasmid to introduce genes for several foreign proteins (including animal proteins) into plants. The bacterium is *Agrobacterium tumefaciens*, which can cause tumors in many plants, but which can be treated so that its tumor-causing ability is eliminated. One practical application of its plasmids would be to enhance a plant's nutritional value by transferring into it the gene necessary for the synthesis of an amino acid in which the plant is normally deficient (for example, transferring the gene for methionine synthesis into pinto beans, which normally do not synthesize high levels of methionine).

Restriction enzymes have been isolated from a number of bacteria and are named after the bacterium of origin. *EcoRI* is a restriction enzyme obtained from the R strain of *E. coli*. The roman numeral I indicates that it was the first restriction enzyme obtained from this strain of bacteria.

✔ Example 9.5.1

A portion of the coding strand of a gene was found to have the sequence 5′-ATGAGCGACTTTCGCCCATTA-3′. A mutation occurred in the gene, making the sequence 5′-ATGAGCGACCTTCGCCCATTA-3′.

a. Identify the mutation as a substitution, an insertion, or a deletion.
b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (refer to the codon chart)?

Solution

a. substitution
b. Phenylalanine (UUU) would be replaced with leucine (CUU).

? Exercise 9.5.1

A portion of the coding strand of a gene was found to have the sequence 5′-ATGAGCGACTTTCGCCCATTA-3′. A mutation occurred in the gene, making the sequence 5′-ATGGCAATCCTCAACGCTGT-3′.

a. Identify the mutation as a substitution, an insertion, or a deletion.
b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (refer to the codon chart)?

Summary

- The nucleotide sequence in DNA may be modified either spontaneously or from exposure to heat, radiation, or certain chemicals and can lead to mutations.
- Mutagens are the chemical or physical agents that cause mutations.
- Genetic diseases are hereditary diseases that occur because of a mutation in a critical gene.

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9.6: Viruses

Learning Objectives

- To explain how viruses reproduce in cells.

Viruses are visible only under an electron microscope. They come in a variety of shapes, ranging from spherical to rod shaped. The fact that they contain either deoxyribonucleic acid (DNA) or ribonucleic acid (RNA)—*but never both*—allows them to be divided into two major classes: **DNA viruses** and **RNA viruses**.

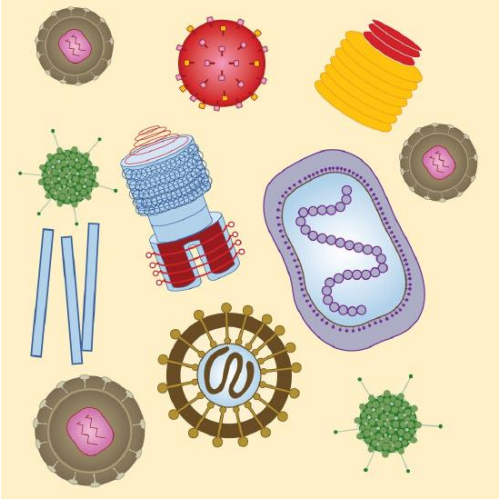


Figure **9.6.1**: Viruses. Viruses come in a variety of shapes that are determined by their protein coats.

Most *RNA viruses* use their nucleic acids in much the same way as the DNA viruses, penetrating a host cell and inducing it to replicate the viral RNA and synthesize viral proteins. The new RNA strands and viral proteins are then assembled into new viruses. Some RNA viruses, however, called **retroviruses** (Figure **9.6.2**), synthesize DNA in the host cell, in a process that is the reverse of the DNA-to-RNA transcription that normally occurs in cells. The synthesis of DNA from an RNA template is catalyzed by the enzyme **reverse transcriptase**.

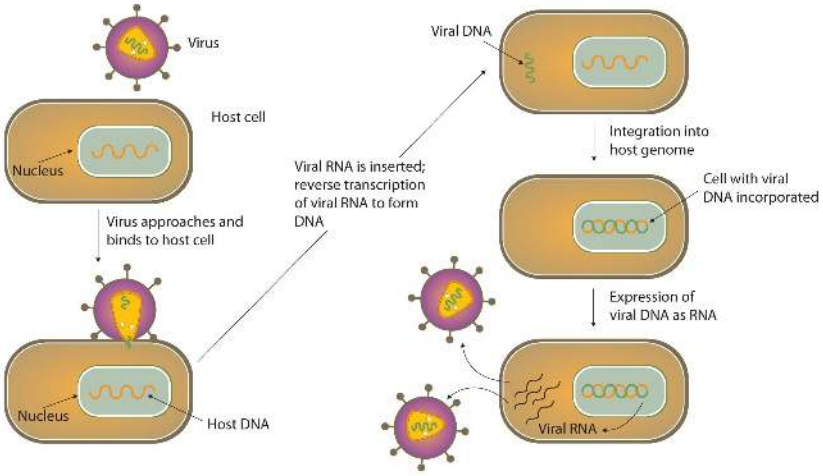
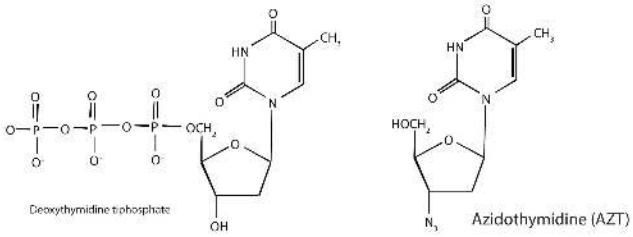
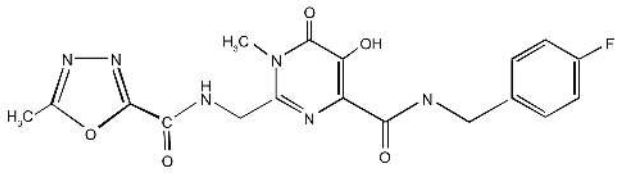


Figure **9.6.2**: Life Cycle of a Retrovirus

In 1987, azidothymidine (AZT, also known as zidovudine or the brand name Retrovir) became the first drug approved for the treatment of AIDS. It works by binding to reverse transcriptase in place of deoxythymidine triphosphate, after which, because AZT does not have a 3′OH group, further replication is blocked. In the past 10 years, several other drugs have been approved that also act by inhibiting the viral reverse transcriptase.



Raltegravir (Isentress) is a newer anti-AIDS drug that was approved by the FDA in October 2007. This drug inhibits the integrase enzyme that is needed to integrate the HIV DNA into cellular DNA, an essential step in the production of more HIV particles.



A major problem in treating HIV infections is that the virus can become resistant to any of these drugs. One way to combat the problem has been to administer a “cocktail” of drugs, typically a combination of two reverse transcriptase inhibitors along with a protease inhibitor. These treatments can significantly reduce the amount of HIV in an infected person.

Career Focus: Genetics Counselor

A genetics counselor works with individuals and families who have birth defects or genetic disorders or a family history of a disease, such as cancer, with a genetic link. A genetics counselor may work in a variety of health-care settings (such as a hospital) to obtain family medical and reproductive histories; explain how genetic conditions are inherited; explain the causes, diagnosis, and care of these conditions; interpret the results of genetic tests; and aid the individual or family in making decisions regarding genetic diseases or conditions. A certified genetics counselor must obtain a master’s degree from an accredited program. Applicants to these graduate programs usually have an undergraduate degree in biology, psychology, or genetics.



Photo courtesy of the United States National Institutes for Health, commons.wikimedia.org/wiki/File:Geneticcounseling.jpg.

Example 9.6.1

Describe the general structure of a virus.

Solution

A virus consists of a central core of nucleic acid enclosed in a protective shell of proteins. There may be lipid or carbohydrate molecules on the surface.

Example 9.6.1

Why is HIV known as a retrovirus?

Solution

In a cell, a retrovirus synthesizes a DNA copy of its RNA genetic material.

Summary

Viruses are very small infectious agents that contain either DNA or RNA as their genetic material. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

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9.E: Nucleic Acids (Exercises)

19.1: Nucleotides

Concept Review Exercises

1. Identify the three molecules needed to form the nucleotides in each nucleic acid.
   a. DNA
   b. RNA
2. Classify each compound as a pentose sugar, a purine, or a pyrimidine.
   a. adenine
   b. guanine
   c. deoxyribose
   d. thymine
   e. ribose
   f. cytosine

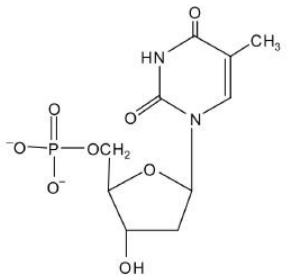
Answers

1. a. nitrogenous base (adenine, guanine, cytosine, and thymine), 2-deoxyribose, and H_3PO_4
   b. nitrogenous base (adenine, guanine, cytosine, and uracil), ribose, and H_3PO_4
2. a. purine
   b. purine
   c. pentose sugar
   d. pyrimidine
   e. pentose sugar
   f. pyrimidine

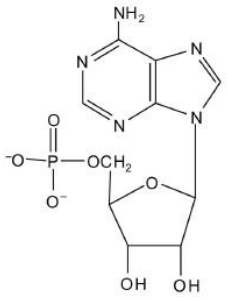
Exercises

1. What is the sugar unit in each nucleic acid?
   a. RNA
   b. DNA
2. Identify the major nitrogenous bases in each nucleic acid.
   a. DNA
   b. RNA
3. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

   a.

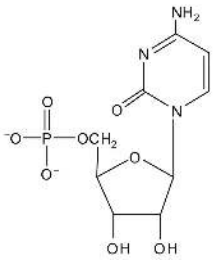


b.

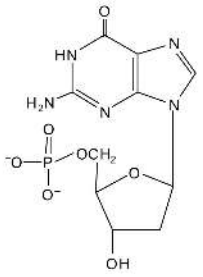


4. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

a.

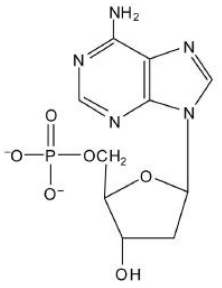


b.

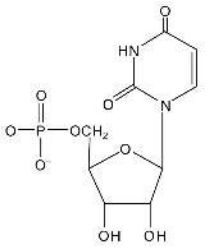


5. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a.

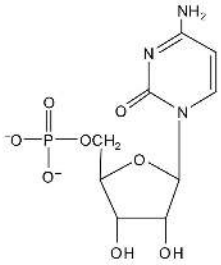


b.

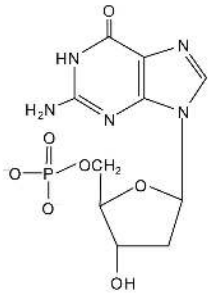


6. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a.



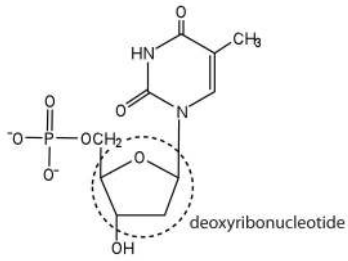
b.



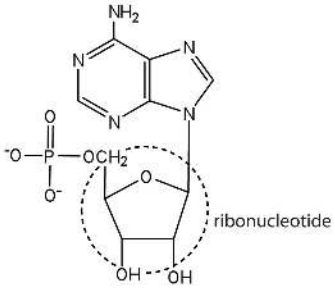
Answers

1. a. ribose
   b. deoxyribose

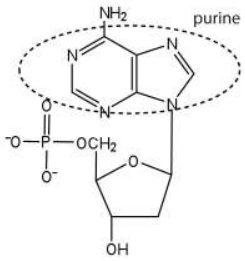
3. a.



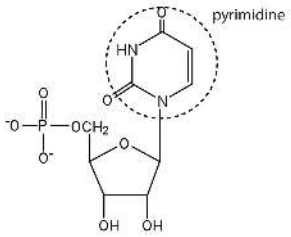
b.



a.



b.



19.2: Nucleic Acid Structure

Concept Review Exercises

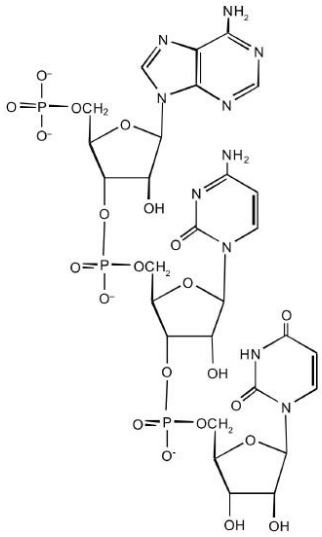
1. a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

1. a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

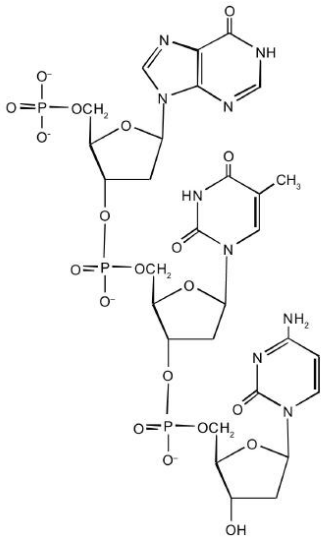
Exercises

1. For this short RNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this DNA segment.

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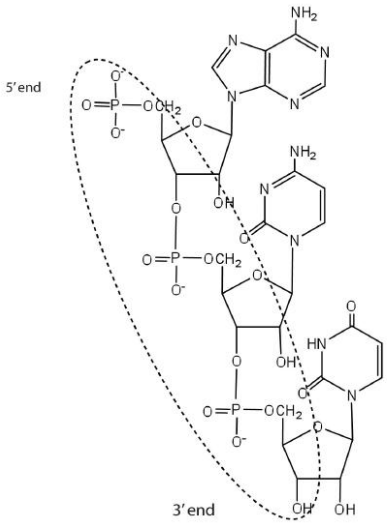


3. Which nitrogenous base in DNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′
6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

Answers

1. 

    c. ACU

3. a. guanine
   b. thymine
   c. cytosine
   d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

19.3: Replication and Expression of Genetic Information

Concept Review Exercises

1. In DNA replication, a parent DNA molecule produces two daughter molecules. What is the fate of each strand of the parent DNA double helix?
2. What is the role of DNA in transcription? What is produced in transcription?
3. Which type of RNA contains the codon? Which type of RNA contains the anticodon?

Answers

1. Each strand of the parent DNA double helix remains associated with the newly synthesized DNA strand.
2. DNA serves as a template for the synthesis of an RNA strand (the product of transcription).
3. codon: mRNA; anticodon: tRNA

Exercises

1. Describe how replication and transcription are similar.
2. Describe how replication and transcription differ.
3. A portion of the coding strand for a given gene has the sequence 5′-ATGAGCGACTTTGCGGGATTA-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?
4. A portion of the coding strand for a given gene has the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?

Answers

1. Both processes require a template from which a complementary strand is synthesized.

3.

a. 3′-TACTCGCTGAAACGCCCTAAT-5′
b. 5′-AUGAGCGACUUUGCGGGAUUA-3′

19.4: Protein Synthesis and the Genetic Code

Concept Review Exercises

1. What are the roles of mRNA and tRNA in protein synthesis?
2. What is the initiation codon?
3. What are the termination codons and how are they recognized?

Answers

1. mRNA provides the code that determines the order of amino acids in the protein; tRNA transports the amino acids to the ribosome to incorporate into the growing protein chain.
2. AUG
3. UAA, UAG, and UGA; they are recognized by special proteins called release factors, which signal the end of the translation process.

Exercises

1. Write the anticodon on tRNA that would pair with each mRNA codon.
   a. 5′-UUU-3′
   b. 5′-CAU-3′
   c. 5′-AGC-3′
   d. 5′-CCG-3′
2. Write the codon on mRNA that would pair with each tRNA anticodon.
   a. 5′-UUG-3′
   b. 5′-GAA-3′
   c. 5′-UCC-3′
   d. 5′-CAC-3′
3. The peptide hormone oxytocin contains 9 amino acid units. What is the minimum number of nucleotides needed to code for this peptide?
4. Myoglobin, a protein that stores oxygen in muscle cells, has been purified from a number of organisms. The protein from a sperm whale is composed of 153 amino acid units. What is the minimum number of nucleotides that must be present in the mRNA that codes for this protein?
5. Use Figure **9.*E*.3** to identify the amino acids carried by each tRNA molecule in Exercise 1.
6. Use Figure **9.*E*.3** to identify the amino acids carried by each tRNA molecule in Exercise 2.
7. Use Figure **9.*E*.3** to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGAGCGACUUUGCGGGAUUA-3′.
8. Use Figure **9.*E*.3** to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGGCAAUCCUCAAACGCUGU-3′

Answers

1. a. 3′-AAA-5′
   b. 3′-GUA-5′
   c. 3′-UCG-5′
   d. 3′-GGC-5′
3. 27 nucleotides (3 nucleotides/codon)
5. 1a: phenyalanine; 1b: histidine; 1c: serine; 1d: proline
7. met-ser-asp-phe-ala-gly-leu

19.5: Mutations and Genetic Diseases

Concept Review Exercises

1. a. What effect can UV radiation have on DNA?
   b. Is UV radiation an example of a physical mutagen or a chemical mutagen?
2. a. What causes PKU?
   b. How is PKU detected and treated?

Answers

1. a. It can lead to the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer.
   b. physical mutagen
2. a. the absence of the enzyme phenylalanine hydroxylase
   b. PKU is diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites; treatment calls for an individual to be placed on a diet containing little or no phenylalanine.

Exercises

1. A portion of the coding strand of a gene was found to have the sequence 5′-ATGAGCGACTTTCGCCCATTA-3′. A mutation occurred in the gene, making the sequence 5′-ATGAGCGACCTTCGCCCATTA-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
2. A portion of the coding strand of a gene was found to have the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′. A mutation occurred in the gene, making the sequence 5′-ATGGCAATCCTCAACGCTGT-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
3. a. What is a mutagen?
   b. Give two examples of mutagens.
4. For each genetic disease, indicate which enzyme is lacking or defective and the characteristic symptoms of the disease.
   a. PKU
   b. Tay-Sachs disease

Answers

1. a. substitution
   b. Phenylalanine (UUU) would be replaced with leucine (CUU).
3. a. a chemical or physical agent that can cause a mutation
   b. UV radiation and gamma radiation (answers will vary)

19.6: Viruses

Questions

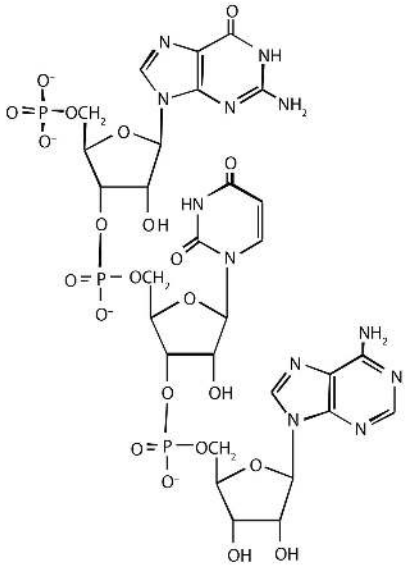
1. Describe the general structure of a virus.
2. How does a DNA virus differ from an RNA virus?
3. Why is HIV known as a retrovirus?
4. Describe how a DNA virus invades and destroys a cell.
5. a. Describe how an RNA virus invades and destroys a cell.
   b. How does this differ from a DNA virus?
6. What HIV enzyme does AZT inhibit?
7. What HIV enzyme does raltegravir inhibit?

Answers

1. A virus consists of a central core of nucleic acid enclosed in a protective shell of proteins. There may be lipid or carbohydrate molecules on the surface.
2. A DNA virus has DNA as its genetic material, while an RNA virus has RNA as its genetic material.
3. In a cell, a retrovirus synthesizes a DNA copy of its RNA genetic material.
4. The DNA virus enters a host cell and induces the cell to replicate the viral DNA and produce viral proteins. These proteins and DNA assemble into new viruses that are released by the host cell, which may die in the process.
5. -
6. reverse transcriptase
7. -

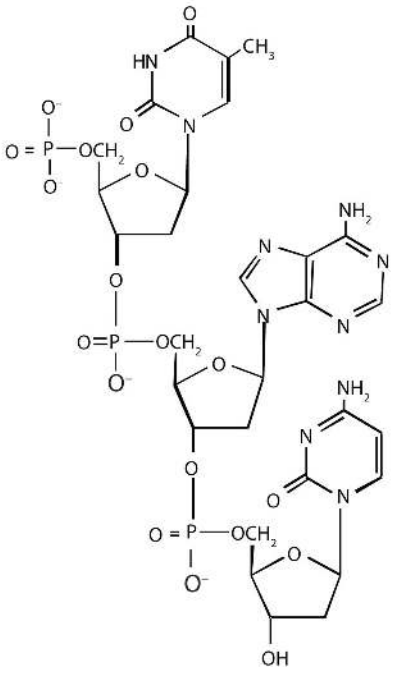
Additional Exercises

1. For this nucleic acid segment,



   a. classify this segment as RNA or DNA and justify your choice.
   b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

2. For this nucleic acid segment,



   a. classify this segment as RNA or DNA and justify your choice.
   b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

3. One of the key pieces of information that Watson and Crick used in determining the secondary structure of DNA came from experiments done by E. Chargaff, in which he studied the nucleotide composition of DNA from many different species. Chargaff noted that the molar quantity of A was always approximately equal to the molar quantity of T, and the molar quantity of C was always approximately equal to the molar quantity of G. How were Chargaff's results explained by the structural model of DNA proposed by Watson and Crick?

4. Suppose Chargaff (see Exercise 3) had used RNA instead of DNA. Would his results have been the same; that is, would the molar quantity of A approximately equal the molar quantity of T? Explain.
5. In the DNA segment

   5′-ATGAGGCATGAGACG-3′ (coding strand) 3′-TACTCCGTACTCTGC-5′ (template strand)

   a. What products would be formed from the segment's replication?
   b. Write the mRNA sequence that would be obtained from the segment's transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 5b?
6. In the DNA segment

   5′-ATGACGGTTTACTAAGCC-3′ (coding strand) 3′-TACTGCCAAATGATTCGG-5′ (template strand)

   a. What products would be formed from the segment's replication?
   b. Write the mRNA sequence that would be obtained from the segment's transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 6b?
7. A hypothetical protein has a molar mass of 23,300 Da. Assume that the average molar mass of an amino acid is 120.

   a. How many amino acids are present in this hypothetical protein?
   b. What is the minimum number of codons present in the mRNA that codes for this protein?
   c. What is the minimum number of nucleotides needed to code for this protein?
8. Bradykinin is a potent peptide hormone composed of nine amino acids that lowers blood pressure.

   a. The amino acid sequence for bradykinin is arg-pro-pro-gly-phe-ser-pro-phe-arg. Postulate a base sequence in the mRNA that would direct the synthesis of this hormone. Include an initiation codon and a termination codon.
   b. What is the nucleotide sequence of the DNA that codes for this mRNA?
9. A particular DNA coding segment is ACGTTAGCCCCAGCT.

   a. Write the sequence of nucleotides in the corresponding mRNA.
   b. Determine the amino acid sequence formed from the mRNA in Exercise 9a during translation.
   c. What amino acid sequence results from each of the following mutations?

      a. replacement of the underlined guanine by adenine
      b. insertion of thymine immediately after the underlined guanine
      c. deletion of the underlined guanine
10. A particular DNA coding segment is TACGACGTAACAAGC.

    a. Write the sequence of nucleotides in the corresponding mRNA.
    b. Determine the amino acid sequence formed from the mRNA in Exercise 10a during translation.
    c. What amino acid sequence results from each of the following mutations?

       a. replacement of the underlined guanine by adenine
       b. replacement of the underlined adenine by thymine
11. Two possible point mutations are the substitution of lysine for leucine *or* the substitution of serine for threonine. Which is likely to be more serious and why?
12. Two possible point mutations are the substitution of valine for leucine *or* the substitution of glutamic acid for histidine. Which is likely to be more serious and why?

Answers

1.

   a. RNA; the sugar is ribose, rather than deoxyribose
   b. 5′-GUA-3′

3. In the DNA structure, because guanine (G) is always paired with cytosine (C) and adenine (A) is always paired with thymine (T), you would expect to have equal amounts of each.

5.

a. Each strand would be replicated, resulting in two double-stranded segments.
b. 5′-AUGAGGCAUGAGACG-3′
c. met-arg-his-glu-thr

7.

a. 194
b. 194
c. 582

9.

a. 5′-ACGUUAGCCCCAGCU-3′
b. thr-leu-ala-pro-ala
c. a. thr-leu-thr-pro-ala
   b. thr-leu-val-pro-ser
   c. thr-leu-pro-gin

11. substitution of lysine for leucine because you are changing from an amino acid with a nonpolar side chain to one that has a positively charged side chain; both serine and threonine, on the other hand, have polar side chains containing the OH group.

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9.S: Nucleic Acids (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

A cell's hereditary information is encoded in **chromosomes** in the cell's nucleus. Each chromosome is composed of proteins and **deoxyribonucleic acid (DNA)**. The chromosomes contain smaller hereditary units called **genes,** which are relatively short segments of DNA. The hereditary information is expressed or used through the synthesis of **ribonucleic acid (RNA)**. Both **nucleic acids**—DNA and RNA—are polymers composed of monomers known as **nucleotides**, which in turn consist of phosphoric acid (H_3PO_4), a nitrogenous base, and a pentose sugar.

The two types of *nitrogenous bases* most important in nucleic acids are **purines**—adenine (A) and guanine (G)—and **pyrimidines**—cytosine (C), thymine (T), and uracil (U). DNA contains the nitrogenous bases adenine, cytosine, guanine, and thymine, while the bases in RNA are adenine, cytosine, guanine, and uracil. The sugar in the nucleotides of RNA is ribose; the one in DNA is 2-deoxyribose. The sequence of nucleotides in a nucleic acid defines the primary structure of the molecule.

RNA is a single-chain nucleic acid, whereas DNA possesses two nucleic-acid chains intertwined in a secondary structure called a **double helix**. The sugar-phosphate backbone forms the outside the double helix, with the purine and pyrimidine bases tucked inside. Hydrogen bonding between **complementary bases** holds the two strands of the double helix together; A always pairs with T and C always pairs with G.

Cell growth requires **replication**, or reproduction of the cell's DNA. The double helix unwinds, and hydrogen bonding between complementary bases breaks so that there are two single strands of DNA, and each strand is a *template* for the synthesis of a new strand. For protein synthesis, three types of RNA are needed: *messenger RNA* (mRNA), *ribosomal RNA* (rRNA), and *transfer RNA* (tRNA). All are made from a DNA template by a process called **transcription**. The double helix uncoils, and ribonucleotides base-pair to the deoxyribonucleotides on one DNA strand; however, RNA is produced using *uracil* rather than thymine. Once the RNA is formed, it dissociates from the template and leaves the nucleus, and the DNA double helix reforms.

Translation is the process in which proteins are synthesized from the information in mRNA. It occurs at structures called **ribosomes**, which are located outside the nucleus and are composed of rRNA and protein. The 64 possible three-nucleotide combinations of the 4 nucleotides of DNA constitute the **genetic code** that dictates the sequence in which amino acids are joined to make proteins. Each three-nucleotide sequence on mRNA is a **codon**. Each kind of tRNA molecule binds a specific amino acid and has a site containing a three-nucleotide sequence called an **anticodon**.

The general term for any change in the genetic code in an organism's DNA is **mutation**. A change in which a single base is substituted, inserted, or deleted is a **point mutation**. The chemical and/or physical agents that cause mutations are called **mutagens**. Diseases that occur due to mutations in critical DNA sequences are referred to as **genetic diseases**.

Viruses are infectious agents composed of a tightly packed central core of nucleic acids enclosed by a protective shell of proteins. Viruses contain either DNA or RNA as their genetic material but not both. Some RNA viruses, called **retroviruses**, synthesize DNA in the host cell from their RNA genome. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

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CHAPTER OVERVIEW

10: Metabolism

Metabolism is the set of life-sustaining chemical transformations within the cells of living organisms. The three main purposes of metabolism are the conversion of food/fuel to energy to run cellular processes, the conversion of food/fuel to building blocks for proteins, lipids, nucleic acids, and some carbohydrates, and the elimination of nitrogenous wastes. These enzyme-catalyzed reactions allow organisms to grow and reproduce, maintain their structures, and respond to their environments. Metabolism is usually divided into two categories: **catabolism**, the breaking down of organic matter, for example, by cellular respiration, and **anabolism**, the building up of components of cells such as proteins and nucleic acids. Usually, breaking down releases energy and building up consumes energy.

10.1: Prelude to Metabolism
10.2: ATP- the Universal Energy Currency
10.3: Stage I of Catabolism
10.4: Overview of Stage II of Catabolism
10.5: Stage III of Catabolism
10.6: Stage II of Carbohydrate Catabolism
10.7: Stage II of Lipid Catabolism
10.8: Stage II of Protein Catabolism
10.9: Metabolism (Exercises)
10.10: Metabolism (Summary)

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10.1: Prelude to Metabolism

The discovery of the link between insulin and diabetes led to a period of intense research aimed at understanding exactly how insulin works in the body to regulate glucose levels. Hormones in general act by binding to some protein, known as the hormone's receptor, thus initiating a series of events that lead to a desired outcome. In the early 1970s, the insulin receptor was purified, and researchers began to study what happens after insulin binds to its receptor and how those events are linked to the uptake and metabolism of glucose in cells.

The insulin receptor is located in the cell membrane and consists of four polypeptide chains: two identical chains called α chains and two identical chains called β chains. The α chains, positioned on the outer surface of the membrane, consist of 735 amino acids each and contain the binding site for insulin. The β chains are integral membrane proteins, each composed of 620 amino acids. The binding of insulin to its receptor stimulates the β chains to catalyze the addition of phosphate groups to the specific side chains of tyrosine (referred to as phosphorylation) in the β chains and other cell proteins, leading to the activation of reactions that metabolize glucose. In this chapter we will look at the pathway that breaks down glucose—in response to activation by insulin—for the purpose of providing energy for the cell.

GLmol

Figure **10.1.1**: Model of the Structure of the Insulin Receptor (PDB code 4ZXB).

Life requires energy. Animals, for example, require heat energy to maintain body temperature, mechanical energy to move their limbs, and chemical energy to synthesize the compounds needed by their cells. Living cells remain organized and functioning properly only through a continual supply of energy. But only specific forms of energy can be used. Supplying a plant with energy by holding it in a flame will not prolong its life. On the other hand, a green plant is able to absorb radiant energy from the sun, the most abundant source of energy for life on the earth. Plants use this energy first to form glucose and then to make other carbohydrates, as well as lipids and proteins. Unlike plants, animals cannot directly use the sun's energy to synthesize new compounds. They must eat plants or other animals to get carbohydrates, fats, and proteins and the chemical energy stored in them. Once digested and transported to the cells, the nutrient molecules can be used in either of two ways: as building blocks for making new cell parts or repairing old ones or "burned" for energy.

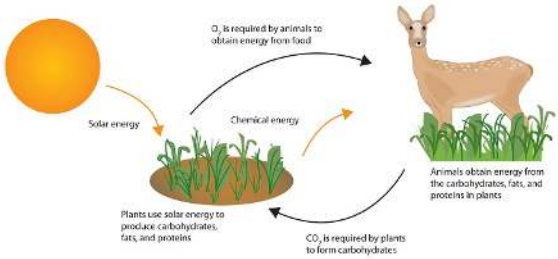


Figure **10.1.2**: Some Energy Transformations in Living Systems. Plants and animals exist in a cycle; each requires products of the other.

The thousands of coordinated chemical reactions that keep cells alive are referred to collectively as **metabolism**. In general, metabolic reactions are divided into two classes: the breaking down of molecules to obtain energy is **catabolism**, and the building of new molecules needed by living systems is **anabolism**.

Definition: Metabolite

Any chemical compound that participates in a metabolic reaction is a *metabolite*.

Most of the energy required by animals is generated from lipids and carbohydrates. These fuels must be oxidized, or "burned," for the energy to be released. The oxidation process ultimately converts the lipid or carbohydrate to carbon dioxide (CO_2) and water (H_2O).

Carbohydrate:

$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + 670\,\text{kcal}$$

Lipid:

$$C_{16}H_{32}O_2 + 23\,O_2 \longrightarrow 16\,CO_2 + 16\,H_2O + 2{,}385\,\text{kcal}$$

These two equations summarize the biological combustion of a carbohydrate and a lipid by the cell through respiration. **Respiration** is the collective name for all metabolic processes in which gaseous oxygen is used to oxidize organic matter to carbon dioxide, water, and energy.

Like the combustion of the common fuels we burn in our homes and cars (wood, coal, gasoline), respiration uses oxygen from the air to break down complex organic substances to carbon dioxide and water. But the energy released in the burning of wood is manifested entirely in the form of heat, and excess heat energy is not only useless but also injurious to the living cell. Living organisms instead conserve much of the energy respiration releases by channeling it into a series of stepwise reactions that produce adenosine triphosphate (ATP) or other compounds that ultimately lead to the synthesis of ATP. The remainder of the energy is released as heat and manifested as body temperature.

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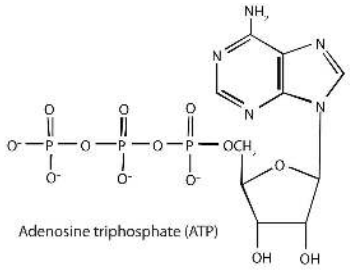
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10.2: ATP- the Universal Energy Currency

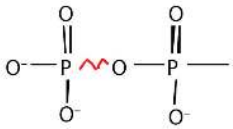
Learning Objectives

- To describe the importance of ATP as a source of energy in living organisms.

Adenosine triphosphate (ATP), a nucleotide composed of adenine, ribose, and three phosphate groups, is perhaps the most important of the so-called energy-rich compounds in a cell. Its concentration in the cell varies from 0.5 to 2.5 mg/mL of cell fluid.



Energy-rich compounds are substances having particular structural features that lead to a release of energy after hydrolysis. As a result, these compounds are able to supply energy for biochemical processes that require energy. The structural feature important in ATP is the phosphoric acid anhydride, or pyrophosphate, linkage:



The pyrophosphate bond, symbolized by a squiggle (~), is hydrolyzed when ATP is converted to adenosine diphosphate (ADP). In this hydrolysis reaction, the products contain less energy than the reactants; there is a release of energy (> 7 kcal/mol). One reason for the amount of energy released is that hydrolysis relieves the electron-electron repulsions experienced by the negatively charged phosphate groups when they are bonded to each other (Figure 20.1.1).

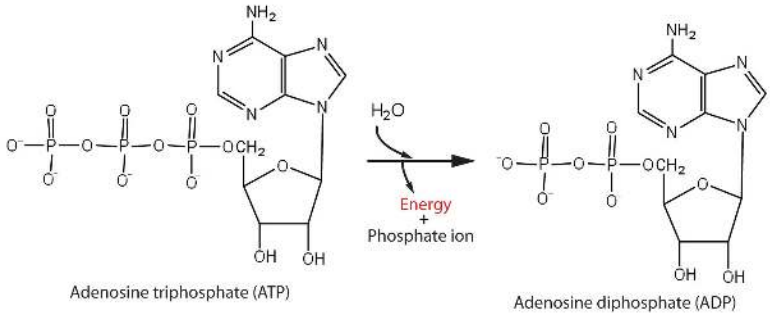


Figure **10.2.1**: Hydrolysis of ATP to Form ADP

Energy is released because the products (ADP and phosphate ion) have less energy than the reactants [ATP and water (H_2O)].

The general equation for ATP hydrolysis is as follows:

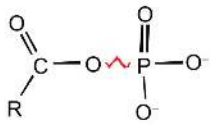
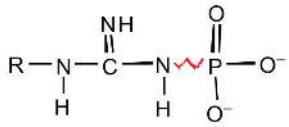
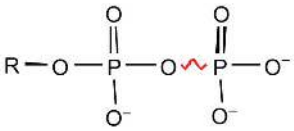
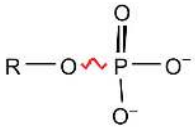
$$ATP + H_2O \rightarrow ADP + P_i + 7.4\ kcal/mol \tag{10.2.1}$$

If the hydrolysis of ATP releases energy, its synthesis (from ADP) requires energy. In the cell, ATP is produced by those processes that supply energy to the organism (absorption of radiant energy from the sun in green plants and breakdown of food in animals), and it is hydrolyzed by those processes that require energy (the syntheses of carbohydrates, lipids, proteins; the transmission of nerve impulses; muscle contractions). In fact, ATP is the principal medium of energy exchange in biological systems. Many scientists call it the energy currency of cells.

> *P_i is the symbol for the inorganic phosphate anions $H_2PO_4^-$ and HPO_4^{2-}.*

ATP is not the only high-energy compound needed for metabolism. Several others are listed in Table **10.2.1**. Notice, however, that the energy released when ATP is hydrolyzed is approximately midway between those of the high-energy and the low-energy phosphate compounds. This means that the hydrolysis of ATP can provide energy for the phosphorylation of the compounds below it in the table. For example, the hydrolysis of ATP provides sufficient energy for the phosphorylation of glucose to form glucose 1-phosphate. By the same token, the hydrolysis of compounds, such as creatine phosphate, that appear *above* ATP in the table can provide the energy needed to resynthesize ATP from ADP.

Table **10.2.1**: Energy Released by Hydrolysis of Some Phosphate Compounds

Type	Example	Energy Released (kcal/mol)
acyl phosphate 	1,3-bisphosphoglycerate (BPG)	−11.8
	acetyl phosphate	−11.3
guanidine phosphates 	creatine phosphate	−10.3
	arginine phosphate	−9.1
pyrophosphates 	$PP_{i*} \rightarrow 2P_i$	−7.8
	$ATP \rightarrow AMP + PP_i$	−7.7
	$ATP \rightarrow ADP + P_i$	−7.5
	$ADP \rightarrow AMP + P_i$	−7.5
sugar phosphates 	glucose 1-phosphate	−5.0
	fructose 6-phosphate	−3.8
	$AMP \rightarrow$ adenosine $+ P_i$	−3.4
	glucose 6-phosphate	−3.3
	glycerol 3-phosphate	−2.2

*PP_i is the pyrophosphate ion.

Example 10.2.1

Identify whether each compound would be classified as a high-energy phosphate compound.

a. ATP
b. glucose 6-phosphate
c. creatine phosphate

Solution

a. yes
b. no
c. yes

? Exercise 10.2.1

Identify whether each compound would be classified as a high-energy phosphate compound.

a. ADP
b. AMP
c. glucose 1-phosphate

Summary

The hydrolysis of ATP releases energy that can be used for cellular processes that require energy.

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10.3: Stage I of Catabolism

Learning Objectives

- To describe how carbohydrates, fats, and proteins are broken down during digestion.

We have said that animals obtain chemical energy from the food—carbohydrates, fats, and proteins—they eat through reactions defined collectively as ***catabolism***. We can think of catabolism as occurring in three stages (Figure **10.3.1**). In stage I, carbohydrates, fats, and proteins are broken down into their individual monomer units: carbohydrates into simple sugars, fats into fatty acids and glycerol, and proteins into amino acids. One part of stage I of catabolism is the breakdown of food molecules by hydrolysis reactions into the individual monomer units—which occurs in the mouth, stomach, and small intestine—and is referred to as **digestion**.

In stage II, these monomer units (or building blocks) are further broken down through different reaction pathways, one of which produces ATP, to form a common end product that can then be used in stage III to produce even more ATP. In this chapter, we will look at each stage of catabolism—as an overview and in detail.

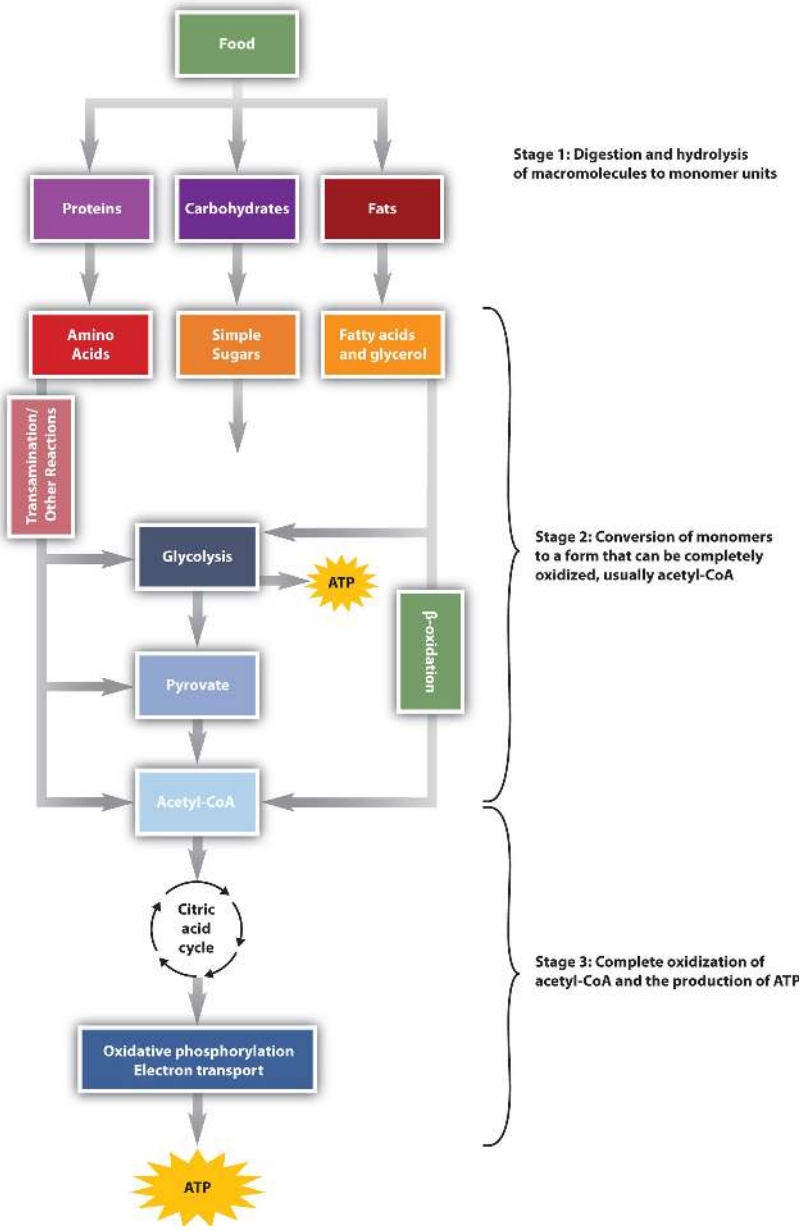


Figure **10.3.1**: Energy Conversions

The conversion of food into cellular energy (as ATP) occurs in three stages.

Digestion of Carbohydrates

Carbohydrate digestion begins in the mouth (Figure **10.3.2**) where salivary α-amylase attacks the α-glycosidic linkages in starch, the main carbohydrate ingested by humans. Cleavage of the glycosidic linkages produces a mixture of dextrins, maltose, and glucose. The α-amylase mixed into the food remains active as the food passes through the esophagus, but it is rapidly inactivated in the acidic environment of the stomach.

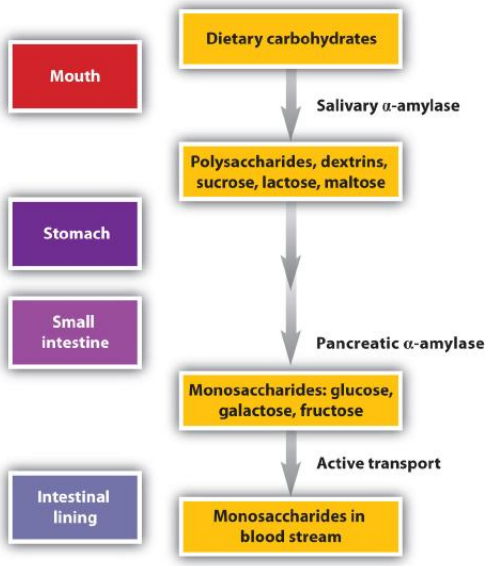


Figure 10.3.2: The Principal Events and Sites of Carbohydrate Digestion

The primary site of carbohydrate digestion is the small intestine. The secretion of α-amylase in the small intestine converts any remaining starch molecules, as well as the dextrins, to maltose. Maltose is then cleaved into two glucose molecules by maltase. Disaccharides such as sucrose and lactose are not digested until they reach the small intestine, where they are acted on by sucrase and lactase, respectively. The major products of the complete hydrolysis of disaccharides and polysaccharides are three monosaccharide units: glucose, fructose, and galactose. These are absorbed through the wall of the small intestine into the bloodstream.

Digestion of Proteins

Protein digestion begins in the stomach (Figure 10.3.3), where the action of gastric juice hydrolyzes about 10% of the peptide bonds. Gastric juice is a mixture of water (more than 99%), inorganic ions, hydrochloric acid, and various enzymes and other proteins.

> The pain of a gastric ulcer is at least partially due to irritation of the ulcerated tissue by acidic gastric juice.

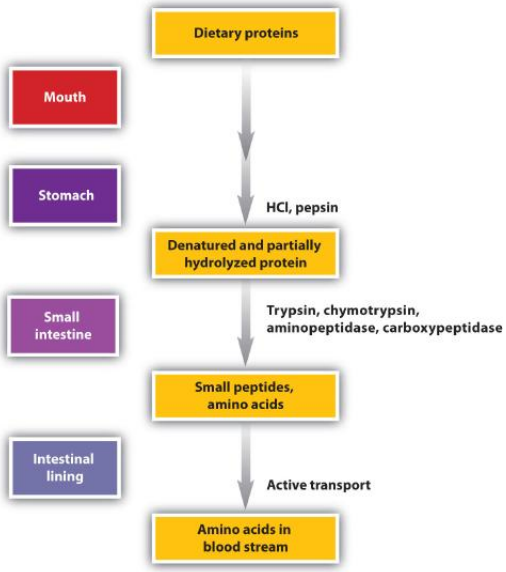


Figure 10.3.3: The Principal Events and Sites of Protein Digestion

The hydrochloric acid (HCl) in gastric juice is secreted by glands in the stomach lining. The pH of freshly secreted gastric juice is about 1.0, but the contents of the stomach may raise the pH to between 1.5 and 2.5. HCl helps to denature food proteins; that is, it unfolds the protein molecules to expose their chains to more efficient enzyme action. The principal digestive component of gastric juice is pepsinogen, an inactive enzyme produced in cells located in the stomach wall. When food enters the stomach after a period of fasting, pepsinogen is converted to its active form—pepsin—in a series of steps initiated by the drop in pH. Pepsin catalyzes the hydrolysis of peptide linkages within protein molecules. It has a fairly broad specificity but acts preferentially on linkages involving the aromatic amino acids tryptophan, tyrosine, and phenylalanine, as well as methionine and leucine.

Protein digestion is completed in the small intestine. Pancreatic juice, carried from the pancreas via the pancreatic duct, contains inactive enzymes such as trypsinogen and chymotrypsinogen. They are activated in the small intestine as follows (Figure **10.3.4**): The intestinal mucosal cells secrete the proteolytic enzyme enteropeptidase, which converts trypsinogen to trypsin; trypsin then activates chymotrypsinogen to chymotrypsin (and also completes the activation of trypsinogen). Both of these active enzymes catalyze the hydrolysis of peptide bonds in protein chains. Chymotrypsin preferentially attacks peptide bonds involving the carboxyl groups of the aromatic amino acids (phenylalanine, tryptophan, and tyrosine). Trypsin attacks peptide bonds involving the carboxyl groups of the basic amino acids (lysine and arginine). Pancreatic juice also contains procarboxypeptidase, which is cleaved by trypsin to carboxypeptidase. The latter is an enzyme that catalyzes the hydrolysis of peptide linkages at the free carboxyl end of the peptide chain, resulting in the stepwise liberation of free amino acids from the carboxyl end of the polypeptide.

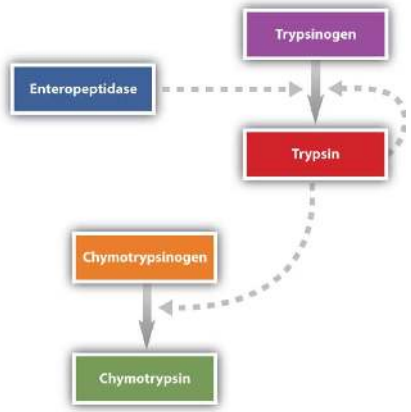


Figure **10.3.4**: Activation of Some Pancreatic Enzymes in the Small Intestine

Aminopeptidases in the intestinal juice remove amino acids from the N-terminal end of peptides and proteins possessing a free amino group. Figure **10.3.5** illustrates the specificity of these protein-digesting enzymes. The amino acids that are released by protein digestion are absorbed across the intestinal wall into the circulatory system, where they can be used for protein synthesis.

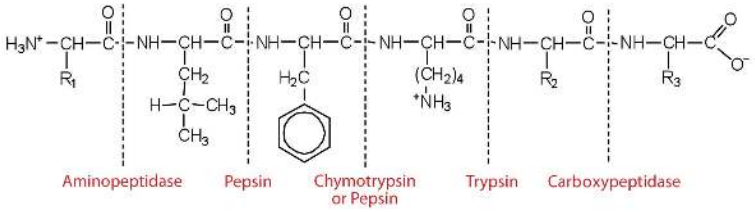


Figure **10.3.5**: Hydrolysis of a Peptide by Several Peptidases

This diagram illustrates where in a peptide the different peptidases we have discussed would catalyze hydrolysis the peptide bonds.

Digestion of Lipids

Lipid digestion begins in the upper portion of the small intestine. A hormone secreted in this region stimulates the gallbladder to discharge bile into the duodenum. The principal constituents of bile are the bile salts, which emulsify large, water-insoluble lipid droplets, disrupting some of the hydrophobic interactions holding the lipid molecules together and suspending the resulting smaller globules (micelles) in the aqueous digestive medium. These changes greatly increase the surface area of the lipid particles, allowing

for more intimate contact with the lipases and thus rapid digestion of the fats. Another hormone promotes the secretion of pancreatic juice, which contains these enzymes.

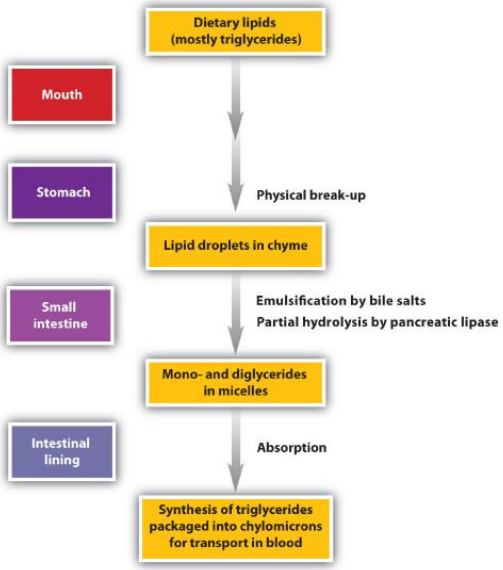


Figure 10.3.6: The Principal Events and Sites of Lipid (Primarily Triglyceride) Digestion

The lipases in pancreatic juice catalyze the digestion of triglycerides first to diglycerides and then to 2-monoglycerides and fatty acids:

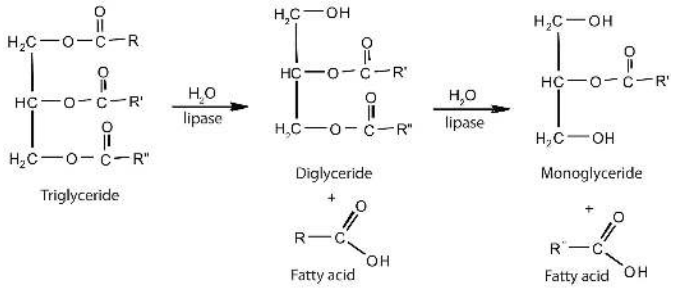


Figure 10.3.7: Digestion of triglycerides.

The monoglycerides and fatty acids cross the intestinal lining into the bloodstream, where they are resynthesized into triglycerides and transported as lipoprotein complexes known as chylomicrons. Phospholipids and cholesteryl esters undergo similar hydrolysis in the small intestine, and their component molecules are also absorbed through the intestinal lining.

The further metabolism of monosaccharides, fatty acids, and amino acids released in stage I of catabolism occurs in stages II and III of catabolism.

Example 10.3.1

Distinguish between each pair of compounds.

a. pepsin and pepsinogen
b. chymotrypsin and trypsin
c. aminopeptidase and carboxypeptidase

Solution

a. Pepsinogen is an inactive form of pepsin; pepsin is the active form of the enzyme.
b. Both enzymes catalyze the hydrolysis of peptide bonds. Chymotrypsin catalyzes the hydrolysis of peptide bonds following aromatic amino acids, while trypsin catalyzes the hydrolysis of peptide bonds following lysine and arginine.

c. Aminopeptidase catalyzes the hydrolysis of amino acids from the N-terminal end of a protein, while carboxypeptidase catalyzes the hydrolysis of amino acids from the C-terminal end of a protein.

Example 10.3.2

What are the primary end products of each form of digestion?

a. carbohydrate digestion
b. lipid digestion
c. protein digestion

Solution

a. glucose, fructose, and galactose
b. monoglycerides and fatty acids
c. amino acids

Summary

- During digestion, carbohydrates are broken down into monosaccharides, proteins are broken down into amino acids, and triglycerides are broken down into glycerol and fatty acids.
- Most of the digestion reactions occur in the small intestine.

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10.4: Overview of Stage II of Catabolism

Learning Objectives

- To describe the role of acetyl-CoA in metabolism.

A **metabolic pathway** is a series of biochemical reactions by which an organism converts a given reactant to a specific end product. There are specific metabolic pathways—which are different for carbohydrates, triglycerides, and proteins—that break down the products of stage I of catabolism (monosaccharides, fatty acids, and amino acids) to produce a common end product, **acetyl-coenzyme A (acetyl-CoA)** in stage II of catabolism.

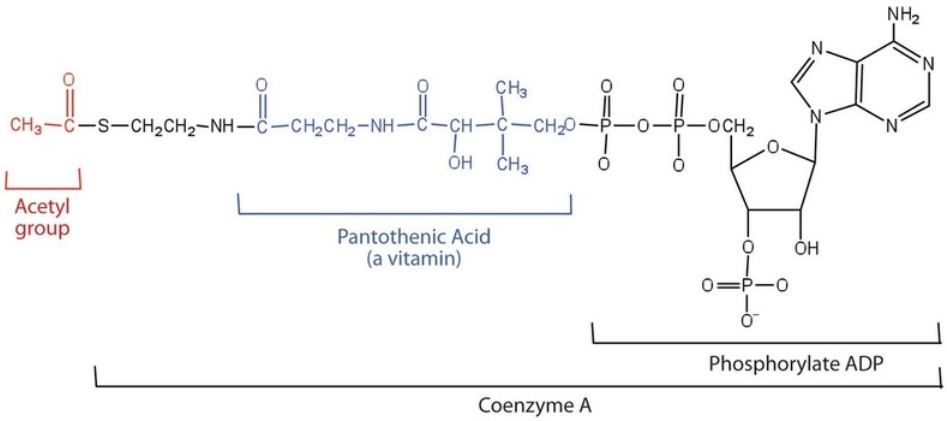


Figure **10.4.1**: The Structure of Acetyl-Coenzyme A (Acetyl-CoA)

Acetyl-CoA has an acetyl unit (derived from the breakdown of carbohydrates, lipids, and proteins) that is attached to coenzyme A, making the acetyl unit more reactive. Acetyl-CoA is used in a myriad of biochemical pathways. For example, it may be used as the starting material for the biosynthesis of lipids (such as triglycerides, phospholipids, or cholesterol and other steroids). Most importantly for energy generation, it may enter the citric acid cycle and be oxidized to produce energy, if energy is needed and oxygen is available. The various fates or uses of acetyl-CoA are summarized in Figure **10.4.2**.

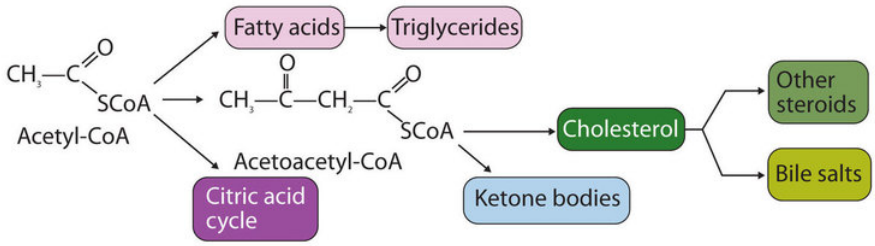


Figure **10.4.2**: Cell Chemistry. Acetyl-CoA plays a variety of roles in cell chemistry.

Glycolysis

Glycolysis is the catabolic process in which glucose is converted into **pyruvate** via ten enzymatic steps. There are three regulatory steps, each of which is highly regulated that are separated into two phases:

1. the "**priming phase**" because it requires an input of energy in the form of 2 ATPs per glucose molecule and
2. the "**pay off phase**" because energy is released in the form of 4 ATPs, 2 per glyceraldehyde molecules.

The end result of Glycolysis is two new pyruvate molecules which can then be fed into the **Citric Acid cycle** (also known as the **Kreb's Cycle**) if oxygen is present, or can be reduced to lactate or ethanol in the absence of of oxygen using a process known as **fermentation**.



Video 10.4.1: Glycolysis: An Overview. Glycolysis is a series of 10 reactions that converts sugars, like glucose, into 3-carbon molecules called pyruvate. This animation provides an overview of the energy consumed and produced by the pathway. NDSU VCell Production's animation; for more information please see http://vcell.ndsu.edu/animations.

Glycolysis occurs within almost all living cells and is the primary source of Acetyl-CoA, which is the molecule responsible for the majority of energy output under aerobic conditions (with oxygen). The structures of Glycolysis intermediates can be found in Figure 10.4.3.

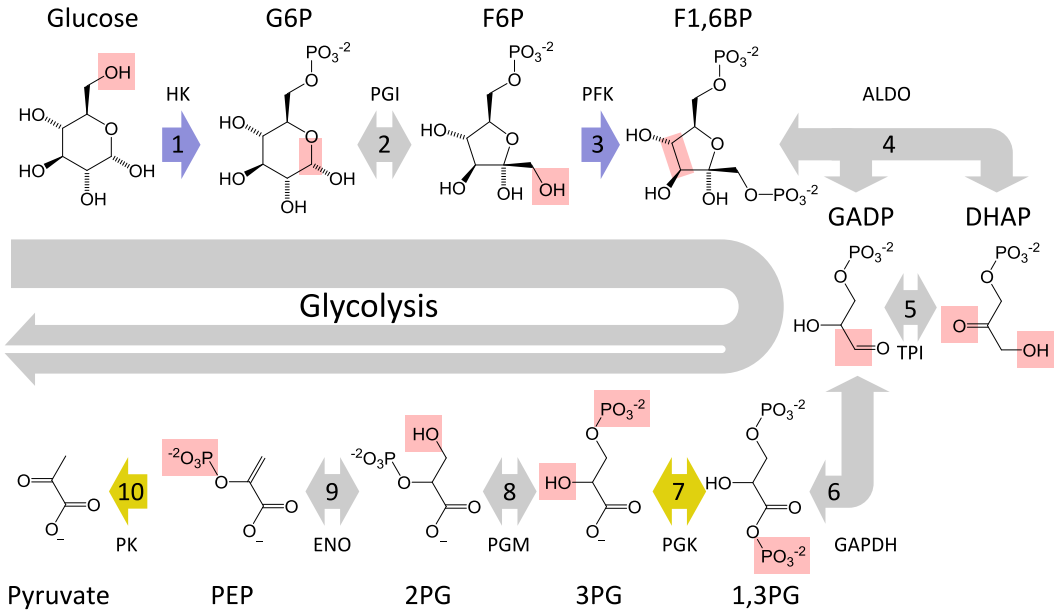


Figure 10.4.3: Glycolysis pathway. (CC BY-SA 4.0; International; Thomas Shafee via Wikipedia)

Phase 1: The "Priming Step"

The first phase of Glycolysis requires an input of energy in the form of ATP (adenosine triphosphate).

1. alpha-D-Glucose is phosphorolated at the 6 carbon by ATP via the enzyme Hexokinase (Class: Transferase) to yield alpha-D-Glucose-6-phosphate (G-6-P). This is a regulatory step which is negatively regulated by the presence of glucose-6-phosphate.
2. alpha-D-Glucose-6-phosphate is then converted into D-Fructose-6-phosphate (F-6-P) by Phosphoglucoisomerase (Class: Isomerase)
3. D-Fructose-6-phosphate is once again phosphorolated this time at the 1 carbon position by ATP via the enzyme Phosphofructokinase (Class: Transferase) to yield D-Fructose-1,6-bisphosphate (FBP). This is the committed step of glycolysis because of its large ΔG value.
4. D-Fructose-1,6-bisphosphate is then cleaved into two, three carbon molecules; Dihydroxyacetone phosphate (DHAP) and D-Glyceraldehyde-3-phosphate (G-3-P) by the enzyme Fructose bisphosphate aldolase (Class: Lyase)

5. Because the next portion of Glycolysis requires the molecule D-Glyceraldehyde-3-phosphate to continue Dihydroxyacetone phosphate is converted into D-Glyceraldehyde-3-phosphate by the enzyme Triose phosphate isomerase (Class: Isomerase)

Phase 2: The "Pay Off Step"

The second phase of Glycolysis where 4 molecules of ATP are produced per molecule of glucose. Enzymes appear in red:

1. D-Glyceraldehyde-3-phosphate is phosphorolated at the 1 carbon by the enzyme Glyceraldehyde-3-phosphate dehodrogenase to yield the high energy molecule 1,3-Bisphosphoglycerate (BPG)
2. ADP is then phosphorolated at the expense of 1,3-Bisphosphoglycerate by the enzyme Phosphoglycerate kinase (Class: Transferase) to yield ATP and 3-Phosphoglycerate (3-PG)
3. 3-Phosphoglycerate is then converted into 2-Phosphoglycerate by Phosphoglycerate mutase in preparation to yield another high energy molecule
4. 2-Phosphoglycerate is then converted to phosphoenolpyruvate (PEP) by Enolase. H_2O, potassium, and magnesium are all released as a result.
5. ADP is once again phosphorolated, this time at the expense of PEP by the enzyme pyruvate kinase to yield another molecule of ATP and and pyruvate. This step is regulated by the energy in the cell. The higher the energy of the cell the more inhibited pyruvate kinase becomes. Indicators of high energy levels within the cell are high concentrations of ATP, Acetyl-CoA, Alanine, and cAMP.

Because Glucose is split to yield two molecules of D-Glyceraldehyde-3-phosphate, each step in the "Pay Off" phase occurs twice per molecule of glucose.

Beta-Oxidation

During the second stage of catabolism, fatty acids are converted to acetyl CoA in a biochemical pathway known as **beta-Oxidation (ß-oxidation)**. The best source of energy for eukaryotic organisms are fats. Glucose offers a ratio 6.3 moles of ATP per carbon while saturated fatty acids offer 8.1 ATP per carbon. Also the complete oxidation of fats yields enormous amounts of water for those organisms that do not have adequate access to drinkable water. Camels and killer whales are good example of this, they obtain their water requirements from the complete oxidation of fats.



Video **10.4.2**: Fatty acid metabolism / beta oxidation / β-Oxidation

There are four distinct stages in the oxidation of fatty acids. Fatty acid degradation takes place within the mitochondria and requires the help of several different enzymes. In order for fatty acids to enter the mitochondria the assistance of two carrier proteins is required, Carnitine acyltransferase I and II. It is also interesting to note the similarities between the four steps of beta-oxidation and the later four steps of the TCA cycle.

Entry into Beta-oxidation

Most fats stored in eukaryotic organisms are stored as triglycerides as seen below. In order to enter into beta-oxidation bonds must be broken usually with the use of a Lipase. The end result of these broken bonds are a glycerol molecule and three fatty acids in the case of triglycerides. Other lipids are capable of being degraded as well.

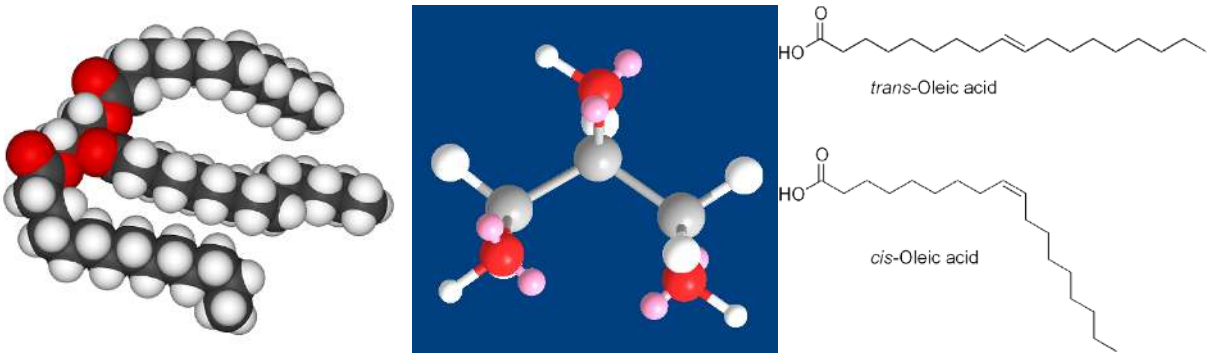


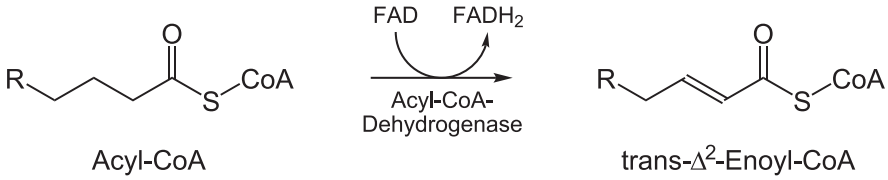
Figure 10.4.4: Key molecules in beta-oxidation: (left) A triglyceride molecule, (middle) Glycerol, (right) Fatty Acids (unsaturated)

Activation Step

- Once the triglycerides are broken down into glycerol and fatty acids they must be activated before they can enter into the mitochondria and proceed on with beta-oxidation. This is done by Acyl-CoA synthetase to yield fatty acyl-CoA.
- After the fatty acid has been acylated it is now ready to enter into the mitochondria.
- There are two carrier proteins (Carnitine acyltransferase I and II), one located on the outer membrane and one on the inner membrane of the mitochondria. Both are required for entry of the Acyl-CoA into the mitochondria.
- Once inside the mitochondria the fatty acyl-CoA can enter into beta-oxidation.

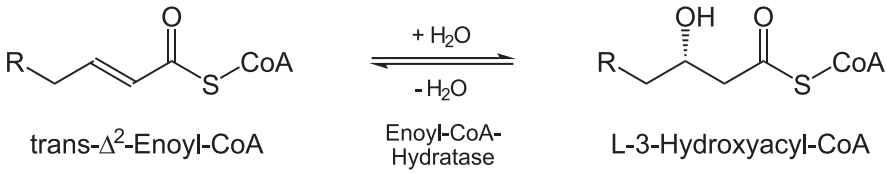
Oxidation Step

A fatty acyl-CoA is oxidized by Acyl-CoA dehydrogenase to yield a trans alkene. This is done with the aid of an [FAD] prosthetic group.



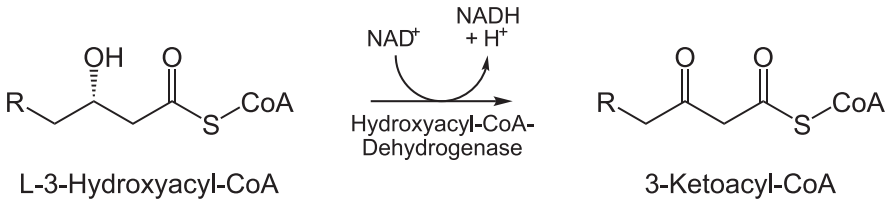
Hydration Step

The trans alkene is then hydrated with the help of Enoyl-CoA hydratase



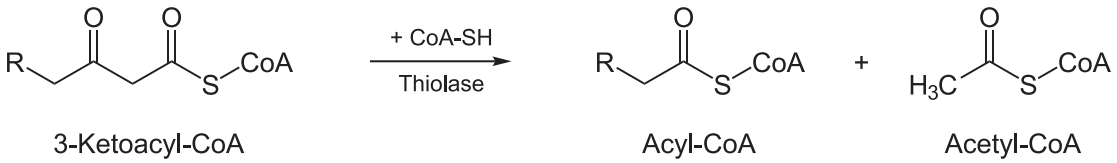
Oxidation Step

The alcohol of the hydroxyacly-CoA is then oxidized by NAD^+ to a carbonyl with the help of Hydroxyacyl-CoA dehydrogenase. NAD^+ is used to oxidize the alcohol rather then [FAD] because NAD^+ is capable of the alcohol while [FAD] is not.



Cleavage

Finally acetyl-CoA is cleaved off with the help of Thiolase to yield an Acyl-CoA that is two carbons shorter than before. The cleaved acetyl-CoA can then enter into the TCA and ETC because it is already within the mitochondria.



3-Ketoacyl-CoA | Acyl-CoA | Acetyl-CoA

Example 10.4.1

What vitamin is required to make coenzyme A?

Solution

pantothenic acid

Summary

- Acetyl-CoA is formed from the breakdown of carbohydrates, lipids, and proteins. It is used in many biochemical pathways.
- Glycolysis

References

1. Garrett, H., Reginald and Charles Grisham. Biochemistry. Boston: Twayne Publishers, 2008.
2. Raven, Peter. Biology. Boston: Twayne Publishers, 2005.

Contributors and Attributions

- Darik Benson, (University California Davis)

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10.5: Stage III of Catabolism

Learning Objectives

- Describe the reactions of the citric acid cycle.
- Describe the function of the citric acid cycle and identify the products produced.
- Describe the role of the electron transport chain in energy metabolism.
- Describe the role of oxidative phosphorylation in energy metabolism.

The acetyl group enters a cyclic sequence of reactions known collectively as the **citric acid cycle (or Krebs cycle or tricarboxylic acid [TCA] cycle)**. The cyclical design of this complex series of reactions, which bring about the oxidation of the acetyl group of acetyl-CoA to carbon dioxide and water, was first proposed by Hans Krebs in 1937. (He was awarded the 1953 Nobel Prize in Physiology or Medicine.) Acetyl-CoA's entrance into the citric acid cycle is the beginning of stage III of catabolism. The citric acid cycle produces adenosine triphosphate (**ATP**), reduced nicotinamide adenine dinucleotide (**NADH**), reduced flavin adenine dinucleotide (**$FADH_2$**), and metabolic intermediates for the synthesis of needed compounds.

Steps of the Citric Acid Cycle

At first glance, the citric acid cycle appears rather complex (Figure 10.5.1). All the reactions, however, are familiar types in organic chemistry: hydration, oxidation, decarboxylation, and hydrolysis. Each reaction of the citric acid cycle is numbered, and in Figure 10.5.1, the two acetyl carbon atoms are highlighted in red. Each intermediate in the cycle is a carboxylic acid, existing as an anion at physiological pH. All the reactions occur within the mitochondria, which are small organelles within the cells of plants and animals.

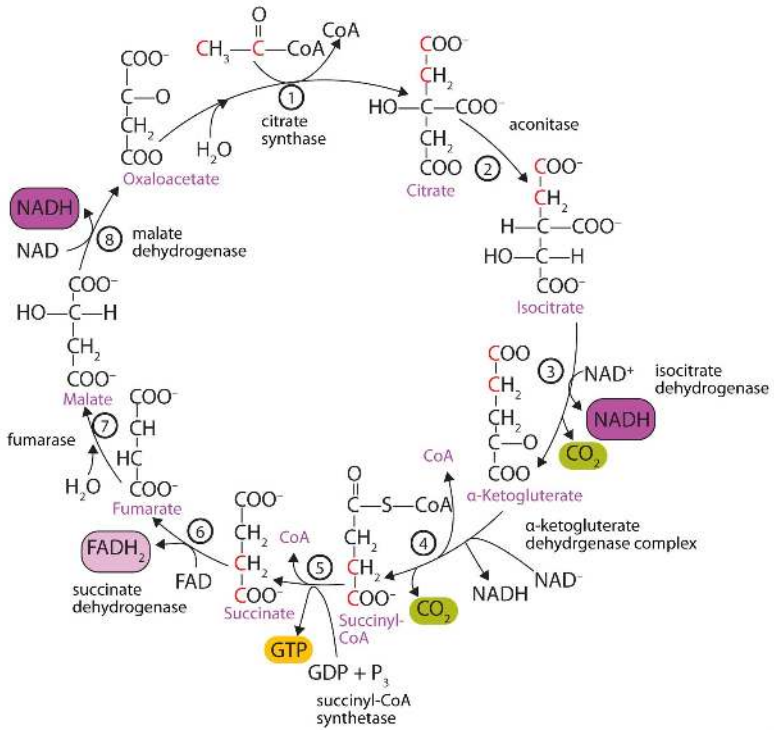


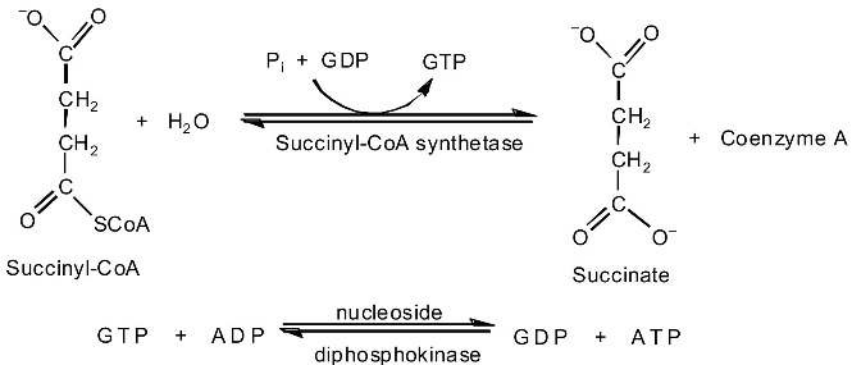
Figure 10.5.1: Reactions of the Citric Acid Cycle

1. In the first step, acetyl-CoA enters the citric acid cycle, and the acetyl group is transferred onto oxaloacetate, yielding citrate. Note that this step releases coenzyme A. The reaction is catalyzed by *citrate synthase*.
2. In the next step, *aconitase* catalyzes the isomerization of citrate to isocitrate. In this reaction, a tertiary alcohol, which cannot be oxidized, is converted to a secondary alcohol, which can be oxidized in the next step.

3. Isocitrate then undergoes a reaction known as oxidative decarboxylation because the alcohol is oxidized and the molecule is shortened by one carbon atom with the release of carbon dioxide (decarboxylation). The reaction is catalyzed by *isocitrate dehydrogenase*, and the product of the reaction is α-ketoglutarate. An important reaction linked to this is the reduction of the coenzyme nicotinamide adenine dinucleotide (NAD^+) to NADH. The NADH is ultimately reoxidized, and the energy released is used in the synthesis of ATP, as we shall see.
4. The fourth step is another oxidative decarboxylation. This time α-ketoglutarate is converted to succinyl-CoA, and another molecule of NAD^+ is reduced to NADH. The *α-ketoglutarate dehydrogenase complex* catalyzes this reaction. This is the only irreversible reaction in the citric acid cycle. As such, it prevents the cycle from operating in the reverse direction, in which acetyl-CoA would be synthesized from carbon dioxide.

> So far, in the first four steps, two carbon atoms have entered the cycle as an acetyl group, and two carbon atoms have been released as molecules of carbon dioxide. The remaining reactions of the citric acid cycle use the four carbon atoms of the succinyl group to resynthesize a molecule of oxaloacetate, which is the compound needed to combine with an incoming acetyl group and begin another round of the cycle.

In the fifth reaction, the energy released by the hydrolysis of the high-energy thioester bond of succinyl-CoA is used to form guanosine triphosphate (GTP) from guanosine diphosphate (GDP) and inorganic phosphate in a reaction catalyzed by *succinyl-CoA synthetase*. This step is the only reaction in the citric acid cycle that directly forms a high-energy phosphate compound. GTP can readily transfer its terminal phosphate group to adenosine diphosphate (ADP) to generate ATP in the presence of *nucleoside diphosphokinase*.



Succinate dehydrogenase then catalyzes the removal of two hydrogen atoms from succinate, forming fumarate. This oxidation-reduction reaction uses flavin adenine dinucleotide (FAD), rather than NAD^+, as the oxidizing agent. Succinate dehydrogenase is the only enzyme of the citric acid cycle located within the inner mitochondrial membrane. We will see soon the importance of this.

In the following step, a molecule of water is added to the double bond of fumarate to form L-malate in a reaction catalyzed by *fumarase*.

One revolution of the cycle is completed with the oxidation of L-malate to oxaloacetate, brought about by *malate dehydrogenase*. This is the third oxidation-reduction reaction that uses NAD^+ as the oxidizing agent. Oxaloacetate can accept an acetyl group from acetyl-CoA, allowing the cycle to begin again.



Video 10.5.1:: "The Citric Acid Cycle: An Overview". In the matrix of the mitochondrion, the Citric Acid Cycle uses Acetyl CoA molecules to produce energy through eight chemical reactions. This animation provides an overview of the pathway and its products. NDSU VCell Production's animation; for more information please see http://vcell.ndsu.edu/animations.

Cellular Respiration

Respiration can be defined as the process by which cells oxidize organic molecules in the presence of gaseous oxygen to produce carbon dioxide, water, and energy in the form of ATP. We have seen that two carbon atoms enter the citric acid cycle from acetyl-CoA (step 1), and two different carbon atoms exit the cycle as carbon dioxide (steps 3 and 4). Yet nowhere in our discussion of the citric acid cycle have we indicated how oxygen is used. Recall, however, that in the four oxidation-reduction steps occurring in the citric acid cycle, the coenzyme NAD^+ or FAD is reduced to NADH or $FADH_2$, respectively. *Oxygen is needed to reoxidize these coenzymes*. Recall, too, that very little ATP is obtained directly from the citric acid cycle. Instead, oxygen participation and significant ATP production occur subsequent to the citric acid cycle, in two pathways that are closely linked: electron transport and oxidative phosphorylation.

All the enzymes and coenzymes for the citric acid cycle, the reoxidation of NADH and $FADH_2$, and the production of ATP are located in the **mitochondria**, which are small, oval organelles with double membranes, often referred to as the “power plants” of the cell (Figure 10.5.2). A cell may contain 100–5,000 mitochondria, depending on its function, and the mitochondria can reproduce themselves if the energy requirements of the cell increase.

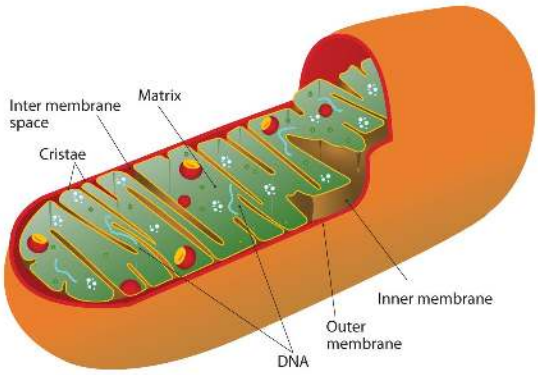


Figure 10.5.2: Respiration

Cellular respiration occurs in the mitochondria

Figure 10.5.2 shows the mitochondrion’s two membranes: *outer* and *inner*. The inner membrane is extensively folded into a series of internal ridges called *cristae*. Thus there are two compartments in mitochondria: the *intermembrane space*, which lies between the membranes, and the *matrix*, which lies inside the inner membrane. The outer membrane is permeable, whereas the inner membrane is impermeable to most molecules and ions, although water, oxygen, and carbon dioxide can freely penetrate both membranes. The matrix contains all the enzymes of the citric acid cycle with the exception of succinate dehydrogenase, which is

embedded in the inner membrane. The enzymes that are needed for the reoxidation of NADH and $FADH_2$ and ATP production are also located in the inner membrane. They are arranged in specific positions so that they function in a manner analogous to a bucket brigade. This highly organized sequence of oxidation-reduction enzymes is known as the **electron transport chain (or respiratory chain)**.

Electron Transport

Figure 10.5.3 illustrates the organization of the electron transport chain. The components of the chain are organized into four complexes designated I, II, III, and IV. Each complex contains several enzymes, other proteins, and metal ions. The metal ions can be reduced and then oxidized repeatedly as electrons are passed from one component to the next. Recall that a compound is reduced when it gains electrons or hydrogen atoms and is oxidized when it loses electrons or hydrogen atoms.

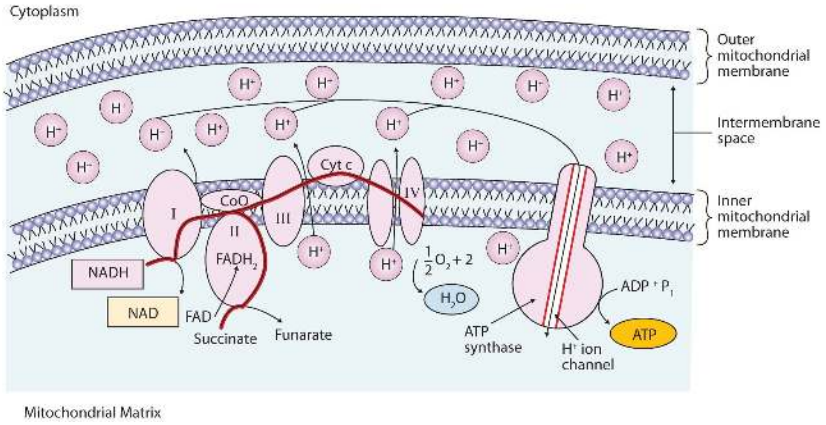
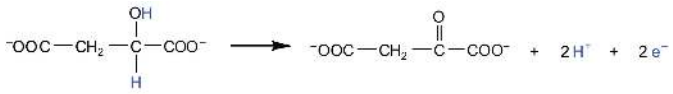


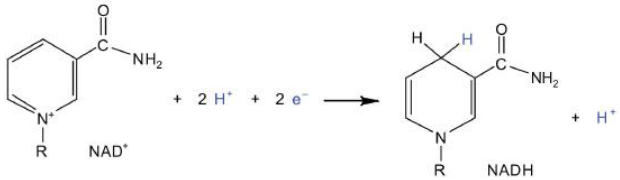
Figure 10.5.3: The Mitochondrial Electron Transport Chain and ATP Synthase. The red line shows the path of electrons.

Electrons can enter the electron transport chain through either complex I or II. We will look first at electrons entering at complex I. These electrons come from NADH, which is formed in three reactions of the citric acid cycle. Let's use step 8 as an example, the reaction in which L-malate is oxidized to oxaloacetate and NAD^+ is reduced to NADH. This reaction can be divided into two half reactions:

- *Oxidation half-reaction*:

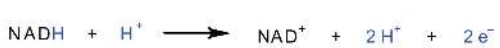


- *Reduction half-reaction*:

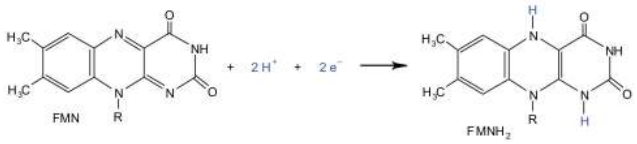


In the oxidation half-reaction, two hydrogen (H^+) ions and two electrons are removed from the substrate. In the reduction half-reaction, the NAD^+ molecule accepts both of those electrons and one of the H^+ ions. The other H^+ ion is transported from the matrix, across the inner mitochondrial membrane, and into the intermembrane space. The NADH diffuses through the matrix and is bound by complex I of the electron transport chain. In the complex, the coenzyme flavin mononucleotide (FMN) accepts both electrons from NADH. By passing the electrons along, NADH is oxidized back to NAD^+ and FMN is reduced to $FMNH_2$ (reduced form of flavin mononucleotide). Again, the reaction can be illustrated by dividing it into its respective half-reactions.

- *Oxidation half-reaction*:



- *Reduction half-reaction*:



Complex I contains several proteins that have iron-sulfur (Fe·S) centers. The electrons that reduced FMN to $FMNH_2$ are now transferred to these proteins. The iron ions in the Fe·S centers are in the Fe(III) form at first, but by accepting an electron, each ion is reduced to the Fe(II) form. Because each Fe·S center can transfer only one electron, two centers are needed to accept the two electrons that will regenerate FMN.

- *Oxidation half-reaction*:

$$FMNH_2 \rightarrow FMN + 2H^+ + 2e^- \tag{10.5.1}$$

- *Reduction half-reaction*:

$$2Fe(III) \cdot S + 2e^- \rightarrow 2Fe(II) \cdot S \tag{10.5.2}$$

Electrons from $FADH_2$, formed in step 6 of the citric acid cycle, enter the electron transport chain through complex II. Succinate dehydrogenase, the enzyme in the citric acid cycle that catalyzes the formation of $FADH_2$ from FAD is part of complex II. The electrons from $FADH_2$ are then transferred to an Fe·S protein.

- *Oxidation half-reaction*:

$$FADH_2 \rightarrow FAD + 2H^+ + 2e^- \tag{10.5.3}$$

- *Reduction half-reaction*:

$$2Fe(III) \cdot S + 2e^- \rightarrow 2Fe(II) \cdot S \tag{10.5.4}$$

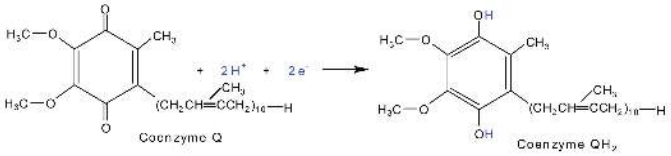
Electrons from complexes I and II are then transferred from the $Fe \cdot S$ protein to coenzyme Q (CoQ), a mobile electron carrier that acts as the electron shuttle between complexes I or II and complex III.

> *Coenzyme Q is also called ubiquinone because it is ubiquitous in living systems.*

- *Oxidation half-reaction*:

$$2Fe(II) \cdot S \rightarrow 2Fe(III) \cdot S + 2e^- \tag{10.5.5}$$

- *Reduction half-reaction*:



Complexes III and IV include several iron-containing proteins known as **cytochromes**. The iron in these enzymes is located in substructures known as iron porphyrins (Figure **10.5.4**). Like the Fe·S centers, the characteristic feature of the cytochromes is the ability of their iron atoms to exist as either Fe(II) or Fe(III). Thus, each cytochrome in its oxidized form—Fe(III)—can accept one electron and be reduced to the Fe(II) form. This change in oxidation state is reversible, so the reduced form can donate its electron to the next cytochrome, and so on. Complex III contains cytochromes b and c, as well as Fe·S proteins, with cytochrome c acting as the electron shuttle between complex III and IV. Complex IV contains cytochromes a and a_3 in an enzyme known as *cytochrome oxidase*. This enzyme has the ability to transfer electrons to molecular oxygen, the last electron acceptor in the chain of electron transport reactions. In this final step, water (H_2O) is formed.

- *Oxidation half-reaction*:

$$4Cyt\,a_3\text{–}Fe(II) \rightarrow 4Cyt\,a_3\text{–}Fe(III) + 4e^- \tag{10.5.6}$$

- *Reduction half-reaction*:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

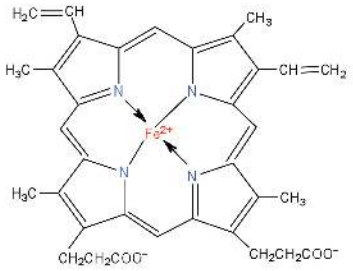


Figure **10.5.4**: An Iron Porphyrin. Iron porphyrins are present in cytochromes as well as in myoglobin and hemoglobin.



Video **10.5.2**:: Cellular Respiration (Electron Transport Chain). Cellular respiration occurs in the mitochondria and provides both animals and plants with the energy needed to power other cellular processes. This section covers the electron transport chain.NDSU Virtual Cell Animations Project animation; ror more information please see http://vcell.ndsu.edu/animations

Oxidative Phosphorylation

Each intermediate compound in the electron transport chain is reduced by the addition of one or two electrons in one reaction and then subsequently restored to its original form by delivering the electron(s) to the next compound along the chain. The successive electron transfers result in energy production. But how is this energy used for the synthesis of ATP? The process that links ATP synthesis to the operation of the electron transport chain is referred to as **oxidative phosphorylation**.

Electron transport is tightly coupled to oxidative phosphorylation. The coenzymes NADH and $FADH_2$ are oxidized by the respiratory chain *only* if ADP is simultaneously phosphorylated to ATP. The currently accepted model explaining how these two processes are linked is known as the *chemiosmotic hypothesis*, which was proposed by Peter Mitchell, resulting in Mitchell being awarded the 1978 Nobel Prize in Chemistry.

Looking again at Figure **10.5.3**, we see that as electrons are being transferred through the electron transport chain, hydrogen (H^+) ions are being transported across the inner mitochondrial membrane from the matrix to the intermembrane space. The concentration of H^+ is already higher in the intermembrane space than in the matrix, so energy is required to transport the additional H^+ there. This energy comes from the electron transfer reactions in the electron transport chain. But how does the extreme difference in H^+ concentration then lead to ATP synthesis? The buildup of H^+ ions in the intermembrane space results in an H^+ ion gradient that is a large energy source, like water behind a dam (because, given the opportunity, the protons will flow out of the intermembrane space and into the less concentrated matrix). Current research indicates that the flow of H^+ down this concentration gradient through a fifth enzyme complex, known as ATP synthase, leads to a change in the structure of the synthase, causing the synthesis and release of ATP.

In cells that are using energy, the turnover of ATP is very high, so these cells contain high levels of ADP. They must therefore consume large quantities of oxygen continuously, so as to have the energy necessary to phosphorylate ADP to form ATP. Consider, for example, that resting skeletal muscles use about 30% of a resting adult's oxygen consumption, but when the same muscles are working strenuously, they account for almost 90% of the total oxygen consumption of the organism.

Experiment has shown that 2.5–3 ATP molecules are formed for every molecule of NADH oxidized in the electron transport chain, and 1.5–2 ATP molecules are formed for every molecule of $FADH_2$ oxidized. Table **10.5.1** summarizes the theoretical maximum yield of ATP produced by the complete oxidation of 1 mol of acetyl-CoA through the sequential action of the citric acid cycle, the electron transport chain, and oxidative phosphorylation.

Table **10.5.1**: Maximum Yield of ATP from the Complete Oxidation of 1 mol of Acetyl-CoA

Reaction	Comments	Yield of ATP (moles)
Isocitrate → α-ketoglutarate + CO_2	produces 1 mol NADH	
α-ketoglutarate → succinyl-CoA + CO_2	produces 1 mol NADH	
Succinyl-CoA → succinate	produces 1 mol GTP	+1
Succinate → fumarate	produces 1 mol $FADH_2$	
Malate → oxaloacetate	produces 1 mol NADH	
1 $FADH_2$ from the citric acid cycle	yields 2 mol ATP	+2
3 NADH from the citric acid cycle	yields 3 mol ATP/NADH	+9
Net yield of ATP:		+12

Example 10.5.1

Two carbon atoms are fed into the citric acid cycle as acetyl-CoA. In what form are two carbon atoms removed from the cycle?

Solution

as carbon dioxide

Example 10.5.2

Replace each question mark with the correct compound.

a. $? \xrightarrow{\text{aconitase}} \textbf{isocitrate}$

b. $? + ? \xrightarrow{\text{citrate synthase}} \textbf{citrate} + \textbf{coenzyme A}$

c. $\textbf{fumarate} \xrightarrow{\text{fumarase}} ?$

d. $\textbf{isocitrate} + \textbf{NAD}^+ \xrightarrow{?} \alpha\textbf{-ketoglurate} + \textbf{NADH} + \textbf{CO}_2$

Solution

a. citrate

b. oxaloacetate + acetyl-CoA

c. malate

d. α-ketoglutarate hydrogenase complex

? Exercise 10.5.1

Replace each question mark with the correct compound.

a. $\text{malate} + \text{NAD}^+ \xrightarrow{?} \text{oxaloacetate} + \text{NADH}$

b. $? + ? \xrightarrow{\text{nucleoside diphosphokinase}} \text{GDP} + \text{ATP}$

c. $\text{succinyl-CoA} \xrightarrow{\text{succinyl-CoA synthetase}} ? + ?$

d. $\text{succinate} + \text{FAD} \xrightarrow{\text{succinate dehydrogenase}} ? + \text{FADH}_2$

Key Takeaways

- The acetyl group of acetyl-CoA enters the citric acid cycle. For each acetyl-CoA that enters the citric acid cycle, 2 molecules of carbon dioxide, 3 molecules of NADH, 1 molecule of ATP, and 1 molecule of $FADH_2$ are produced.
- The reduced coenzymes (NADH and $FADH_2$) produced by the citric acid cycle are reoxidized by the reactions of the electron transport chain. This series of reactions also produces a pH gradient across the inner mitochondrial membrane.
- The pH gradient produced by the electron transport chain drives the synthesis of ATP from ADP. For each NADH reoxidized, 2.5–3 molecules of ATP are produced; for each $FADH_2$ reoxidized, 1.5–2 molecules of ATP are produced.

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10.6: Stage II of Carbohydrate Catabolism

Learning Objectives

- Describe the function of glycolysis and identify its major products.
- Describe how the presence or absence of oxygen determines what happens to the pyruvate and the NADH that are produced in glycolysis.
- Determine the amount of ATP produced by the oxidation of glucose in the presence and absence of oxygen.

In stage II of catabolism, the metabolic pathway known as **glycolysis** converts glucose into two molecules of **pyruvate** (a three-carbon compound with three carbon atoms) with the corresponding production of adenosine triphosphate (ATP). The individual reactions in glycolysis were determined during the first part of the 20th century. It was the first metabolic pathway to be elucidated, in part because the participating enzymes are found in soluble form in the cell and are readily isolated and purified. The pathway is structured so that the product of one enzyme-catalyzed reaction becomes the substrate of the next. The transfer of intermediates from one enzyme to the next occurs by diffusion.

Steps in Glycolysis

The 10 reactions of glycolysis, summarized in Figure **10.6.1** can be divided into two phases. In the first 5 reactions—phase I—glucose is broken down into two molecules of glyceraldehyde 3-phosphate. In the last five reactions—phase II—each glyceraldehyde 3-phosphate is converted into pyruvate, and ATP is generated. Notice that all the intermediates in glycolysis are phosphorylated and contain either six or three carbon atoms.

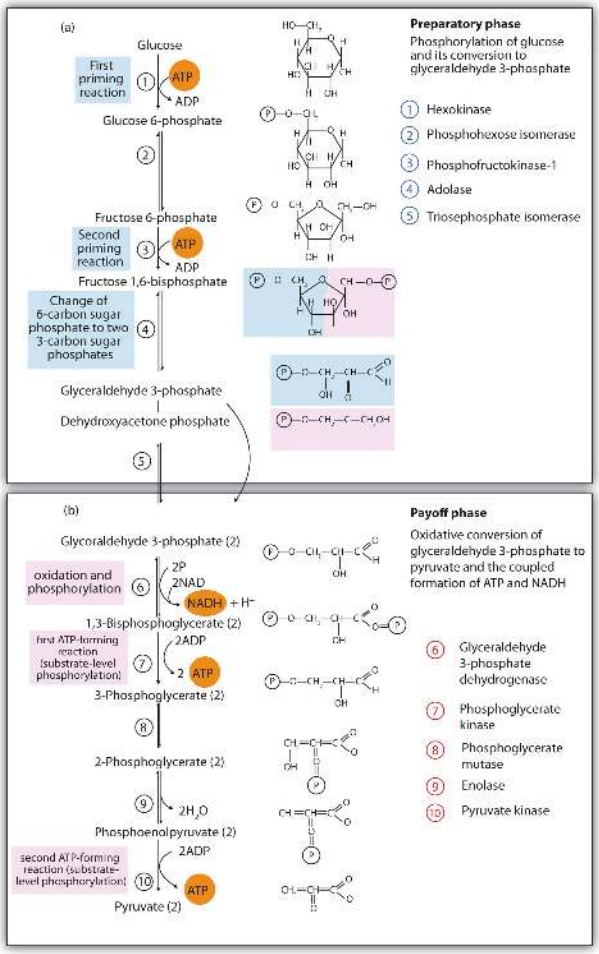


Figure **10.6.1**: Glycolysis reaction process.

When glucose enters a cell, it is immediately phosphorylated to form glucose 6-phosphate, in the first reaction of phase I. The phosphate donor in this reaction is ATP, and the enzyme—which requires magnesium ions for its activity—is *hexokinase*. In this reaction, ATP is being used rather than being synthesized. The presence of such a reaction in a catabolic pathway that is supposed to *generate* energy may surprise you. However, in addition to activating the glucose molecule, this initial reaction is essentially irreversible, an added benefit that keeps the overall process moving in the right direction. Furthermore, the addition of the negatively charged phosphate group prevents the intermediates formed in glycolysis from diffusing through the cell membrane, as neutral molecules such as glucose can do.

In the next reaction, *phosphoglucose isomerase* catalyzes the isomerization of glucose 6-phosphate to fructose 6-phosphate. This reaction is important because it creates a primary alcohol, which can be readily phosphorylated.

The subsequent phosphorylation of fructose 6-phosphate to form fructose 1,6-bisphosphate is catalyzed by *phosphofructokinase*, which requires magnesium ions for activity. ATP is again the phosphate donor.

> *When a molecule contains two phosphate groups on different carbon atoms, the convention is to use the prefix bis. When the two phosphate groups are bonded to each other on the same carbon atom (for example, adenosine diphosphate [ADP]), the prefix is di.*

Fructose 1,6-bisphosphate is enzymatically cleaved by *aldolase* to form two triose phosphates: dihydroxyacetone phosphate and glyceraldehyde 3-phosphate.

Isomerization of dihydroxyacetone phosphate into a second molecule of glyceraldehyde 3-phosphate is the final step in phase I. The enzyme catalyzing this reaction is *triose phosphate isomerase*.

In steps 4 and 5, aldolase and triose phosphate isomerase effectively convert one molecule of fructose 1,6-bisphosphate into *two* molecules of glyceraldehyde 3-phosphate. Thus, phase I of glycolysis requires energy in the form of two molecules of ATP and releases none of the energy stored in glucose.

In the initial step of phase II, glyceraldehyde 3-phosphate is both oxidized and phosphorylated in a reaction catalyzed by *glyceraldehyde-3-phosphate dehydrogenase*, an enzyme that requires nicotinamide adenine dinucleotide (NAD^+) as the oxidizing agent and inorganic phosphate as the phosphate donor. In the reaction, NAD^+ is reduced to reduced nicotinamide adenine dinucleotide (NADH), and 1,3-bisphosphoglycerate (BPG) is formed.

BPG has a high-energy phosphate bond joining a phosphate group to C1. This phosphate group is now transferred directly to a molecule of ADP, thus forming ATP and 3-phosphoglycerate. The enzyme that catalyzes the reaction is *phosphoglycerate kinase*, which, like all other kinases, requires magnesium ions to function. This is the first reaction to produce ATP in the pathway. Because the ATP is formed by a direct transfer of a phosphate group from a metabolite to ADP—that is, from one substrate to another—the process is referred to as **substrate-level phosphorylation**, to distinguish it from the *oxidative phosphorylation.*

In the next reaction, the phosphate group on 3-phosphoglycerate is transferred from the OH group of C3 to the OH group of C2, forming 2-phosphoglycerate in a reaction catalyzed by *phosphoglyceromutase*.

A dehydration reaction, catalyzed by *enolase*, forms phosphoenolpyruvate (PEP), another compound possessing a high-energy phosphate group.

The final step is irreversible and is the second reaction in which substrate-level phosphorylation occurs. The phosphate group of PEP is transferred to ADP, with one molecule of ATP being produced per molecule of PEP. The reaction is catalyzed by *pyruvate kinase*, which requires both magnesium and potassium ions to be active.

In phase II, two molecules of glyceraldehyde 3-phosphate are converted to two molecules of pyruvate, along with the production of four molecules of ATP and two molecules of NADH.

To Your Health: Diabetes

Many topics covered in the course have touched on different aspects of diabetes and the role of insulin in its causation and treatment. Although medical science has made significant progress against this disease, it continues to be a major health threat. Some of the serious complications of diabetes are as follows:

- It is the leading cause of lower limb amputations in the United States.
- It is the leading cause of blindness in adults over age 20.
- It is the leading cause of kidney failure.
- It increases the risk of having a heart attack or stroke by two to four times.

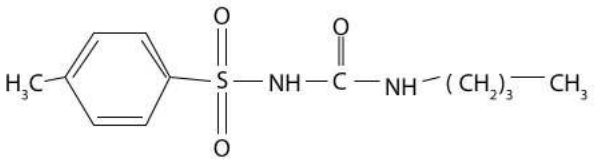
Because a person with diabetes is unable to use glucose properly, excessive quantities accumulate in the blood and the urine. Other characteristic symptoms are constant hunger, weight loss, extreme thirst, and frequent urination because the kidneys excrete large amounts of water in an attempt to remove excess sugar from the blood.

There are two types of diabetes. In immune-mediated diabetes, insufficient amounts of insulin are produced. This type of diabetes develops early in life and is also known as *Type 1 diabetes*, as well as insulin-dependent or juvenile-onset diabetes. Symptoms are rapidly reversed by the administration of insulin, and Type 1 diabetics can lead active lives provided they receive insulin as needed. Because insulin is a protein that is readily digested in the small intestine, it cannot be taken orally and must be injected at least once a day.

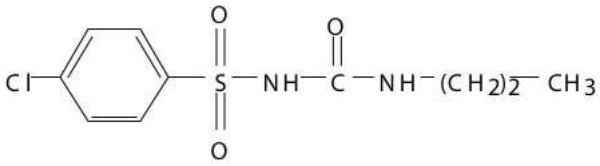
In Type 1 diabetes, insulin-producing cells of the pancreas are destroyed by the body's immune system. Researchers are still trying to find out why. Meanwhile, they have developed a simple blood test capable of predicting who will develop Type 1 diabetes several years before the disease becomes apparent. The blood test reveals the presence of antibodies that destroy the body's insulin-producing cells.

Type 2 diabetes, also known as noninsulin-dependent or adult-onset diabetes, is by far the more common, representing about 95% of diagnosed diabetic cases. (This translates to about 16 million Americans.) Type 2 diabetics usually produce sufficient amounts of insulin, but either the insulin-producing cells in the pancreas do not release enough of it, or it is not used properly because of defective insulin receptors or a lack of insulin receptors on the target cells. In many of these people, the disease can be controlled with a combination of diet and exercise alone. For some people who are overweight, losing weight is sufficient to bring their blood sugar level into the normal range, after which medication is not required if they exercise regularly and eat wisely.

Those who require medication may use oral antidiabetic drugs that stimulate the islet cells to secrete insulin. First-generation antidiabetic drugs stimulated the release of insulin. Newer second-generation drugs, such as glyburide, do as well, but they also increase the sensitivity of cell receptors to insulin. Some individuals with Type 2 diabetes do not produce enough insulin and thus do not respond to these oral medications; they must use insulin. In both Type 1 and Type 2 diabetes, the blood sugar level must be carefully monitored and adjustments made in diet or medication to keep the level as normal as possible (70–120 mg/dL).

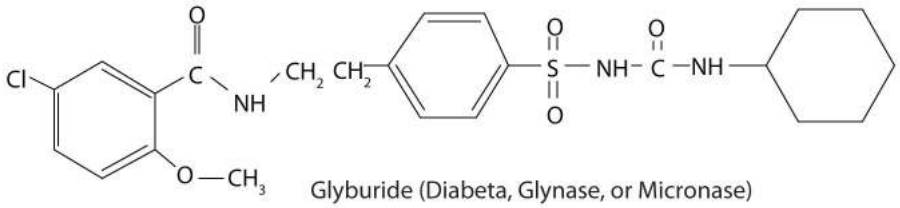


Tolbutamide (Orinase)



Chlorpropamide (Diabinese)

First-Generation Antidiabetic Drugs



Glyburide (Diabeta, Glynase, or Micronase)

Second-Generation Antidiabetic Drugs

Metabolism of Pyruvate

The presence or absence of oxygen determines the fates of the pyruvate and the NADH produced in glycolysis. When plenty of oxygen is available (**aerobic conditions**) pyruvate is completely oxidized to carbon dioxide, with the release of much greater amounts of ATP through the combined actions of the citric acid cycle, the electron transport chain, and oxidative phosphorylation. However, in the absence of oxygen (**anaerobic conditions**), the fate of pyruvate is different in different organisms. In vertebrates, pyruvate is converted to lactate, while other organisms, such as yeast, convert pyruvate to ethanol and carbon dioxide. These possible fates of pyruvate are summarized in Figure **10.6.2**. The conversion to lactate or ethanol under anaerobic conditions allows for the reoxidation of NADH to NAD^+ in the absence of oxygen.

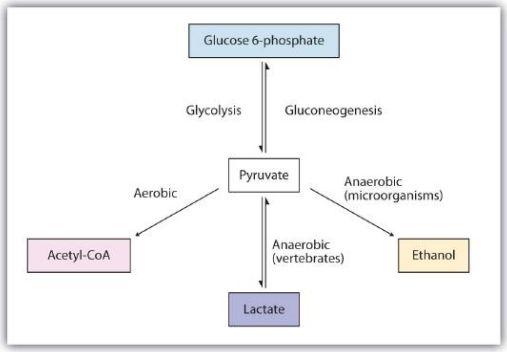


Figure **10.6.2**: Metabolic Fates of Pyruvate.

ATP Yield from Glycolysis

The net energy yield from anaerobic glucose metabolism can readily be calculated in moles of ATP. In the initial phosphorylation of glucose (step 1), 1 mol of ATP is expended, along with another in the phosphorylation of fructose 6-phosphate (step 3). In step 7, 2 mol of BPG (recall that 2 mol of 1,3-BPG are formed for each mole of glucose) are converted to 2 mol of 3-phosphoglycerate, and 2 mol of ATP are produced. In step 10, 2 mol of pyruvate and 2 mol of ATP are formed per mole of glucose.

For every mole of glucose degraded, 2 mol of ATP are initially consumed and 4 mol of ATP are ultimately produced. The net production of ATP is thus 2 mol for each mole of glucose converted to lactate or ethanol. If 7.4 kcal of energy is conserved per mole of ATP produced, and the total amount of energy that can theoretically be obtained from the complete oxidation of 1 mol of

glucose is 670 kcal (as stated in the chapter introduction), the energy conserved in the anaerobic catabolism of glucose to two molecules of lactate (or ethanol) is as follows:

Thus anaerobic cells extract only a very small fraction of the total energy of the glucose molecule.

Contrast this result with the amount of energy obtained when glucose is completely oxidized to carbon dioxide and water through glycolysis, the citric acid cycle, the electron transport chain, and oxidative phosphorylation as summarized in Table **10.6.1**. Note the indication in the table that a variable amount of ATP is synthesized, depending on the tissue, from the NADH formed in the cytoplasm during glycolysis. This is because NADH is not transported into the inner mitochondrial membrane where the enzymes for the electron transport chain are located. Instead, brain and muscle cells use a transport mechanism that passes electrons from the cytoplasmic NADH through the membrane to flavin adenine dinucleotide (FAD) molecules inside the mitochondria, forming reduced flavin adenine dinucleotide ($FADH_2$), which then feeds the electrons into the electron transport chain. This route lowers the yield of ATP to 1.5–2 molecules of ATP, rather than the usual 2.5–3 molecules. A more efficient transport system is found in liver, heart, and kidney cells where the formation of one cytoplasmic NADH molecule results in the formation of one mitochondrial NADH molecule, which leads to the formation of 2.5–3 molecules of ATP.

Table **10.6.1**. Maximum Yield of ATP from the Complete Oxidation of 1 Mol of Glucose

Reaction	Comments	Yield of ATP (moles)
glucose → glucose 6-phosphate	consumes 1 mol ATP	−1
fructose 6-phosphate → fructose 1,6-bisphosphate	consumes 1 mol ATP	−1
glyceraldehyde 3-phosphate → BPG	produces 2 mol of cytoplasmic NADH	
BPG → 3-phosphoglycerate	produces 2 mol ATP	+2
phosphoenolpyruvate → pyruvate	produces 2 mol ATP	+2
pyruvate → acetyl-CoA + CO_2	produces 2 mol NADH	
isocitrate → α-ketoglutarate + CO_2	produces 2 mol NADH	
α-ketoglutarate → succinyl-CoA + CO_2	produces 2 mol NADH	
succinyl-CoA → succinate	produces 2 mol GTP	+2
succinate → fumarate	produces 2 mol $FADH_2$	
malate → oxaloacetate	produces 2 mol NADH	
2 cytoplasmic NADH from glycolysis	yields 2–3 mol ATP per NADH (depending on tissue)	+4 to +6
2 NADH from the oxidation of pyruvate	yields 3 mol ATP per NADH	+6
2 $FADH_2$ from the citric acid cycle	yields 2 ATP per $FADH_2$	+4
3 NADH from the citric acid cycle	yields 3 ATP per NADH	+18
Net yield of ATP:		+36 to +38

The total amount of energy conserved in the aerobic catabolism of glucose in the liver is as follows:

Conservation of 42% of the total energy released compares favorably with the efficiency of any machine. In comparison, automobiles are only about 20%–25% efficient in using the energy released by the combustion of gasoline.

As indicated earlier, the 58% of released energy that is not conserved enters the surroundings (that is, the cell) as heat that helps to maintain body temperature. If we are exercising strenuously and our metabolism speeds up to provide the energy needed for muscle

contraction, more heat is produced. We begin to perspire to dissipate some of that heat. As the perspiration evaporates, the excess heat is carried away from the body by the departing water vapor.

Example 10.6.1

In glycolysis, how many molecules of pyruvate are produced from one molecule of glucose?

Solution

two

Exercise 10.6.1

In anaerobic glycolysis, how many molecules of ATP are produced from one molecule of glucose?

KEY TAKEAWAYS

- The monosaccharide glucose is broken down through a series of enzyme-catalyzed reactions known as glycolysis.
- For each molecule of glucose that is broken down, two molecules of pyruvate, two molecules of ATP, and two molecules of NADH are produced.
- In the absence of oxygen, pyruvate is converted to lactate, and NADH is reoxidized to NAD^+. In the presence of oxygen, pyruvate is converted to acetyl-CoA and then enters the citric acid cycle.
- More ATP can be formed from the breakdown of glucose when oxygen is present.

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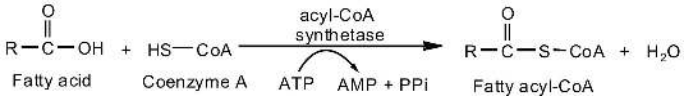
10.7: Stage II of Lipid Catabolism

Learning Objectives

- To describe the reactions needed to completely oxidize a fatty acid to carbon dioxide and water.

Like glucose, the fatty acids released in the digestion of triglycerides and other lipids are broken down in a series of sequential reactions accompanied by the gradual release of usable energy. Some of these reactions are oxidative and require nicotinamide adenine dinucleotide (NAD^+) and flavin adenine dinucleotide (FAD). The enzymes that participate in fatty acid catabolism are located in the mitochondria, along with the enzymes of the citric acid cycle, the electron transport chain, and oxidative phosphorylation. This localization of enzymes in the mitochondria is of the utmost importance because it facilitates efficient utilization of energy stored in fatty acids and other molecules.

Fatty acid oxidation is initiated on the outer mitochondrial membrane. There the fatty acids, which like carbohydrates are relatively inert, must first be activated by conversion to an energy-rich fatty acid derivative of coenzyme A called *fatty acyl-coenzyme A* (CoA). The activation is catalyzed by *acyl-CoA synthetase*. For each molecule of fatty acid activated, one molecule of coenzyme A and one molecule of adenosine triphosphate (ATP) are used, equaling a net utilization of the two high-energy bonds in one ATP molecule (which is therefore converted to adenosine monophosphate [AMP] rather than adenosine diphosphate [ADP]):



The fatty acyl-CoA diffuses to the inner mitochondrial membrane, where it combines with a carrier molecule known as carnitine in a reaction catalyzed by *carnitine acyltransferase*. The acyl-carnitine derivative is transported into the mitochondrial matrix and converted back to the fatty acyl-CoA.

Steps in the β-Oxidation of Fatty Acids

Further oxidation of the fatty acyl-CoA occurs in the mitochondrial matrix via a sequence of four reactions known collectively as **β-oxidation** because the β-carbon undergoes successive oxidations in the progressive removal of two carbon atoms from the carboxyl end of the fatty acyl-CoA (Figure 10.7.1).

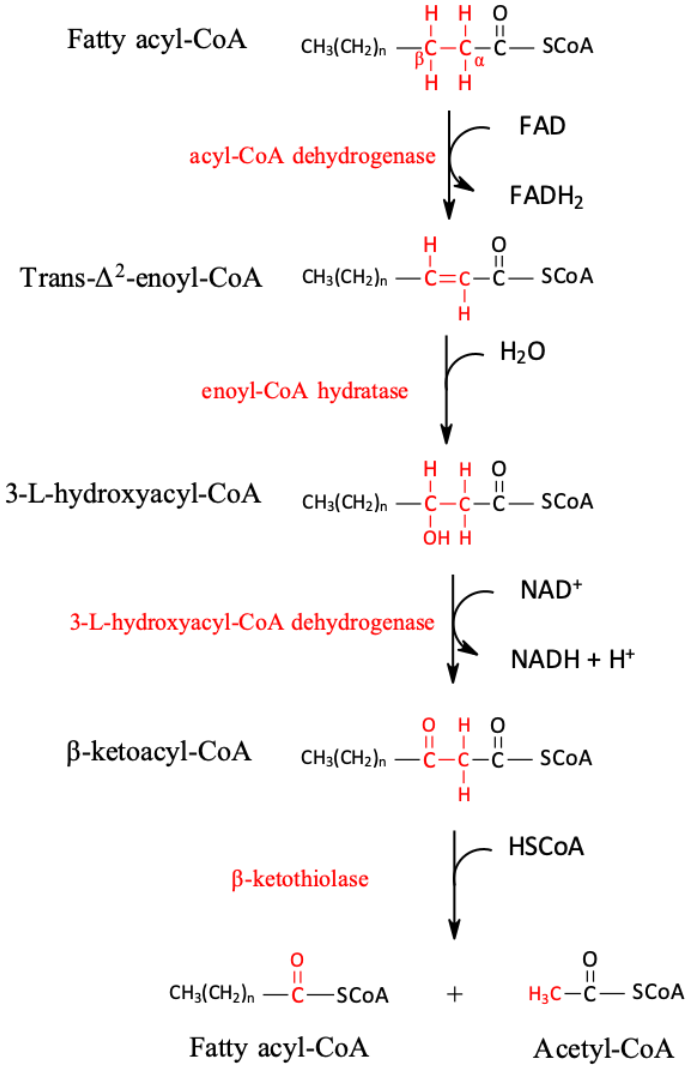


Figure **10.7.1**: Fatty Acid Oxidation. The fatty acyl-CoA formed in the final step becomes the substrate for the first step in the next round of β-oxidation. β-oxidation continues until two acetyl-CoA molecules are produced in the final step.

The first step in the catabolism of fatty acids is the formation of an alkene in an oxidation reaction catalyzed by *acyl-CoA dehydrogenase*. In this reaction, the coenzyme FAD accepts two hydrogen atoms from the acyl-CoA, one from the α-carbon and one from the β-carbon, forming reduced flavin adenine dinucleotide ($FADH_2$).

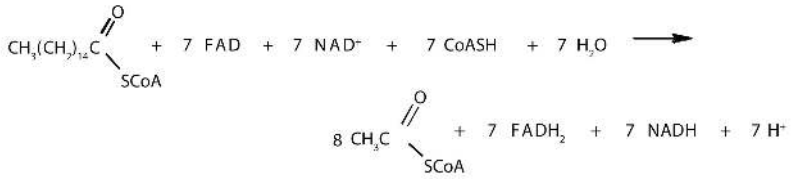
> *The $FADH_2$ is reoxidized back to FAD via the electron transport chain that supplies energy to form 1.5–2 molecules of ATP.*

Next, the *trans*-alkene is hydrated to form a secondary alcohol in a reaction catalyzed by *enoyl-CoA hydratase*. The enzyme forms only the L-isomer.

The secondary alcohol is then oxidized to a ketone by *β-hydroxyacyl-CoA dehydrogenase*, with NAD^+ acting as the oxidizing agent. The reoxidation of each molecule of NADH to NAD^+ by the electron transport chain furnishes 2.5–3 molecules of ATP.

The final reaction is cleavage of the β-ketoacyl-CoA by a molecule of coenzyme A. The products are acetyl-CoA and a fatty acyl-CoA that has been shortened by two carbon atoms. The reaction is catalyzed by *thiolase*.

The shortened fatty acyl-CoA is then degraded by repetitions of these four steps, each time releasing a molecule of acetyl-CoA. The overall equation for the β-oxidation of palmitoyl-CoA (16 carbon atoms) is as follows:

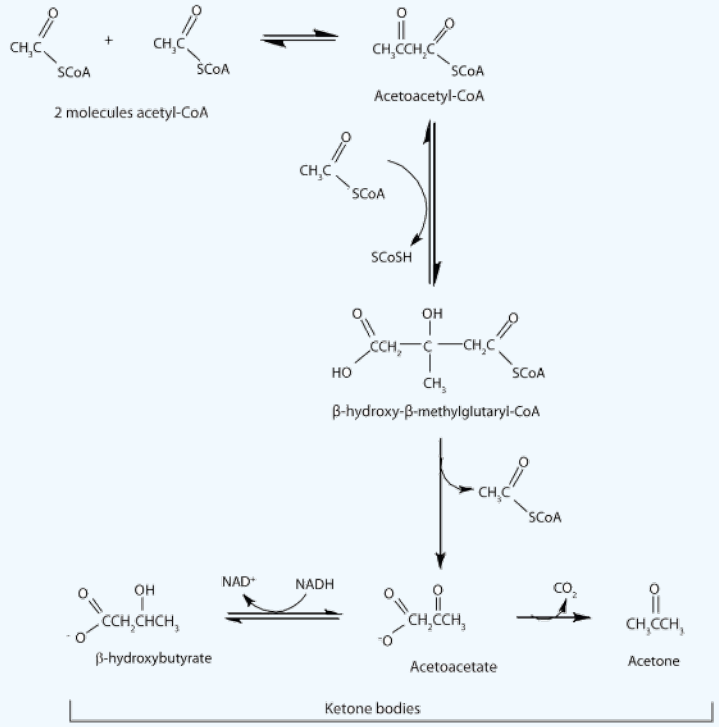


> *Because each shortened fatty acyl-CoA cycles back to the beginning of the pathway, β-oxidation is sometimes referred to as the fatty acid spiral.*

The fate of the acetyl-CoA obtained from fatty acid oxidation depends on the needs of an organism. It may enter the citric acid cycle and be oxidized to produce energy, it may be used for the formation of water-soluble derivatives known as ketone bodies, or it may serve as the starting material for the synthesis of fatty acids. For more information about the citric acid cycle.

Looking Closer: Ketone Bodies

In the liver, most of the acetyl-CoA obtained from fatty acid oxidation is oxidized by the citric acid cycle. However, some of the acetyl-CoA is used to synthesize a group of compounds known as *ketone bodies*: acetoacetate, β-hydroxybutyrate, and acetone. Two acetyl-CoA molecules combine, in a reversal of the final step of β-oxidation, to produce acetoacetyl-CoA. The acetoacetyl-CoA reacts with another molecule of acetyl-CoA and water to form β-hydroxy-β-methylglutaryl-CoA, which is then cleaved to acetoacetate and acetyl-CoA. Most of the acetoacetate is reduced to β-hydroxybutyrate, while a small amount is decarboxylated to carbon dioxide and acetone.



The acetoacetate and β-hydroxybutyrate synthesized by the liver are released into the blood for use as a metabolic fuel (to be converted back to acetyl-CoA) by other tissues, particularly the kidney and the heart. Thus, during prolonged starvation, ketone bodies provide about 70% of the energy requirements of the brain. Under normal conditions, the kidneys excrete about 20 mg of ketone bodies each day, and the blood levels are maintained at about 1 mg of ketone bodies per 100 mL of blood.

In starvation, diabetes mellitus, and certain other physiological conditions in which cells do not receive sufficient amounts of carbohydrate, the rate of fatty acid oxidation increases to provide energy. This leads to an increase in the concentration of acetyl-CoA. The increased acetyl-CoA cannot be oxidized by the citric acid cycle because of a decrease in the concentration of oxaloacetate, which is diverted to glucose synthesis. In response, the rate of ketone body formation in the liver increases

further, to a level much higher than can be used by other tissues. The excess ketone bodies accumulate in the blood and the urine, a condition referred to as *ketosis*. When the acetone in the blood reaches the lungs, its volatility causes it to be expelled in the breath. The sweet smell of acetone, a characteristic of ketosis, is frequently noticed on the breath of severely diabetic patients.

Because two of the three kinds of ketone bodies are weak acids, their presence in the blood in excessive amounts overwhelms the blood buffers and causes a marked decrease in blood pH (to 6.9 from a normal value of 7.4). This decrease in pH leads to a serious condition known as *acidosis*. One of the effects of acidosis is a decrease in the ability of hemoglobin to transport oxygen in the blood. In moderate to severe acidosis, breathing becomes labored and very painful. The body also loses fluids and becomes dehydrated as the kidneys attempt to get rid of the acids by eliminating large quantities of water. The lowered oxygen supply and dehydration lead to depression; even mild acidosis leads to lethargy, loss of appetite, and a generally run-down feeling. Untreated patients may go into a coma. At that point, prompt treatment is necessary if the person's life is to be saved.

ATP Yield from Fatty Acid Oxidation

The amount of ATP obtained from fatty acid oxidation depends on the size of the fatty acid being oxidized. For our purposes here. we'll study palmitic acid, a saturated fatty acid with 16 carbon atoms, as a typical fatty acid in the human diet. Calculating its energy yield provides a model for determining the ATP yield of all other fatty acids.

The breakdown by an organism of 1 mol of palmitic acid requires 1 mol of ATP (for activation) and forms 8 mol of acetyl-CoA. Recall that each mole of acetyl-CoA metabolized by the citric acid cycle yields 10 mol of ATP. The complete degradation of 1 mol of palmitic acid requires the β-oxidation reactions to be repeated seven times. Thus, 7 mol of NADH and 7 mol of $FADH_2$ are produced. Reoxidation of these compounds through respiration yields 2.5–3 and 1.5–2 mol of ATP, respectively. The energy calculations can be summarized as follows:

1 mol of ATP is split to AMP and $2P_i$	−2 ATP
8 mol of acetyl-CoA formed (8 × 12)	96 ATP
7 mol of $FADH_2$ formed (7 × 2)	14 ATP
7 mol of NADH formed (7 × 3)	21 ATP
Total	129 ATP

> *The number of times β-oxidation is repeated for a fatty acid containing n carbon atoms is n/2 – 1 because the final turn yields two acetyl-CoA molecules.*

The combustion of 1 mol of palmitic acid releases a considerable amount of energy:

$$C_{16}H_{32}O_2 + 23O_2 \rightarrow 16CO_2 + 16H_2O + 2,340\ kcal \tag{10.7.1}$$

The percentage of this energy that is conserved by the cell in the form of ATP is as follows:

$$\frac{\text{energy conserved}}{\text{total energy available}} \times 100 = \frac{(129\ \text{ATP})(7.4\ \text{kcal/ATP})}{2,340\ \text{kcal}} \times 100 = 41\% \tag{10.7.2}$$

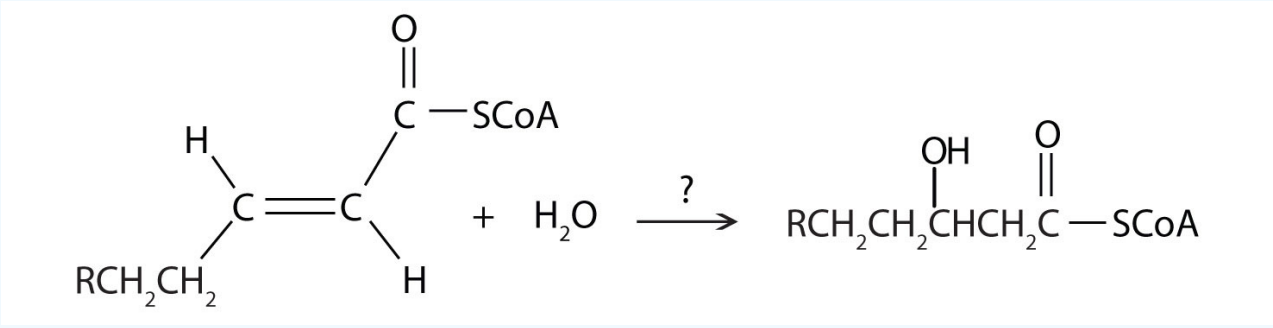
The efficiency of fatty acid metabolism is comparable to that of carbohydrate metabolism, which we calculated to be 42%. For more information about the efficiency of fatty acid metabolism.

> *The oxidation of fatty acids produces large quantities of water. This water, which sustains migratory birds and animals (such as the camel) for long periods of time.*

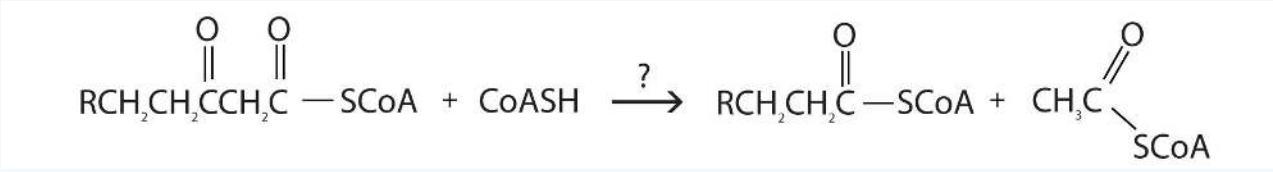
Example 10.7.1

For each reaction found in β-oxidation, identify the enzyme that catalyzes the reaction and classify the reaction as oxidation-reduction, hydration, or cleavage.

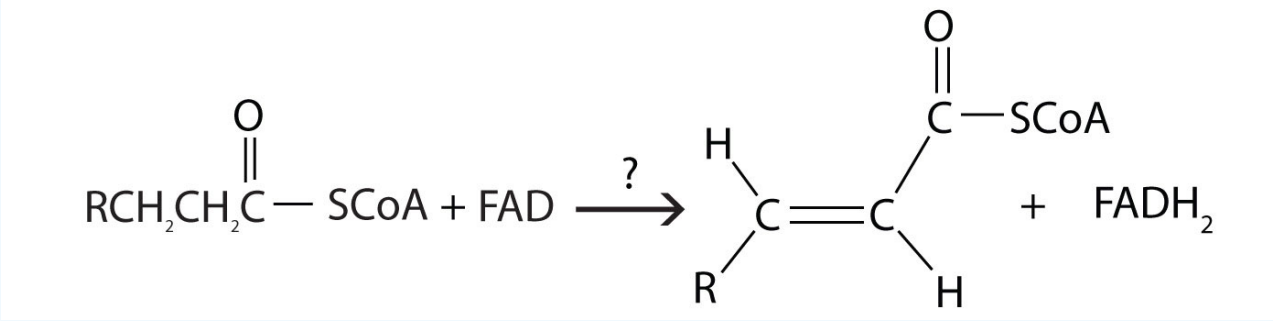
a.



b.



c.



Solution

a. enoyl-CoA hydratase; hydration
b. thiolase; cleavage
c. acyl-CoA dehydrogenase; oxidation-reduction

Example 10.7.2

How many rounds of β-oxidation are necessary to metabolize lauric acid (a saturated fatty acid with 12 carbon atoms)?

Solution

five rounds

Exercise 10.7.1

How many rounds of β-oxidation are necessary to metabolize arachidic acid (a saturated fatty acid with 20 carbon atoms)?

Example 10.7.3

When myristic acid (a saturated fatty acid with 14 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?

a. acetyl-CoA

b. $FADH_2$

Solution

a. 7 molecules
b. 6 molecules

Exercise 10.7.2

When myristic acid (a saturated fatty acid with 14 carbon atoms) is completely oxidized by β-oxidation, how many NADH molecules are formed?

Key Takeaways

- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β-oxidation.
- In each round of β-oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

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10.8: Stage II of Protein Catabolism

Learning Objectives

- To describe how excess amino acids are degraded.

The liver is the principal site of amino acid metabolism, but other tissues, such as the kidney, the small intestine, muscles, and adipose tissue, take part. Generally, the first step in the breakdown of amino acids is the separation of the amino group from the carbon skeleton, usually by a transamination reaction. The carbon skeletons resulting from the deaminated amino acids are used to form either glucose or fats, or they are converted to a metabolic intermediate that can be oxidized by the citric acid cycle. The latter alternative, amino acid catabolism, is more likely to occur when glucose levels are low—for example, when a person is fasting or starving.

Transamination

Transamination is an exchange of functional groups between any amino acid (except lysine, proline, and threonine) and an α-keto acid. The amino group is usually transferred to the keto carbon atom of pyruvate, oxaloacetate, or α-ketoglutarate, converting the α-keto acid to alanine, aspartate, or glutamate, respectively. Transamination reactions are catalyzed by specific transaminases (also called aminotransferases), which require pyridoxal phosphate as a coenzyme.

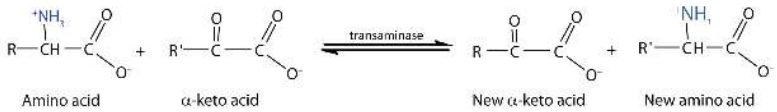


Figure 10.8.1): Transamination reaction.

> *In an α-keto acid, the carbonyl or keto group is located on the carbon atom adjacent to the carboxyl group of the acid.*

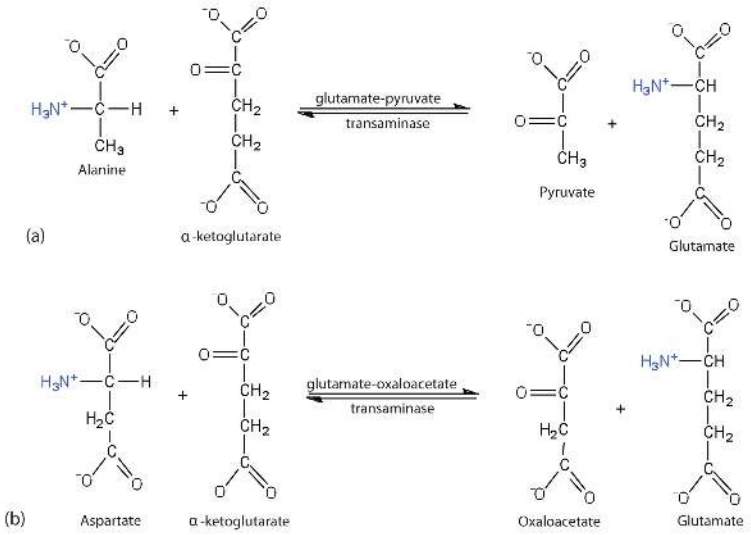
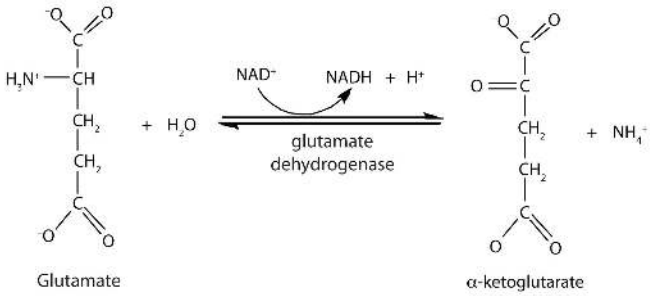


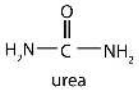
Figure 10.8.2: Two Transamination Reactions. In both reactions, the final acceptor of the amino group is α-ketoglutarate, and the final product is glutamate.

Oxidative Deamination

In the breakdown of amino acids for energy, the final acceptor of the α-amino group is α-ketoglutarate, forming glutamate. Glutamate can then undergo **oxidative deamination**, in which it loses its amino group as an ammonium (NH_4^+) ion and is oxidized back to α-ketoglutarate (ready to accept another amino group):



This reaction occurs primarily in liver mitochondria. Most of the NH_4^+ ion formed by oxidative deamination of glutamate is converted to urea and excreted in the urine in a series of reactions known as the **urea cycle**.



The synthesis of glutamate occurs in animal cells by reversing the reaction catalyzed by glutamate dehydrogenase. For this reaction nicotinamide adenine dinucleotide phosphate (NADPH) acts as the reducing agent. The synthesis of glutamate is significant because it is one of the few reactions in animals that can incorporate inorganic nitrogen (NH_4^+) into an α-keto acid to form an amino acid. The amino group can then be passed on through transamination reactions, to produce other amino acids from the appropriate α-keto acids.

The Fate of the Carbon Skeleton

Any amino acid can be converted into an intermediate of the citric acid cycle. Once the amino group is removed, usually by transamination, the α-keto acid that remains is catabolized by a pathway unique to that acid and consisting of one or more reactions. For example, phenylalanine undergoes a series of six reactions before it splits into fumarate and acetoacetate. Fumarate is an intermediate in the citric acid cycle, while acetoacetate must be converted to acetoacetyl-coenzyme A (CoA) and then to acetyl-CoA before it enters the citric acid cycle.

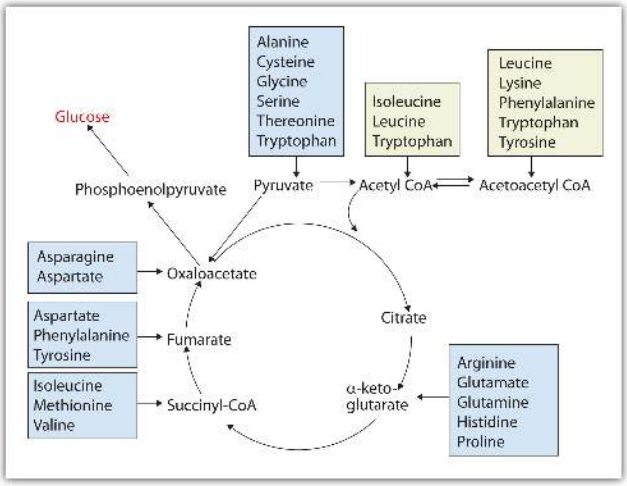


Figure **10.8.3**: Fates of the Carbon Skeletons of Amino Acids

Those amino acids that can form any of the intermediates of carbohydrate metabolism can subsequently be converted to glucose via a metabolic pathway known as **gluconeogenesis**. These amino acids are called **glucogenic amino acids**. Amino acids that are converted to acetoacetyl-CoA or acetyl-CoA, which can be used for the synthesis of ketone bodies but not glucose, are called **ketogenic amino acids**. Some amino acids fall into both categories. Leucine and lysine are the only amino acids that are exclusively ketogenic. Figure **10.8.3** summarizes the ultimate fates of the carbon skeletons of the 20 amino acids.

https://chem.libretexts.org/@go/page/342879

Career Focus: Exercise Physiologist

An exercise physiologist works with individuals who have or wish to prevent developing a wide variety of chronic diseases, such as diabetes, in which exercise has been shown to be beneficial. Each individual must be referred by a licensed physician. An exercise physiologist works in a variety of settings, such as a hospital or in a wellness program at a commercial business, to design and monitor individual exercise plans. A registered clinical exercise physiologist must have an undergraduate degree in exercise physiology or a related degree. Some job opportunities require a master's degree in exercise physiology or a related degree.



Ergospirometry laboratory for the measurement of metabolic changes during a graded exercise test on a treadmill. from Wikipedia.

Example 10.8.1

Determine if each amino acid is glucogenic, ketogenic, or both.

a. asparagine
b. tyrosine
c. valine

Solution

a. glucogenic
b. both
c. glucogenic

Exercise 10.8.1

Determine if each amino acid is glucogenic, ketogenic, or both.

a. phenylalanine
b. leucine
c. serine

Summary

Generally the first step in the breakdown of amino acids is the removal of the amino group, usually through a reaction known as transamination. The carbon skeletons of the amino acids undergo further reactions to form compounds that can either be used for the synthesis of glucose or the synthesis of ketone bodies.

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10.9: Metabolism (Exercises)

20.1: ATP- the Universal Energy Currency

Concept Review Exercise

1. Why is ATP referred to as the energy currency of the cell?

Answer

1. ATP is the principal molecule involved in energy exchange reactions in biological systems.

Exercises

1. How do ATP and ADP differ in structure?
2. Why does the hydrolysis of ATP to ADP involve the release of energy?
3. Identify whether each compound would be classified as a high-energy phosphate compound.
   a. ATP
   b. glucose 6-phosphate
   c. creatine phosphate
4. Identify whether each compound would be classified as a high-energy phosphate compound.
   a. ADP
   b. AMP
   c. glucose 1-phosphate

Answers

1. ATP has a triphosphate group attached, while ADP has only a diphosphate group attached.

3. a. yes
   b. no
   c. yes

20.2: Stage I of Catabolism

Concept Review Exercises

1. Distinguish between each pair of compounds.
   a. pepsin and pepsinogen
   b. chymotrypsin and trypsin
   c. aminopeptidase and carboxypeptidase
2. What are the primary end products of each form of digestion?
   a. carbohydrate digestion
   b. lipid digestion
   c. protein digestion
3. In what section of the digestive tract does most of the carbohydrate, lipid, and protein digestion take place?

Answers

1. a. Pepsinogen is an inactive form of pepsin; pepsin is the active form of the enzyme.
   b. Both enzymes catalyze the hydrolysis of peptide bonds. Chymotrypsin catalyzes the hydrolysis of peptide bonds following aromatic amino acids, while trypsin catalyzes the hydrolysis of peptide bonds following lysine and arginine.
   c. Aminopeptidase catalyzes the hydrolysis of amino acids from the N-terminal end of a protein, while carboxypeptidase catalyzes the hydrolysis of amino acids from the C-terminal end of a protein.
2. a. glucose, fructose, and galactose

b. monoglycerides and fatty acids
c. amino acids

3. the small intestine

Exercises

1. What are the products of digestion (or stage I of catabolism)?
2. What is the general type of reaction used in digestion?
3. Give the site of action and the function of each enzyme.
   a. chymotrypsin
   b. lactase
   c. pepsin
   d. maltase
4. Give the site of action and the function of each enzyme.
   a. α-amylase
   b. trypsin
   c. sucrase
   d. aminopeptidase
5. a. What is the meaning of the following statement? “Bile salts act to emulsify lipids in the small intestine.”
   b. Why is emulsification important?
6. Using chemical equations, describe the chemical changes that triglycerides undergo during digestion.
7. What are the expected products from the enzymatic action of chymotrypsin on each amino acid segment?
   a. gly-ala-phe-thr-leu
   b. ala-ile-tyr-ser-arg
   c. val-trp-arg-leu-cys
8. What are the expected products from the enzymatic action of trypsin on each amino acid segment?
   a. leu-thr-glu-lys-ala
   b. phe-arg-ala-leu-val
   c. ala-arg-glu-trp-lys

Answers

1. proteins: amino acids; carbohydrates: monosaccharides; fats: fatty acids and glycerol
3. a. Chymotrypsin is found in the small intestine and catalyzes the hydrolysis of peptide bonds following aromatic amino acids.
   b. Lactase is found in the small intestine and catalyzes the hydrolysis of lactose.
   c. Pepsin is found in the stomach and catalyzes the hydrolysis of peptide bonds, primarily those that occur after aromatic amino acids.
   d. Maltase is found in the small intestine and catalyzes the hydrolysis of maltose.
5. a. Bile salts aid in digestion by dispersing lipids throughout the aqueous solution in the small intestine.
   b. Emulsification is important because lipids are not soluble in water; it breaks lipids up into smaller particles that can be more readily hydrolyzed by lipases.
7. a. gly-ala-phe and thr-leu
   b. ala-ile-tyr and ser-arg
   c. val-trp and arg-leu-cys

20.3: Overview of Stage II of Catabolism

Concept Review Exercises

1. What is a metabolic pathway?
2. What vitamin is required to make coenzyme A?
3. What is the net yield of Glycolysis as far as ATP?
4. Name the enzymes that are key regulatory sites in Glycolysis.
5. Why are the enzymes in the previous question targets for regulation?
6. Why is the priming phase necessary?
7. Draw the entire pathway for glycolysis including enzymes, reactants and products for each step.
8. Where does beta-oxidation occur?
9. What is the average net yield of ATP per carbon?
10. Where exactly is water formed during the process of fatty acid degradation? (Hint: H_2O is formed when when the one of the products of beta-oxidation is passed through another of the metabolic pathways)
11. During the process of beta-oxidation, why is it that [FAD] is used to oxidize an alkane to an alkene while NAD^+ is used to oxidize an alchol to a carbonyl
12. Draw out the entire process of the degradation of a triglyceride, include enzymes and products and reactants for each step.

Answers

1. A metabolic pathway is a series of biochemical reactions by which an organism converts a given reactant to a specific end product.
2. pantothenic acid

20.4: Stage III of Catabolism

Concept Review Exercises

1. What is the main function of the citric acid cycle?
2. Two carbon atoms are fed into the citric acid cycle as acetyl-CoA. In what form are two carbon atoms removed from the cycle?
3. What are mitochondria and what is their function in the cell?

Answers

1. the complete oxidation of carbon atoms to carbon dioxide and the formation of a high-energy phosphate compound, energy rich reduced coenzymes (NADH and $FADH_2$), and metabolic intermediates for the synthesis of other compounds
2. as carbon dioxide
3. Mitochondria are small organelles with a double membrane that contain the enzymes and other molecules needed for the production of most of the ATP needed by the body.

Exercises

1. Replace each question mark with the correct compound.
   a. $\text{?} \xrightarrow{\text{aconitase}} \text{isocitrate}$
   b. $\text{?} + \text{?} \xrightarrow{\text{citrate synthase}} \text{citrate} + \text{coenzyme A}$
   c. $\text{fumarate} \xrightarrow{\text{fumarase}} \text{?}$
   d. $\text{isocitrate} + \text{NAD}^+ \xrightarrow{\text{?}} \alpha\text{-ketoglurate} + \text{NADH} + \text{CO}_2$

2. Replace each question mark with the correct compound.

   a. $\text{malate} + \text{NAD}^+ \xrightarrow{?} \text{oxaloacetate} + \text{NADH}$

   b. $? + ? \xrightarrow{\text{nucleoside diphosphokinase}} \text{GDP} + \text{ATP}$

   c. $\text{succinyl-CoA} \xrightarrow{\text{succinyl-CoA synthetase}} ? + ?$

   d. $\text{succinate} + \text{FAD} \xrightarrow{\text{succinate dehydrogenase}} ? + \text{FADH}_2$

3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

   a. isomerization

   b. hydration

   c. synthesis

4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

   a. oxidation

   b. decarboxylation

   c. phosphorylation

5. What similar role do coenzyme Q and cytochrome c serve in the electron transport chain?

6. What is the electron acceptor at the end of the electron transport chain? To what product is this compound reduced?

7. What is the function of the cytochromes in the electron transport chain?

8. a. What is meant by this statement? “Electron transport is tightly coupled to oxidative phosphorylation.”

   b. How are electron transport and oxidative phosphorylation coupled or linked?

Answers

1. a. citrate

   b. oxaloacetate + acetyl-CoA

   c. malate

   d. α-ketoglutarate hydrogenase complex

3. a. reaction in 1a

   b. reaction in 1c

   c. reaction in 1b

5. Both molecules serve as electron shuttles between the complexes of the electron transport chain.

7. Cytochromes are proteins in the electron transport chain and serve as one-electron carriers.

20.5: Stage II of Carbohydrate Catabolism

- ### Concept Review Exercises

  1. In glycolysis, how many molecules of pyruvate are produced from one molecule of glucose?

  2. In vertebrates, what happens to pyruvate when

     a. plenty of oxygen is available?

     b. oxygen supplies are limited?

  3. In anaerobic glycolysis, how many molecules of ATP are produced from one molecule of glucose?

  #### Answers

  1. two

  2. a. Pyruvate is completely oxidized to carbon dioxide.

     b. Pyruvate is reduced to lactate, allowing for the reoxidation of NADH to NAD^+.

  3. There is a net production of two molecules of ATP.

Exercises

1. Replace each question mark with the correct compound.

   a. $\text{fructose 1, 6-bisphosphate} \xrightarrow{\text{aldolase}} ? + ?$

   b. $? + \text{ADP} \xrightarrow{\text{pyruvate kinase}} \text{pyruvate} + \text{ATP}$

   c. $\text{dihydroxyacetone phosphate} \xrightarrow{?} \text{glyceraldehyde 3-phosphate}$

   d. $\text{glucose} + \text{ATP} \xrightarrow{\text{hexokinase}} ? + \text{ADP}$

2. Replace each question mark with the correct compound.

   a. $\text{fructose 6-phosphate} + \text{ATP} \xrightarrow{?} \text{fructose 1, 6-bisphosphate} + \text{ADP}$

   b. $? \xrightarrow{\text{phosphoglucose isomerase}} \text{fructose 6-phosphate}$

   c. $\text{glyceraldehyde 3-phosphate} + \text{NAD}^+ + \text{P}_\text{i} \xrightarrow{?} \text{1, 3-bisphosphoglycerate} + \text{NADH}$

   d. $\text{3-phosphoglycerate} \xrightarrow{\text{phosphoglyceromutase}} ?$

3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

   a. hydrolysis of a high-energy phosphate compound

   b. synthesis of ATP

4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

   a. isomerization

   b. oxidation

5. What coenzyme is needed as an oxidizing agent in glycolysis?

6. Calculate

   a. the *total* number of molecules of ATP produced for each molecule of glucose converted to pyruvate in glycolysis.

   b. the number of molecules of ATP hydrolyzed in phase I of glycolysis.

   c. the *net* ATP production from glycolysis alone.

7. How is the NADH produced in glycolysis reoxidized when oxygen supplies are limited in

   a. muscle cells?

   b. yeast?

8. a. Calculate the number of moles of ATP produced by the aerobic oxidation of 1 mol of glucose in a liver cell.

   b. Of the total calculated in Exercise 9a, determine the number of moles of ATP produced in each process.

      a. glycolysis alone

      b. the citric acid cycle

      c. the electron transport chain and oxidative phosphorylation

Answers

1. a. glyceraldehyde 3-phosphate + dihydroxyacetone phosphate

   b. phosphoenolpyruvate

   c. triose phosphate isomerase

   d. glucose 6-phosphate

3. a. reactions 1b, 1d, and 2a

   b. reaction 1b

5. NAD^+

7. a. Pyruvate is reduced to lactate, and NADH is reoxidized to NAD^+.

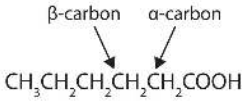
   b. Pyruvate is converted to ethanol and carbon dioxide, and NADH is reoxidized to NAD^+.

20.6: Stage II of Lipid Catabolism

- ### Concept Review Exercises

1. How are fatty acids activated prior to being transported into the mitochondria and oxidized?
2. Draw the structure of hexanoic (caproic) acid and identify the α-carbon and the β-carbon.

Answers

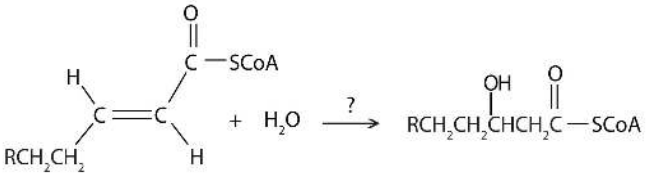
1. They react with CoA to form fatty acyl-CoA molecules.
2. 

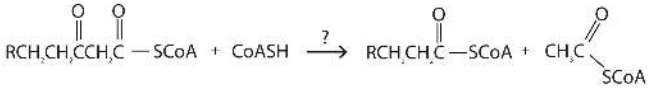
Key Takeaways

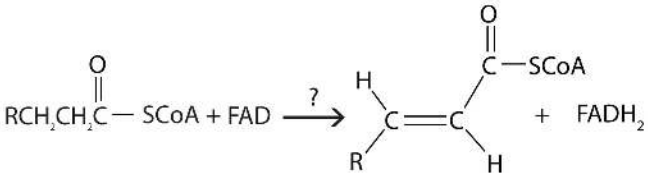
- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β-oxidation.
- In each round of β-oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

Exercises

1. For each reaction found in β-oxidation, identify the enzyme that catalyzes the reaction and classify the reaction as oxidation-reduction, hydration, or cleavage.

a. 

b. 

c. 

2. What are the products of β-oxidation?
3. How many rounds of β-oxidation are necessary to metabolize lauric acid (a saturated fatty acid with 12 carbon atoms)?
4. How many rounds of β-oxidation are necessary to metabolize arachidic acid (a saturated fatty acid with 20 carbon atoms)?
5. When myristic acid (a saturated fatty acid with 14 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA
   b. $FADH_2$
   c. NADH
6. When stearic acid (a saturated fatty acid with 18 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA

b. $FADH_2$

c. NADH

7. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of myristic acid?
8. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of stearic acid?

Answers

1. a. enoyl-CoA hydratase; hydration

   b. thiolase; cleavage

   c. acyl-CoA dehydrogenase; oxidation-reduction

3. five rounds
5. a. 7 molecules

   b. 6 molecules

   c. 6 molecules

7. 112 molecules

20.7: Stage II of Protein Catabolism

Concept Review Exercises

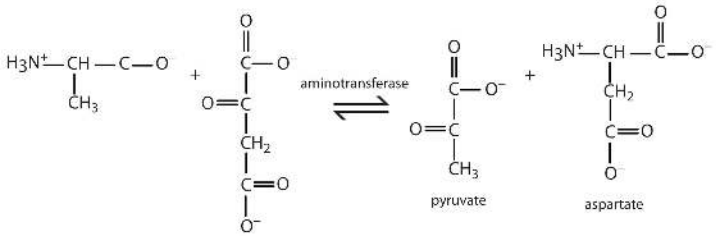
1. a. Write the equation for the transamination reaction between alanine and oxaloacetate.

   b. Name the two products that are formed.

2. What is the purpose of oxidative deamination?

Answers

1. a.



   b. pyruvate and aspartate

2. Oxidative deamination provides a reaction in which the amino group [as the ammonium (NH_4^+) ion] is removed from a molecule, not simply transferred from one molecule to another. Most of the NH_4^+ ion is converted to urea and excreted from the body.

Exercises

1. Write the equation for the transamination reaction between valine and pyruvate.
2. Write the equation for the transamination reaction between phenylalanine and oxaloacetate.
3. What products are formed in the oxidative deamination of glutamate?
4. Determine if each amino acid is glucogenic, ketogenic, or both.

   a. phenylalanine

   b. leucine

   c. serine

5. Determine if each amino acid is glucogenic, ketogenic, or both.

   a. asparagine

   b. tyrosine

   c. valine

Answers



1.

3. α-ketoglutarate, NADH, and NH_4^+

5. a. glucogenic
   b. both
   c. glucogenic

Additional Exercises

1. Hydrolysis of which compound—arginine phosphate or glucose 6-phosphate—would provide enough energy for the phosphorylation of ATP? Why?
2. If a cracker, which is rich in starch, is chewed for a long time, it begins to develop a sweet, sugary taste. Why?
3. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.

   a. aminopeptidase
   b. chymotrypsin

4. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.

   a. trypsin
   b. carboxypeptidase

5. If the methyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?
6. If the carbonyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?
7. The average adult consumes about 65 g of fructose daily (either as the free sugar or from the breakdown of sucrose). In the liver, fructose is first phosphorylated to fructose 1-phosphate, which is then split into dihydroxyacetone phosphate and glyceraldehyde. Glyceraldehyde is then phosphorylated to glyceraldehyde 3-phosphate, with ATP as the phosphate group donor. Write the equations (using structural formulas) for these three steps. Indicate the type of enzyme that catalyzes each step.
8. What critical role is played by both BPG and PEP in glycolysis?
9. How is the NADH produced in glycolysis reoxidized when oxygen supplies are abundant?
10. When a triglyceride is hydrolyzed to form three fatty acids and glycerol, the glycerol can be converted to glycerol 3-phosphate and then oxidized to form dihydroxyacetone phosphate, an intermediate of glycolysis. (In this reaction, NAD^+ is reduced to NADH.) If you assume that there is sufficient oxygen to completely oxidize the pyruvate formed from dihydroxyacetone phosphate, what is the maximum amount of ATP formed from the complete oxidation of 1 mol of glycerol?
11. How is the $FADH_2$ from β-oxidation converted back to FAD?
12. If 1 mol of alanine is converted to pyruvate in a muscle cell (through transamination) and the pyruvate is then metabolized via the citric acid cycle, the electron transport chain, and oxidative phosphorylation, how many moles of ATP are produced?
13. If the essential amino acid leucine (2-amino-4-methylpentanoic acid) is lacking in the diet, an α-keto acid can substitute for it. Give the structure of the α-keto acid and the probable reaction used to form leucine from this α-keto acid.

Answers

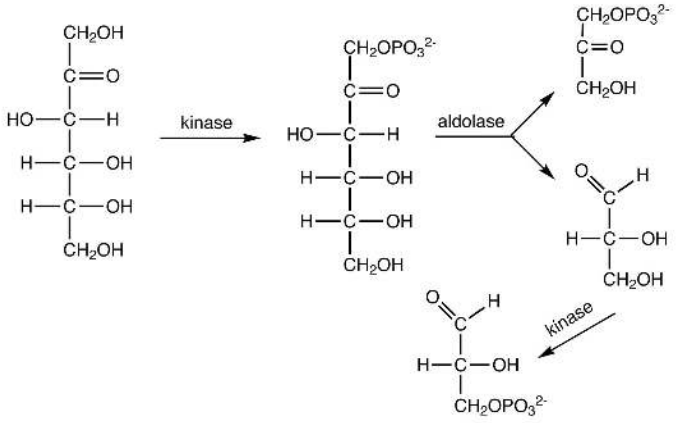
1. The hydrolysis of arginine phosphate releases more energy than is needed for the synthesis of ATP, while hydrolysis of glucose 6-phosphate does not.

3.

a. The enzyme will cleave off amino acids one at a time beginning with alanine (the N-terminal end).
b. following phenylalanine

5. Half of the label will be on the second carbon atom of oxaloacetate, while the other half will be on the third carbon atom.

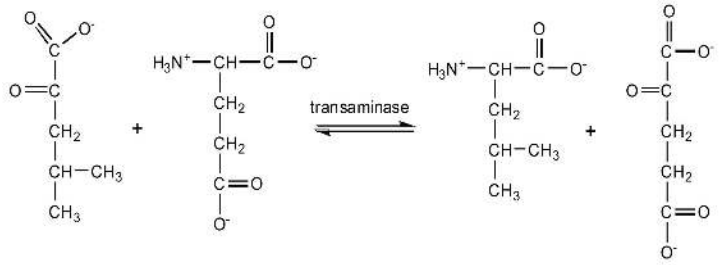
7.



9. When oxygen is abundant, NADH is reoxidized through the reactions of the electron transport chain.

11. $FADH_2$ is reoxidized back to FAD via the electron transport chain.

13.



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10.10: Metabolism (Summary)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Metabolism is the general term for all chemical reactions in living organisms. The two types of metabolism are **catabolism**—those reactions in which complex molecules (carbohydrates, lipids, and proteins) are broken down to simpler ones with the concomitant release of energy—and **anabolism**—those reactions that consume energy to build complex molecules. Metabolism is studied by looking at individual **metabolic pathways**, which are a series of biochemical reactions in which a given reactant is converted to a desired end product.

The oxidation of fuel molecules (primarily carbohydrates and lipids), a process called **respiration**, is the source of energy used by cells. Catabolic reactions release energy from food molecules and use some of that energy for the synthesis of *adenosine triphosphate* (ATP); anabolic reactions use the energy in ATP to create new compounds. Catabolism can be divided into three stages. In stage I, carbohydrates, lipids, and proteins are broken down into their individual monomer units—simple sugars, fatty acids, and amino acids, respectively. In stage II, these monomer units are broken down by specific metabolic pathways to form a common end product *acetyl-coenzyme A* (CoA). In stage III, acetyl-CoA is completely oxidized to form carbon dioxide and water, and ATP is produced.

The **digestion** of carbohydrates begins in the mouth as α-amylase breaks glycosidic linkages in carbohydrate molecules. Essentially no carbohydrate digestion occurs in the stomach, and food particles pass through to the small intestine, where α-amylase and intestinal enzymes convert complex carbohydrate molecules (starches) to monosaccharides. The monosaccharides then pass through the lining of the small intestine and into the bloodstream for transport to all body cells.

Protein digestion begins in the stomach as pepsinogen in **gastric juice** is converted to pepsin, the enzyme that hydrolyzes peptide bonds. The partially digested protein then passes to the small intestine, where the remainder of protein digestion takes place through the action of several enzymes. The resulting amino acids cross the intestinal wall into the blood and are carried to the liver.

Lipid digestion begins in the small intestine. Bile salts emulsify the lipid molecules, and then lipases hydrolyze them to fatty acids and monoglycerides. The hydrolysis products pass through the intestine and are repackaged for transport in the bloodstream.

In cells that are operating aerobically, acetyl-CoA produced in stage II of catabolism is oxidized to carbon dioxide. The **citric acid cycle** describes this oxidation, which takes place with the formation of the coenzymes reduced nicotinamide adenine dinucleotide (NADH) and reduced flavin adenine dinucleotide ($FADH_2$). The sequence of reactions needed to oxidize these coenzymes and transfer the resulting electrons to oxygen is called the **electron transport chain**, or the **respiratory chain**. The compounds responsible for this series of oxidation-reduction reactions include proteins known as **cytochromes**, Fe·S proteins, and other molecules that ultimately result in the reduction of molecular oxygen to water. Every time a compound with two carbon atoms is oxidized in the citric acid cycle, a respiratory chain compound accepts the electrons lost in the oxidation (and so is reduced) and then passes them on to the next metabolite in the chain. The energy released by the electron transport chain is used to transport hydrogen (H^+) ions from the mitochondrial matrix to the intermembrane space. The flow of H^+ back through ATP synthase leads to the synthesis and release of ATP from adenosine diphosphate (ADP) and inorganic phosphate ions (P_i) in a process known as **oxidative phosphorylation**. Electron transport and oxidative phosphorylation are tightly coupled to each other. The enzymes and intermediates of the citric acid cycle, the electron transport chain, and oxidative phosphorylation are located in organelles called **mitochondria**.

The oxidation of carbohydrates is the source of over 50% of the energy used by cells. Glucose is oxidized to two molecules of pyruvate through a series of reactions known as **glycolysis**. Some of the energy released in these reactions is conserved by the formation of ATP from ADP. Glycolysis can be divided into two phases: phase I consists of the first five reactions and requires energy to “prime” the glucose molecule for phase II, the last five reactions in which ATP is produced through **substrate-level phosphorylation**.

The pyruvate produced by glycolysis has several possible fates, depending on the organism and whether or not oxygen is present. In animal cells, pyruvate can be further oxidized to acetyl-CoA and then to carbon dioxide (through the citric acid cycle) if oxygen supplies are sufficient. When oxygen supplies are insufficient, pyruvate is reduced to lactate. In yeast and other microorganisms, pyruvate is not converted to lactate in the absence of oxygen but instead is converted to ethanol and carbon dioxide.

The amount of ATP formed by the oxidation of glucose depends on whether or not oxygen is present. If oxygen is present, glucose is oxidized to carbon dioxide, and 36–38 ATP molecules are produced for each glucose molecule oxidized, using the combined pathways of glycolysis, the citric acid cycle, the electron transport chain, and oxidative phosphorylation. Thus, approximately 42% of the energy released by the complete oxidation of glucose is conserved by the synthesis of ATP. In the absence of oxygen, only 2 molecules of ATP are formed for each molecule of glucose converted to lactate (2 molecules), and the amount of energy conserved is much less (2%).

Fatty acids, released by the degradation of triglycerides and other lipids, are converted to fatty acyl-CoA, transported into the mitochondria, and oxidized by repeated cycling through a sequence of four reactions known as **β-oxidation**. In each round of β-oxidation, the fatty acyl-CoA is shortened by two carbon atoms as one molecule of acetyl-CoA is formed. The final round of β-oxidation, once the chain has been shortened to four carbon atoms, forms two molecules of acetyl-CoA. β-oxidation also forms the reduced coenzymes $FADH_2$ and NADH, whose reoxidation through the electron transport chain and oxidative phosphorylation leads to the synthesis of ATP. The efficiency of fatty acid oxidation in the human body is approximately 41%.

Amino acids from the breakdown of proteins can be catabolized to provide energy. Amino acids whose carbon skeletons are converted to intermediates that can be converted to glucose through gluconeogenesis are known as **glucogenic amino acids**. Amino acids whose carbon skeletons are broken down to compounds used to form ketone bodies are known as **ketogenic amino acids**.

The first step in amino acid catabolism is separation of the amino group from the carbon skeleton. In a **transamination**, the amino acid gives its NH_2 to pyruvate, α-ketoglutarate, or oxaloacetate. The products of this reaction are a new amino acid and an α-keto acid containing the carbon skeleton of the original amino acid. Pyruvate is transaminated to alanine, α-ketoglutarate to glutamate, and oxaloacetate to aspartate. The amino groups used to form alanine and aspartate are ultimately transferred to α-ketoglutarate, forming glutamate. The glutamate then undergoes **oxidative deamination** to yield α-ketoglutarate and ammonia.

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Glossary

achiral | objects/molecules have superimposable (identical) mirror images

active transport | occurs when ions and small polar molecules move across the membrane in the opposite direction of diffusion (from low to high concentration); energy is required

addition reaction | reaction in which an atom or molecule is added to an unsaturated molecule, making a single product

adenoside triphosphate (ATP) | energy currency of the cell; nucleotide; undergoes hydrolysis to ADP (low energy) during which energy is released. [NEUROtiker, Public domain, via Wikimedia Commons]

aerobic conditions | with oxygen

alcohols | molecules that contain the hydroxyl (–OH) functional group

aldehyde |

molecules that contain a hydrogen directly bonded to the carbon of a carbonyl group; condensed notation: R–CHO

aldose | monosaccharide that contains an aldehyde group

alkane | hydrocarbons with only C–C and C–H single bonds.

alkenes | Molecules that contain a carbon-carbon double bond (C=C) and general molecular formula: C_nH_{2n}

alkyl halide | organic molecules where a halogen (F, Cl, Br, or I) has replaced a hydrogen

alkynes | Molecules that contain a carbon-carbon triple bond (C≡C) and general molecular formula: C_nH_{2n-2}

amidation | condensation reaction that occurs when a carboxylic acid and amine (or ammonia) combine to form an amide and water [" Condensation Reactions" by LibreTexts is licensed under CC BY-NC .]

amide | molecules that are derivatives of carboxylic acids, formed by replacing the OH of the carboxyl group with ammonia or an amine; condensed notation: R–$CONH_2$'

amine | Molecules derived from ammonia (NH_3), where one or more hydrogen is replaced with a carbon

amino acids | protein building blocks that contain an amino and carboxylic acid group [Benjah-bmm27, Public domain, via Wikimedia Commons]

amphipathetic | contain both polar and nonpolar parts

anabolic pathway |

chemical reactions that convert smaller molecules into larrger molecules;energy is absorbed [CNX OpenStax, CC BY 4.0, via Wikimedia Commons]

anaerobic | without oxygen

anomeric carbon | carbon of the carbonyl group

anomers | diastereomers that differ only at the anomeric carbon

aromatic |

class of cyclic compounds that contain a benzene ring [

Cacycle, Benzene Structure, CC BY-SA 3.0, via WikiMedia Commons]

Benedict's test | qualitative test to determine whether a carbohydrate is a reducing sugar

beta-oxidation (ß-oxidation) | stage II of catabolism where fatty acids are converted to acetyl CoA

carbohydrates |

Sugars composed of carbon, hydrogen and oxygen that provide energy when consumed.

carbonyl group | represents a carbon-oxygen double bond (C=O)

carboxylic acid | molecules that contain a hydroxyl (–OH) directly bonded to the carbon of a carbonyl group; condensed notation: R–COOH

catabolic pathway |

chemical reactions that convert larger molecules into smaller molecules;energy is released [CNX OpenStax, CC BY 4.0, via Wikimedia Commons]

cellular respiration | biochemical process in which energy is transferred from carbohydrates and fats (high potential energy molecules) to ATP

cerebrosides | glycolipids with a monosaccharide. [Epithelyann, CC BY-SA 4.0, via Wikimedia Commons]

chiral | objects/molecules that have nonsuperimposable (not identical) mirror images

chiral center | tetrahedral carbon bonded to four different atoms or group of atoms.

citric acid cycle (or Krebs cycle or the tricarboxylic acid cycle) | series of reactions that degrade the two-carbon acetyl groups from acetyl CoA into carbon dioxide while generating the high-energy molecules NADH and $FADH_2$. [Narayanese, WikiUserPedia, YassineMrabet, TotoBaggins, CC BY-SA 3.0, via Wikimedia Commons]

codon | triplets sequence of nucleotides in mRNA; transcribed from DNA contains a sequence of bases specifying the protein to be made [Thomas Splettstoesser (www.scistyle.com), CC BY-SA 4.0, via Wikimedia Commons]

cofactor | inorganic substances that serve as non-protein helpers

competitive inhibitors |

reversible inhibitors that have structures similar to that of the substrate that compete with a substrate for the active site

condensation reaction | reaction that involves two molecules combining to form one larger organic molecule and water.

Condensed structural formulas | an abbreviated formula that shows all the atoms in a molecule, without showing all of the bonds

conenzyme | organic substances , derived from vitamins, that serve as non-protein helper

conformers | different rotational forms of a molecule

crenation | shrinking/shriveling; water flows out of the cell to dilute the concentration until they are equalize

cycloalkane | Three or more carbon atoms arranged in a ring with only C-C and C-H bonds

cycloalkene | cyclic molecule that contains a C=C

dehalogenation reaction | elimination reaction where a halogen is removed from the molecule to form an alkene

dehydration reaction | elimination reaction where water is removed from the molecule to form an alkene

dehydrogenation reaction | elimination reaction where molecular hydrogen is removed from the molecule to form an alkene

deletion (mutation) | the loss/removal of a nucloetide [Hullo97, CC BY-SA 4.0, via Wikimedia Commons]

denaturation | process that disrupts the stabilizing attractive forces in the secondary, tertiary, and quaternary structures

diastereomers | stereoisomers that are not enantiomers (not exact mirror images) [FlyScienceGuy, CC BY-SA 4.0, via Wikimedia Commons]

diene | molecule that contains two C=C

diffusion | movement of solute molecules from an area of high solute concentration to a low concentration

digestion | stage I of catabolism where food molecules are broken down by hydrolysis reactions into the individual monomer units; occurs in the mouth, stomach, and small intestine

diol | molecules that contain two hydroxyl (–OH) functional groups

dipeptide | peptide containing only two amino acids

disaccharides | carbohydrate consisting of two monosaccharide units chemical combined through a condensation reaction

elimination reaction | reaction that involves the removal of adjacent atoms from a molecule to form an alkene

enantiomers | stereoisomers with nonsuperimposable mirror images. [FlyScienceGuy, CC BY-SA 4.0, via Wikimedia Commons]

enzyme | biological catalyst;biologically active globular proteins that accelerate chemical reactions.

enzyme–substrate (ES) complex | interaction of the enzyme with the substrate; intermediate of an enzyme-catalyzed reaction

epimers | diastereomers that differ only at one chiral carbon

essential amino acids | must be consumed because the body cannot make them.

esterification | condensation reaction that occurs when a carboxylic acid and alcohol combine to form an ester and water [" Condensation Reactions" by LibreTexts is licensed under CC BY-NC .]

esters | molecules that are derivatives of carboxylic acids, formed by replacing the H of the carboxyl group with an alkyl (carbon) group; condensed notation: R–COOR'

ether | molecules contain the R–O–R' functional group

facilitated transport | occurs when small polar molecules and ions pass through a channel formed by integral membrane proteins; no energy required

fat |

consist of triglycerides made up of mostly saturated fatty acids; exist as a solid or semisolid at room temperature.

fatty acids | long-chained carboxylic acids with properties similar to alkanes.

functional group | atoms bonded in a specific way that represents a specific class of organic compounds

furanose | five-membered ring (four carbon atoms and an oxygen) formed from ketoses

genetic code | assigns all 20 amino acids to codons of mRNA [Sarah Greenwood, CC BY-SA 4.0, via Wikimedia Commons]

geometric (cis-trans) isomers | molecues that have different arrangements because of restricted rotation around a carbon-carbon double bond (or ring)

glycerophospholipids (or phospholipids) | lipids that have a glycerol backbone with two fatty acids linked to it through an ester bond and a third group which forms a phosphoester bond with an amino alcohol. [Clbt88 at English Wikibooks, Public domain, via Wikimedia Commons]

glycolipids |

lipids that contain a carbohydrate.

glycolysis | catabolic process in which glucose is converted into pyruvate via ten enzymatic steps [Thomas Shafee, CC BY-SA 4.0, via Wikimedia Commons]

glycosidic bond | connects two molecules to one another through a condensation reaction

halogenation reaction |

addition of a halogen to an alkene to produce a di-substituted alkyl halide

hemolysis (or lysis) | swelling; water flows into the cell to dilute the concentration until they are equalized

hydration reaction |

addition of water to an alkene in the presence of an acid catalyst to produce an alcohol

hydrocarbons | Organic molecules containing only carbon and hydrogen atoms

hydrogenation reaction |

addition of H_2 to an alkene in the presence of a metal catalyst to produce an alkane

hydrohalogenation reaction | addition of a hydrogen halide to an alkene to produce a mono-substituted alkyl halide

hydrolysis reaction |

reaction that involves water reacting with an organic molecule to break it down to form two or more smaller organic molecules; opposite of condensation [FrozenMan, CC BY-SA 4.0, via Wikimedia Commons]

hypertonic solution | solute concentration outside of the cell is higher than that inside of the cell

hypotonic solutions | solute concentration outside of the cell is lower than that inside of the cell

induced-fit model | active site that is flexible and undergoes a conformational change, adjusting to the shape of the substrate when the substrate interacts with the enzyme.

inhibitor | Molecules that cause enzymes to lose activity by preventing the active site from interacting with substrate to form the ES complex

insertion (mutation) | a different nucleotide is substituted [Hullo97, CC BY-SA 4.0, via Wikimedia Commons]

irreversible inhibition | occurs when the inhibitor causes a permanent loss of activity; forms a covalent bond with an amino acid side chain in the enzyme's active site

isotonic solutions | solute concentration inside and outside of the cell are equal

ketone | molecules that contain two carbon groups directly bonded to the carbon of the carbonyl group; condensed notation: R–CO–R'

ketose | monosaccharide that contains a ketone group

Lewis Structure | shows all atoms and electrons (bonding and nonbonding) attaching them

lipid | class of biomolecules defined by low solubility in water and high solubility in nonpolar, organic solvents

lock-and-key model | active site that has a rigid, inflexible shape that is an exact complement to the substrate

messenger RNA (mRNA) | codes for proteins

metabolic pathway | series of steps in the chemical reactions in biological systems

metabolism | chemical reactions occurring in the body during the break down or building up of molecules

molecular formula | shows the type and number of atoms in a molecule

monomer | smaller units that make up a polymer

monosaccharides | simplest carbohydrates that cannot be broken down to smaller carbohydrates; general formula: $C_n(H_2O)_n$

monounsaturated fatty acid | fatty acids that contain only one carbon–carbon double bond

mutagen | chemical or physical agents that cause mutations

mutation | change in a DNA nucleotide sequence

noncompetitive inhibitors | reversible inhibitors that do no have structures similar to that of the substrate and do not compete with a substrate for the active site

nucleic acids | biomolecules composed of nucleotides

nucleoside | sugar/base combination between a pentose and a nitrogen containing purine or pyrimidine base

nucleotide | combination between a pentose, a nitrogen containing purine or pyrimidine base, and phosphate; building blocks of nucleic acids

oil | consist of triglycerides made up of mostly unsaturated fatty acids; exist as a liquid at room temperature

oligosaccharide | carbohydrate consisting of 3-9 monosaccharide units chemical combined through a condensation reaction

organic chemistry | study of the chemistry of the carbon compounds

organic molecule | Compound that contains carbon and hydrogen

osmosis | occurs when water travels across the cell membrane (from a lower to a higher solution concentration) to equalize solute concentrations inside and outside of a cell

oxidation | loss of electrons; or in organic compounds, involves an increase in oxygen and/or decrease in hydrogen

oxidizing agent | undergoes reduction; responsible for something else getting oxidized

parent chain | longest continuous chain of carbon atoms

passive (or simple) diffusion | small molecules and nonpolar molecules use this process to move across the semipermeable membrane; no energy required

peptide | compound containing amino acids joined by a peptide bond

phenol | molecules that contain the hydroxyl (–OH) functional group directly attached to a benzene ring

polyene | molecule that contains more than two C=C

polymer | large molecule formed of repeating smaller units that are covalently bonded to one another in a repeating pattern

polyol | molecules that contain many hydroxyl (–OH) functional groups

polypeptide | peptide containing many amino acids

polysaccharide | carbohydrate consisting of 10 or more monosaccharide units chemical combined through a condensation reaction

polyunsaturated fatty acid | fatty acids that contain more than one carbon–carbon double bond

primary (1°) alcohol | alcohols that have one alkyl group attached to the carbon where the functional group is bonded

primary (1°) amine | amine that has one alkyl group attached to the nitrogen of the functional group

protein | biologically active polypeptide containing 50 or more amino acids

pyranose | six-membered ring (five carbon atoms and an oxygen) formed from aldoses

pyruvate | result of the breakdown of glucose during glycolysis [Pyruvic-acid-2D-skeletal.png: Benjah-bmm27derivative work: Kpengboy (talk)further derivative work GKFXtalk, Public domain, via Wikimedia Commons]

Redox (oxidation-reduction) reaction | reactions involving a transfer of electrons

reducing agent | undergoes oxidation; responsible for something else getting reduced

reducing sugar | carbohydrate that can act as a reducing agent

reduction | gain of electrons; or in organic compounds, involves an decrease in oxygen and/or increase in hydrogen

replication | process of making new copies of DNA

reversible inhibition | occurs when the inhibitor causes a temporary loss of activity

ribosomal RNA (rRNA) | component of ribosomes

saponification | alkaline hydrolysis of an ester resulting in an alcohol and fatty acid salt (ionic compound of the conjugate base) [The original uploader was Rhadamante at French Wikipedia., CC BY-SA 3.0, via Wikimedia Commons]

saturated | maximum number of H atoms

saturated fatty acid | fatty acids that contain only carbon–carbon single bonds

secondary (2°) alcohol | alcohols that have two alkyl groups attached to the carbon where the functional group is bonded

secondary (2°) amine | amine that has two alkyl groups attached to the nitrogen of the functional group

semipermeable | meaning that some things can enter, and some things cannot

Skeletal Structures (or line-angle structures) | shows all the bonds between carbon atoms, but omits some atom labels

sphingolipid | phospholipids that contain an 18-carbon unsaturated amino alcohol called *sphingosine*, instead of glycerol. [Karol Langner at en.Wikipedia, Public domain, via Wikimedia Commons]

sphingosine | an amino alcohol found in all sphingolipids [Ed (Edgar181), Public domain, via Wikimedia Commons]

stereoisomers | molecules that have the same molecular formula and same connectivity/bonding between the atoms.

steroids | lipids that do not contain fatty acids; contain a steroid nucleus with four fused rings

Structural (or constitutional) isomers | molecules with the same molecular formula but a different connectivity.

structural formula | shows all atoms and the bonds attaching them

substituents | groups that replace at least one H in order to branch from the alkane chain.

substitution (mutation) | a different nucleotide is substituted [Hullo97, CC BY-SA 4.0, via Wikimedia Commons]

substitution (mutation) | the addition of a new nucloetide [Hullo97, CC BY-SA 4.0, via Wikimedia Commons]

substrate | reactant in a chemical reaction (typically refers to enzyme-catalyzed reactions)

sugar acid | product of the oxidation of a monosaccharide

sugar alcohol | product of the reduction of a monosaccharide

template strand | DNA sequence that is transcribed to make RNA

tertiary (3°) alcohol | alcohols that have three alkyl groups attached to the carbon where the functional group is bonded

tertiary (3°) amine | amine that has three alkyl groups attached to the nitrogen of the functional group

thiol | molecules that contain the sulfhydryl (–SH) functional group

transcription | a segment of DNA is used to produce RNA; first step of making a protein from DNA is to make a copy of the gene from the DNA

transfer RNA (tRNA) | adapter molecule that brings the amino acid to the ribosome

translation | process in which information in RNA is translated into a protein sequence

triacylglycerol (triglyceride) | fats or oils; produced by the esterification of the hydroxyl groups of glycerol and the carboxyl groups of three fatty acids [Hbf878, CC0, via Wikimedia Commons]

triol | molecules that contain three hydroxyl (–OH) functional groups

wax | lipid produced by the esterification of one fatty acid and a long-chain alcohol each containing 14 to 30 carbons

zwitterion | form of an amino acid that contains the protonated amine and carboxylat e; typically occurs at neutral pH

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