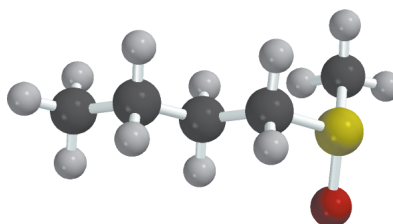


Phosphorus is in the same group of the periodic table as nitrogen, and tricoordinate phosphorus compounds (phosphines), like amines, are trigonal pyramidal. Phosphines, however, undergo pyramidal inversion much more slowly than amines, and a number of optically active phosphines have been prepared.

Tricoordinate sulfur compounds are chiral when sulfur bears three different groups. The rate of pyramidal inversion at sulfur is rather slow. The most common compounds in which sulfur is a chirality center are sulfoxides such as:



Butyl methyl sulfoxide



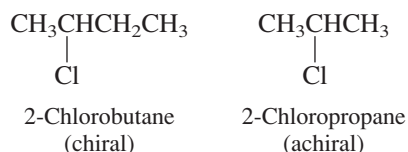
(S)-(+)-Butyl methyl sulfoxide

The absolute configuration at sulfur is specified by the Cahn–Ingold–Prelog method with the provision that the unshared electron pair is considered to be the lowest ranking substituent.

7.17 SUMMARY

Chemistry in three dimensions is known as **stereochemistry**. At its most fundamental level, stereochemistry deals with molecular structure; at another level, it is concerned with chemical reactivity. Table 7.2 summarizes some basic definitions relating to molecular structure and stereochemistry.

Section 7.1 A molecule is **chiral** if it cannot be superimposed on its mirror image. *Nonsuperimposable mirror images* are **enantiomers** of one another. Molecules in which mirror images are superimposable are achiral.



Section 7.2 The most common kind of chiral molecule contains a carbon atom that bears four different atoms or groups. Such an atom is called a **chirality center**. Table 7.2 shows the enantiomers of 2-chlorobutane. C-2 is a chirality center in 2-chlorobutane.

Section 7.3 A molecule that has a plane of symmetry or a center of symmetry is achiral. *cis*-4-Methylcyclohexanol (Table 7.2) has a plane of symmetry that bisects the molecule into two mirror-image halves and is achiral. The same can be said for *trans*-4-methylcyclohexanol.

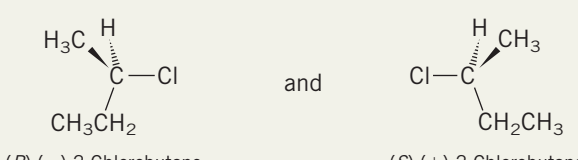
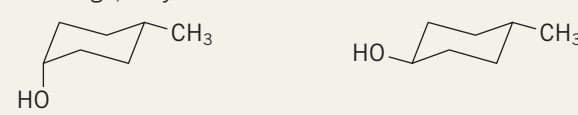
Section 7.4 **Optical activity**, or the degree to which a substance rotates the plane of polarized light, is a physical property used to characterize chiral substances. Enantiomers have equal and opposite **optical rotations**. To be optically active a substance must be chiral, and one enantiomer must be present in excess of the other. A **racemic mixture** is optically inactive and contains equal quantities of enantiomers.

Section 7.5 **Relative configuration** compares the arrangement of atoms in space to some reference. The prefix *cis* in *cis*-4-methylcyclohexanol, for example, describes relative configuration by referencing the orientation of the CH_3 group to the OH. **Absolute configuration** is an exact description of the arrangement of atoms in space.

Section 7.6 Absolute configuration in chiral molecules is best specified using the prefixes *R* and *S* of the Cahn–Ingold–Prelog notational system. Substituents at a

A detailed flowchart describing a more finely divided set of subcategories of isomers appears in the February 1990 issue of the *Journal of Chemical Education*.

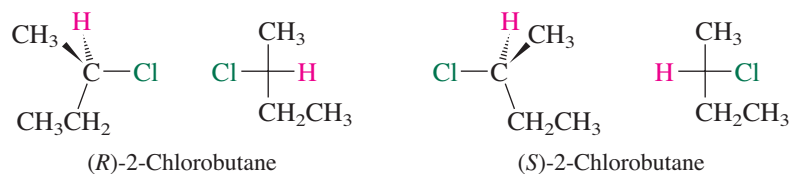
TABLE 7.2 Classification of Isomers

Definition	Example
Isomers are different compounds that have the same molecular formula. They may be either constitutional isomers or stereoisomers.	
1. <i>Constitutional isomers</i> are isomers that differ in the order in which their atoms are connected.	Three constitutionally isomeric compounds have the molecular formula C ₃ H ₈ O: $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \qquad \text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_3 \qquad \text{CH}_3\text{CH}_2\text{OCH}_3$ <p style="text-align: center;">1-Propanol 2-Propanol Ethyl methyl ether</p>
2. <i>Stereoisomers</i> are isomers that have the same constitution but differ in the arrangement of their atoms in space.	
(a) <i>Enantiomers</i> are stereoisomers that are related as an object and its nonsuperimposable mirror image.	The two enantiomeric forms of 2-chlorobutane are  $\begin{array}{ccc} \text{H}_3\text{C} & \text{H} & \\ & & \\ & \text{C} & - \text{Cl} \\ & & \\ \text{CH}_3\text{CH}_2 & & \end{array} \qquad \text{and} \qquad \begin{array}{ccc} & \text{H} & \text{CH}_3 \\ & & \\ \text{Cl} & - \text{C} & \\ & & \\ & \text{CH}_2\text{CH}_3 & \end{array}$ <p style="text-align: center;">(R)-(-)-2-Chlorobutane (S)-(+)-2-Chlorobutane</p>
(b) <i>Diastereomers</i> are stereoisomers that are not mirror images.	The cis and trans isomers of 4-methylcyclohexanol are stereoisomers, but they are not related as an object and its mirror image; they are diastereomers.  $\begin{array}{ccc} & & \text{CH}_3 \\ & & \\ \text{HO} & & \\ & & \\ \text{cis-4-Methylcyclohexanol} & & \text{trans-4-Methylcyclohexanol} \end{array}$

chirality center are ranked in order of decreasing precedence. If the three highest ranked substituents trace a clockwise path (highest→second highest→third highest) when the lowest ranked substituent is held away from you, the configuration is *R*. If the path is counterclockwise, the configuration is *S*. Table 7.2 shows the *R* and *S* enantiomers of 2-chlorobutane.

Section 7.7

A **Fischer projection** shows how a molecule would look if its bonds were projected onto a flat surface. Horizontal lines represent bonds pointing toward you; vertical lines represent bonds pointing away from you. The projection is normally drawn so that the carbon chain is vertical, with the lowest numbered carbon at the top.



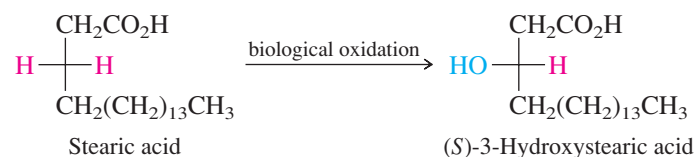
Section 7.8

Both enantiomers of the same substance are identical in most of their physical properties. The most prominent differences are biological ones, such as taste and odor, in which the substance interacts with a chiral receptor site. Enantiomers also have important consequences in medicine, in which the two enantiomeric forms of a drug can have much different effects on a patient.

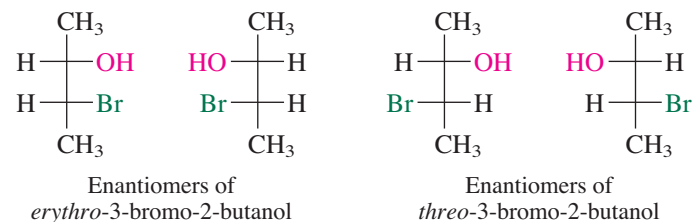
Section 7.9

A chemical reaction can convert an achiral substance to a chiral one. If the product contains a single chirality center, it is formed as a racemic mixture. Optically active products can be formed from optically inactive starting

materials only if some optically active agent is present. The best examples are biological processes in which enzymes catalyze the formation of only a single enantiomer.

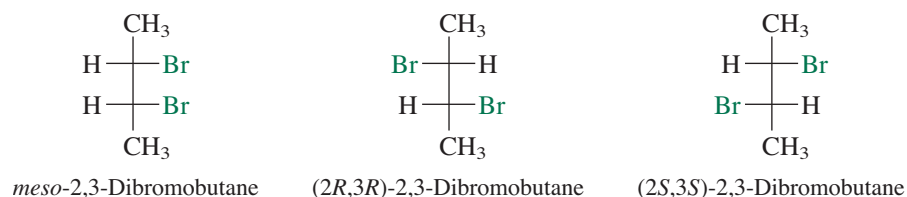


Section 7.10 When a molecule has two chirality centers and these two chirality centers are not equivalent, four stereoisomers are possible.



Stereoisomers that are not mirror images are classified as **diastereomers**. Each enantiomer of *erythro*-3-bromo-2-butanol is a diastereomer of each enantiomer of *threo*-3-bromo-2-butanol.

Section 7.11 Achiral molecules that contain chirality centers are called **meso forms**. Meso forms typically contain (but are not limited to) two equivalently substituted chirality centers. They are optically inactive.



Section 7.12 For a particular constitution, the maximum number of stereoisomers is 2^n , where n is the number of structural units capable of stereochemical variation—usually this is the number of chirality centers, but can include *E* and *Z* double bonds as well. The number of stereoisomers is reduced to less than 2^n when there are meso forms.

Section 7.13 Addition reactions of alkenes may generate one (Section 7.9) or two (Section 7.13) chirality centers. When two chirality centers are produced, their relative stereochemistry depends on the configuration (*E* or *Z*) of the alkene and whether the addition is syn or anti.

Section 7.14 **Resolution** is the separation of a racemic mixture into its enantiomers. It is normally carried out by converting the mixture of enantiomers to a mixture of diastereomers, separating the diastereomers, then regenerating the enantiomers.

Section 7.15 Certain polymers such as polypropylene contain chirality centers, and the relative configurations of these centers affect the physical properties of the polymers. Like substituents appear on the same side of a zigzag carbon chain in an **isotactic** polymer, alternate along the chain in a **syndiotactic** polymer, and appear in a random manner in an **atactic** polymer. Isotactic and syndiotactic polymers are referred to as **stereoregular** polymers.

Section 7.16 Atoms other than carbon can be chirality centers. Examples include those based on tetracoordinate silicon and tricoordinate sulfur as the chirality center. In principle, tricoordinate nitrogen can be a chirality center in compounds of the type $\text{N}(x, y, z)$, where x , y , and z are different, but inversion of the nitrogen pyramid is so fast that racemization occurs virtually instantly at room temperature.