5.8 The Origin of Optical Activity
5.8A Racemic Form (正负号)

- An equimolar mixture of two enantiomers is called a racemic form (either a racemate or a racemic mixture).
- A racemic form shows no rotation of plane-polarized light.
- It is often designated as being (±).

\[
\begin{align*}
\text{(R)-(-)-2-Butanol} & \quad \text{[\(\alpha\)]_D^{25} = -13.52} \\
\text{(S)-(+) 2-Butanol} & \quad \text{[\(\alpha\)]_D^{25} = +13.52} \\
\text{(±)-2-Butanol} & \quad \text{[\(\alpha\)]_D^{25} = 0}
\end{align*}
\]
5.8B Racemic forms and Enantiomeric Excess (外消旋体及对映体过量百分率)

\[
\% \text{ ee} = \frac{\text{moles of one enantiomer} - \text{moles of other enantiomer}}{\text{total moles of both enantiomers}} \times 100\%
\]

\[
= \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}} \times 100\%
\]

\[
= \frac{[R][S]}{[R][S]} \times 100\%
\]

\[
\% \text{ ee} = \% \text{ enantiomeric excess}
\]
5.9 The Synthesis of Chiral Molecules
5.9A Racemic Forms

\[
\text{CH}_3\text{CH}_2\text{CCH}_3 \quad + \quad \text{H-H} \quad \xrightarrow{\text{Ni}} \quad \text{CH}_3\text{CH}_2\text{CHCH}_3 \quad (\pm)
\]

2-butanone \quad (achiral molecules) \quad (\pm)-2-butanone \quad [chiral molecules but 50:50 mixture (R) and (S)]
If a reaction that leads to the formation of enantiomers produces a preponderance of one enantiomer over its mirror image, the reaction is said to be enantioselective.

For a reaction to be enantioselective, a chiral reagent, solvent, or catalyst must assert an influence on the course of the reaction.
5.9B Enantioselective Synthesis

\[
\begin{align*}
\text{O} &= \text{C} - \text{CH}_3 \\
\text{H} &= \text{H} - \text{O} \\
\text{O} &= \text{C} - \text{CH}_3 \\
\text{H} &= \text{H} - \text{O}
\end{align*}
\]

50% (R)-2-Butanol

50% (S)-2-Butanol
(1) LiAlH₄

(2) H₂O

5.0

1

More stable

Less stable

91%

9%
Many enzymes have also found use in the organic chemistry laboratory, where organic chemists take advantage of their properties to bring about enantioselective reactions.

Ethyl (±)-2-fluorohexanoate
[an ester that is a racemate of (R) and (S) forms]
5.10 Chiral Drugs
Ibuprofen, 布洛芬 (抗炎、镇痛药)
Thalidomide, 萨利多胺 (镇静剂, 安眠药)
Adrenaline, 麻黄碱
Nicotine, 尼古丁
5.11 Fischer Projection Formulas
**Fischer projection**

- Vertical lines represent bonds that project behind the plane of the paper.
- Horizontal lines represent bonds that project out of the plane of the paper.
Notes

1. We are permitted to rotate them in the plane of the paper by $180^\circ$ but by no other angle.
Enantiomers
2. We are not allowed to flip them over
5.12 Molecules with More than one Stereocenter
Diastereomers

(erythrose),

(2R,3R)

(2S,3S)

(2R,3S)

(2S,3R)

Enantiomers
酒石酸

(2S,3S)  (2R,3R)  (2R,3S)
对映体

内消旋体

Meso
5.12A Meso Compounds (内消旋化合物)

Meso compounds, because they are achiral, are optically inactive.
5.12B Naming Compounds with More than One Stereocenter

2,3-DiBromobutane

(2R,3R)-2,3-Dibromobutane
CHO
H—OH
H—OH
H—OH
CH₂OH

CHO
HO—H
HO—H
HO—H
CH₂OH

CHO
HO—H
HO—H
H—OH
CH₂OH

CHO
H—OH
HO—H
H—OH
CH₂OH

1
2
3
4

和3是差向异构体
(2R,3r,4S)-2,3,4-三羟基戊二酸

(2R,3s,4S)-2,3,4-三羟基戊二酸

R > S
5.13 Stereoisomerism of Cyclic Compounds
cis-1,2-Dimethylcyclopropane  
(1R,2S)-1,2-Dimethylcyclopropane

trans-1,2-Dimethylcyclopropane  
(1R,2R)-1,2-Dimethylcyclopropane  
(1S,2S)-1,2-Dimethylcyclopropane
1,2-Dimethylcyclopentane

Enantiomers

Meso compound

Plane of symmetry
5.13A  Cyclohexane Derivatives

1,4-Disubstituted cyclohexanes

1,4-Disubstituted cyclohexanes have no stereogenic centers by virtue of a symmetry plane passing through the substituents and through carbons 1 and 4 of the ring. Thus, only cis and trans stereoisomers (diastereomers) are possible.
Both the cis and trans forms have a plane of symmetry.
1,3-Disubstituted cyclohexanes

1,3-Disubstituted cyclohexanes have two stereogenic centers and a maximum of four stereoisomers is therefore possible.
cis-1,3-Dimethylcyclohexane has a symmetry plane
trans-1,3-Dimethylcyclohexane has no symmetry plane

Enantiomers
1,2-Disubstituted cyclohexanes

1,2-Disubstituted cyclohexanes have two stereogenic centers and four stereoisomers are again possible.
(trans)

Optical active
cis-1,2-Dimethylcyclohexane

Two rapidly interconverting chair conformations

Optical inactive