Section 8--Properties of Enantiomers: Optical Activity

Properties of Enantiomers: Optical Activity

Enantiomers are distinct stereoisomers. One structure cannot be superimposed on the other. However, the two stereoisomers are identical in all respects, except that they are mirror images of each other. It is not surprising that enantiomers have identical properties, except when they are in a chiral environment.

Physical Properties of (R) and (S)-2-Butanol

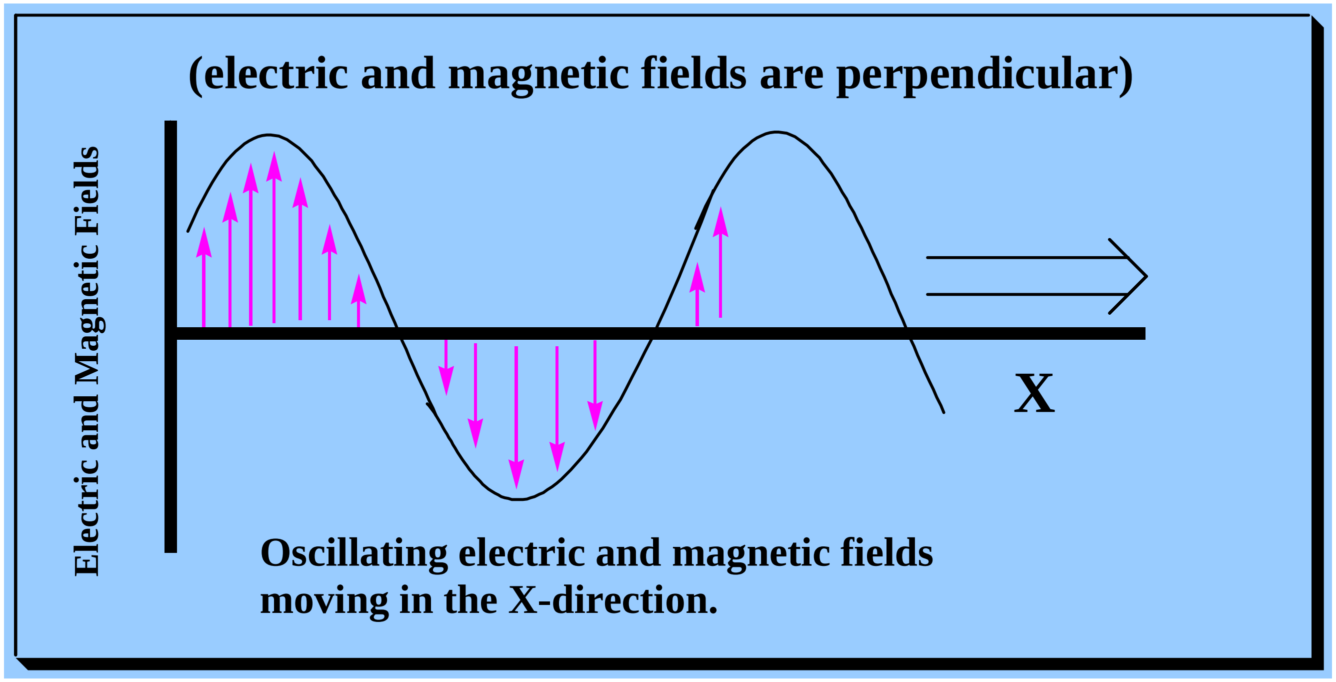
	(R)	(S)
boiling point	99.5^{o}C	99.5^{o}C
density (g/mL, 20^{o}C)	0.808	0.808

Optical Activity

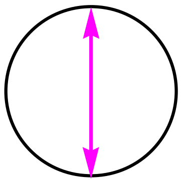
However, when plane-polarized light is passed through a solution of (R)-2-butanol, the plane is rotated in one direction and when plane-polarized light is passed through a solution of (S)-2-butanol, the plane is rotated in the opposite direction.

Plane Polarized Light

Light is a moving wave of electric and magnetic fields called electromagnetic radiation. The strengths of the electric and magnetic fields oscillate in a repeating pattern as the wave moves through space.

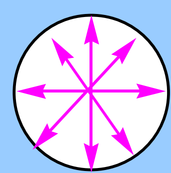


Head-on view of oscillating electric or magnetic field vector.



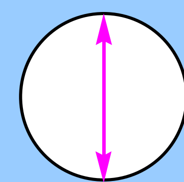
Ordinary and Plane-Polarized Light

Ordinary light is a bundle of waves with electromagnetic field vectors moving in all directions around the propagating axis.



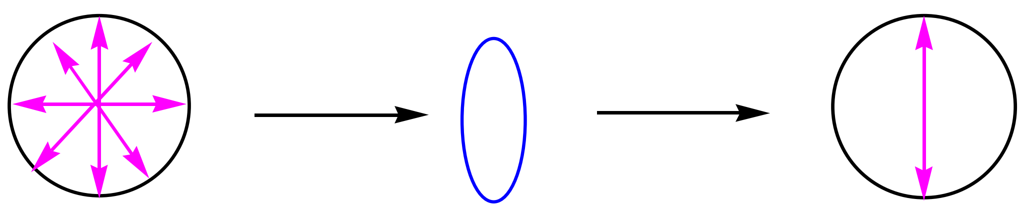
head-on view

Plane-polarized light is a wave with only a single oscillating electromagnetic field vector



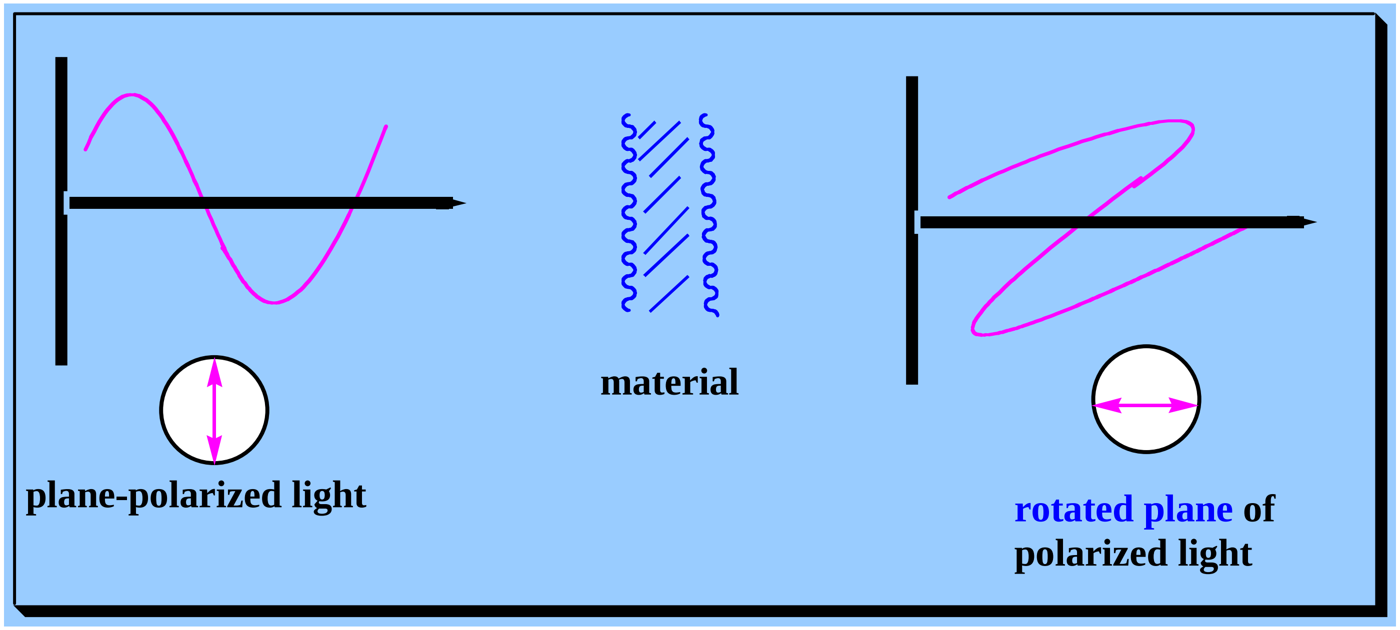
head-on view

Plane-polarized light is obtained by passing ordinary light through a polarizer (material such as Iceland spar).



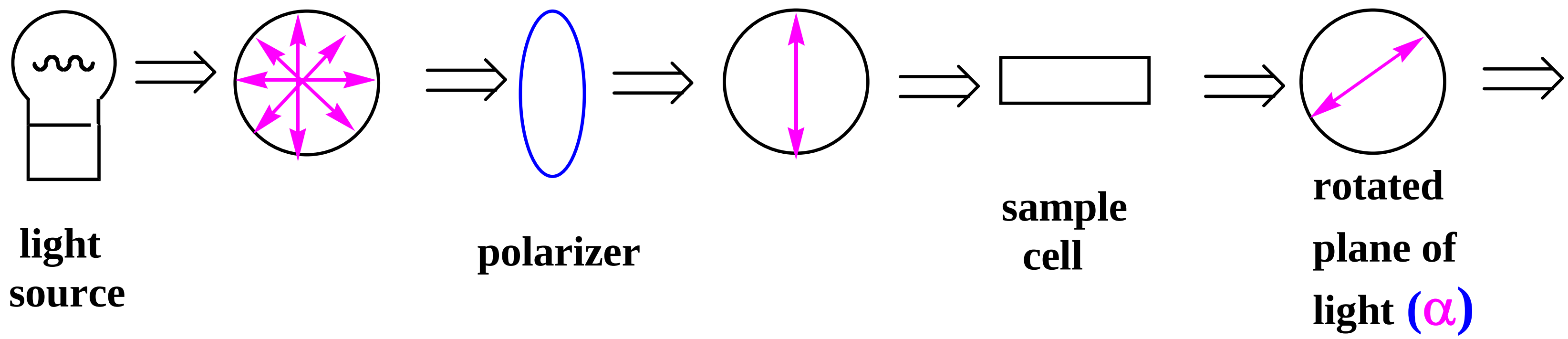
The Interaction of Plane-Polarized Light with Materials

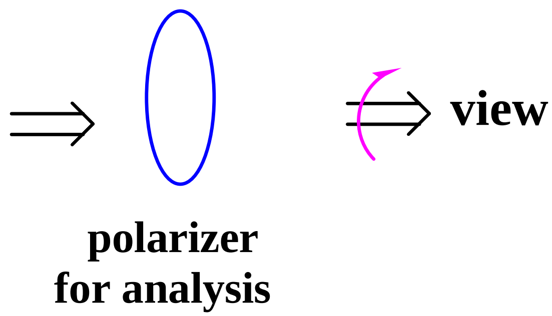
When plane-polarized light is passed through certain materials (gases, liquids or crystalline solids), the plane of the polarized light rotates.



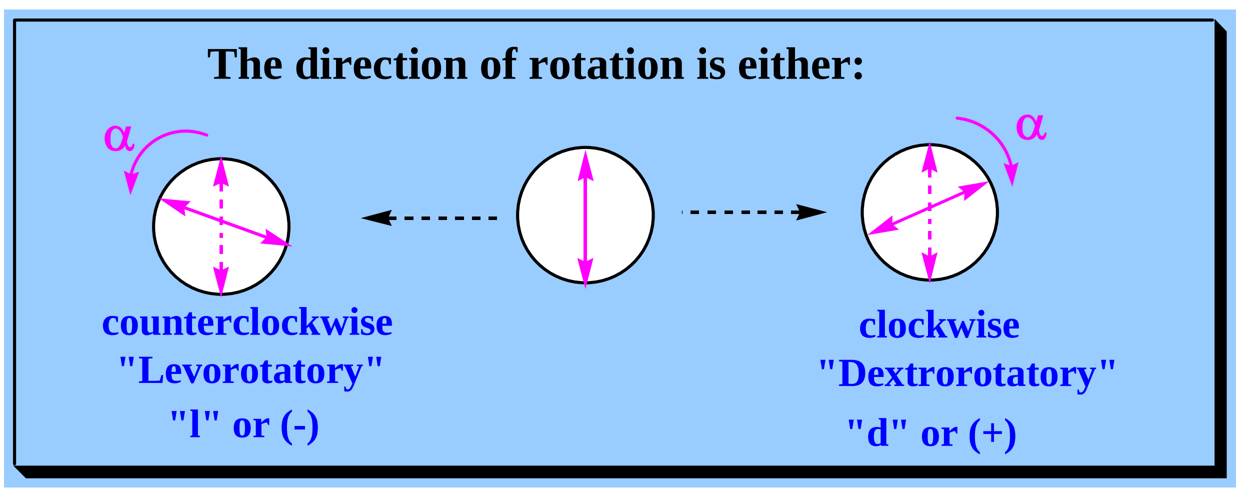
Solutions of certain organic compounds have this capability. The rotatory power is characteristic of the compound and is measured in a polarimeter.

Components of a Polarimeter





The second polarizer is rotated to match the degree of rotation of the plane-polarized light. When a match is achieved, light passes through the polarizer.



Specific Rotation: A Measurement of Rotatory Power

The measured rotation, a, depends on how many molecules the plane-polarized light interacts with in passing through the cell, and experimental variables such as the wavelength of the light, solvent and temperature.

In order to adjust for these experimental variables, the intrinsic rotatory power of a compound is described by its specific rotation, $[\alpha]$:

$$[\alpha]_{l}^{temp} = \frac{\alpha}{L \times C}$$

where α is the observed rotation
L is the cell path length in decimeters
C is the concentration in g/mL

Note: The specific rotation depends on the temperature, the wavelength of the plane-polarized light, and the solvent. These variables must be considered when specific rotation is used for diagnostic purposes.

Some Examples

A sample of a compound A in chloroform (0.500 g/mL) at 25.0°C shows a rotation of +2.5° in a 1.0 decimeter cell. What is the specific rotation?

$$[\alpha]_{l}^{temp} = \frac{\alpha}{L \times C} = \frac{+2.5^{o}}{1.0\ dm \times 0.5\ (g/mL)} = +5.0^{o}\ dm^{-1}\ (g/mL)^{-1}$$

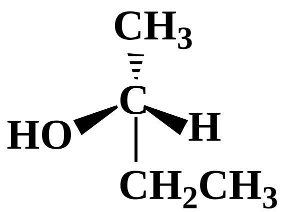
What is the observed rotation of A in a 0.5 dm cell?

$$\alpha = [\alpha] \times L \times C = 5.0^{o}\ dm^{-1}\ (g/mL)^{-1} \times 0.5\ dm \times 0.5\ g/mL = +1.25^{o}$$

What is the observed rotation if C = 0.050 g/mL?

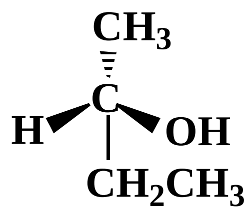
$$\alpha = [\alpha] \times L \times C = 5.0^{o}\ dm^{-1}\ (g/mL)^{-1} \times 1.0\ dm \times 0.050\ g/mL = +0.25^{o}$$

Some Examples of Specific Rotations



(R)-2-butanol

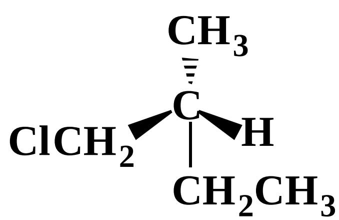
$[\alpha]_D^{25} = -13.52^o$



(S)-2-butanol

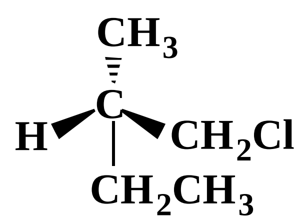
$[\alpha]_D^{25} = +13.52^o$

The subscript "D" refers to the sodium D-line at 589.3 nm.



(R)-(-)-1-chloro-2-methylbutane

$[\alpha]_D^{25} = -1.64^o$



(S)-(+)-1-chloro-2-methylbutane

$[\alpha]_D^{25} = +1.64^o$

NOTE: there is no direct correlation between (R,S) and the sign (+ or -) of the rotation.

Section 9--The Origin of Optical Activity

Optical Purity

Racemic Form or Racemate

A mixture of equal amounts of the two enantiomers of a chiral compound is called a racemic form (or mixture) or simply racemate.

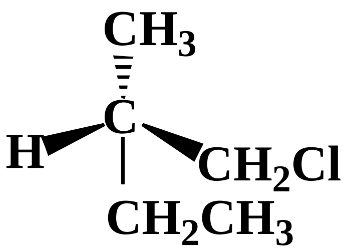
Because the rotatory power is balanced by the equal numbers of the enantiomers, a racemic form shows no net rotation of plane-polarized light.

Optical Purity and Enantiomeric Excess (ee)

If the specific rotation of a single enantiomer of a chiral compound is known, it is possible to determine the enantiomeric mixture of samples of the compound from polarimetric experiments.

A sample of a chiral compound that contains only a single enantiomer is enantiomerically pure, and is said to have an enantiomeric excess (ee) of 100%.

Example: (S)-(+)-1-chloro-2-methylbutane



A sample that is 100% of this enantiomer has a specific rotation of $[a]^{25}_{D} = +1.64°$.

As the levorotatory (R) enantiomer is added to the sample, it cancels the dextrorotatory power of an equal number of (S) molecules.

The rotatory power of the sample is due only to the enantiomers that are in excess.

Enantiomeric Excess (ee)

The enantiomeric excess of a sample is

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

and is directly calculated from the specific rotations by

$$\%(ee) = \left[\frac{\text{(observed specific rotation)}}{\text{(specific rotation of pure enantiomer)}}\right] \times 100$$

Optical Purity of (R)- and (S)-1-Chloro-2-methylbutane

observed specific rotation in degrees	optical purity (ee) in %	% S	% R
+1.64	100	100	0
+0.82	50	75	25
+0.41	25	62.5	37.5
0	0	50	50
-0.41	25	37.5	62.5
- 0.82	50	25	75
-1.64	100	0	100

Quiz Chapter 5 Section 9

A sample of 100% ee (R)-2-butanol shows [α] = -13.5^o. What is the enantiomeric mixture of a sample of 2-butanol that shows [α] = +1.35^o ?

$$\%ee = \left[\frac{+1.35^o}{+13.5^o}\right] \times 100 = 10\% \text{ excess of } S$$

This sample of 2-butanol is 90% racemic form and 10% excess S, or S = (45 + 10) = 55% and R = 45%.