Chapter 5:

Stereochemistry – Part 3 Optical Purity

Today! Chapter 5 (5.4, 5.9-5.11)

Resolving Enantiomers

Wednesday Chapter 6:

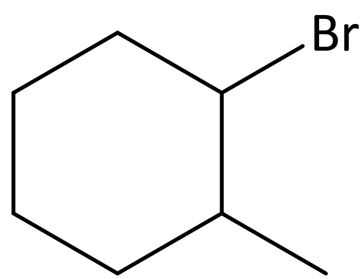
Kinetics and Thermodynamics (6.1-6.6)

Friday Chapter 6: Mechanisms (6.7 - 6.10, 6.12)

(We'll come back to 6.11 later.)

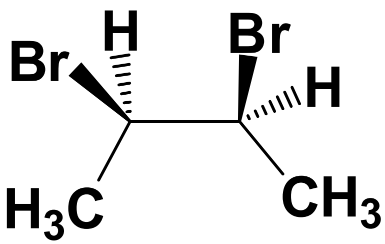
Stereoisomeric Relationships

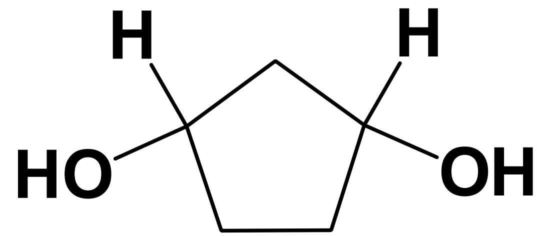
- Draw each of the four possible stereoisomers for the following compound. It might be helpful to also make a handheld model for each isomer.

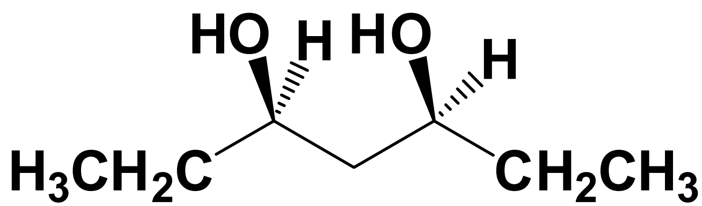


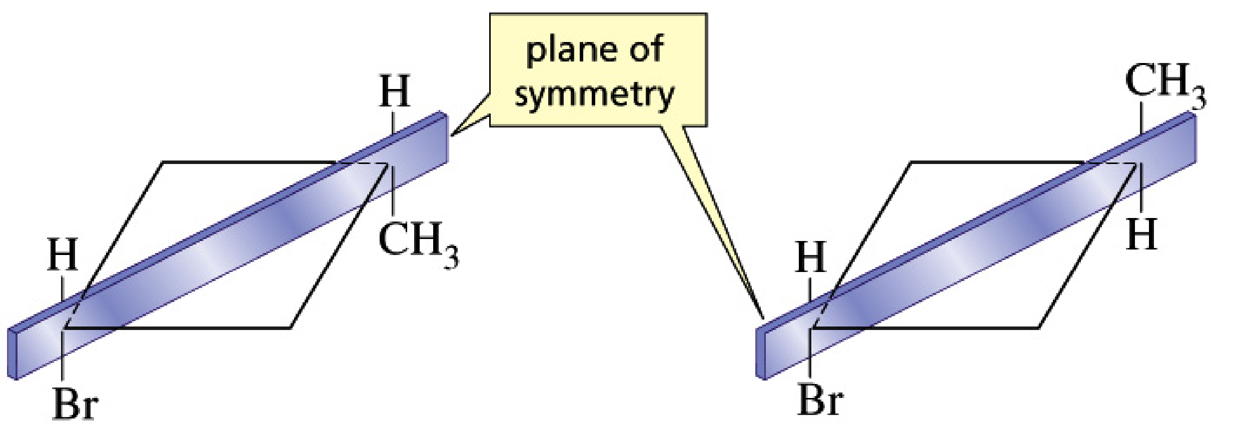
- Pair up the isomers in every possible combination and label the pairs as either enantiomers or diastereomers.

Meso Compounds









cis-1-bromo-3-methylcyclobutane

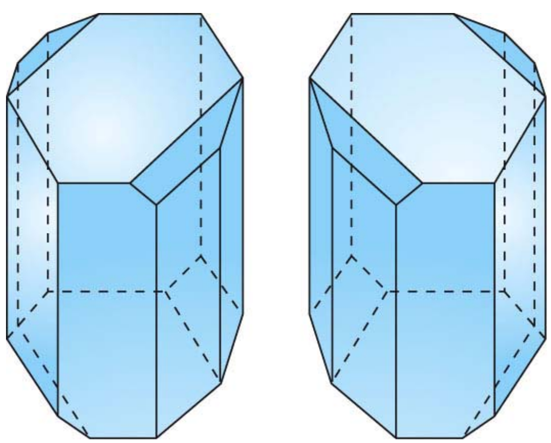
trans-1-bromo-3-methylcyclobutane

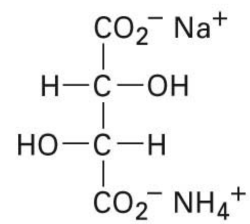
Configuration

- ______________________compares the arrangement of atoms in space of one compound with those of another.
- .
- ______________________ is the precise arrangement of atoms in space.

Pasteur's Discovery of Enantiomers

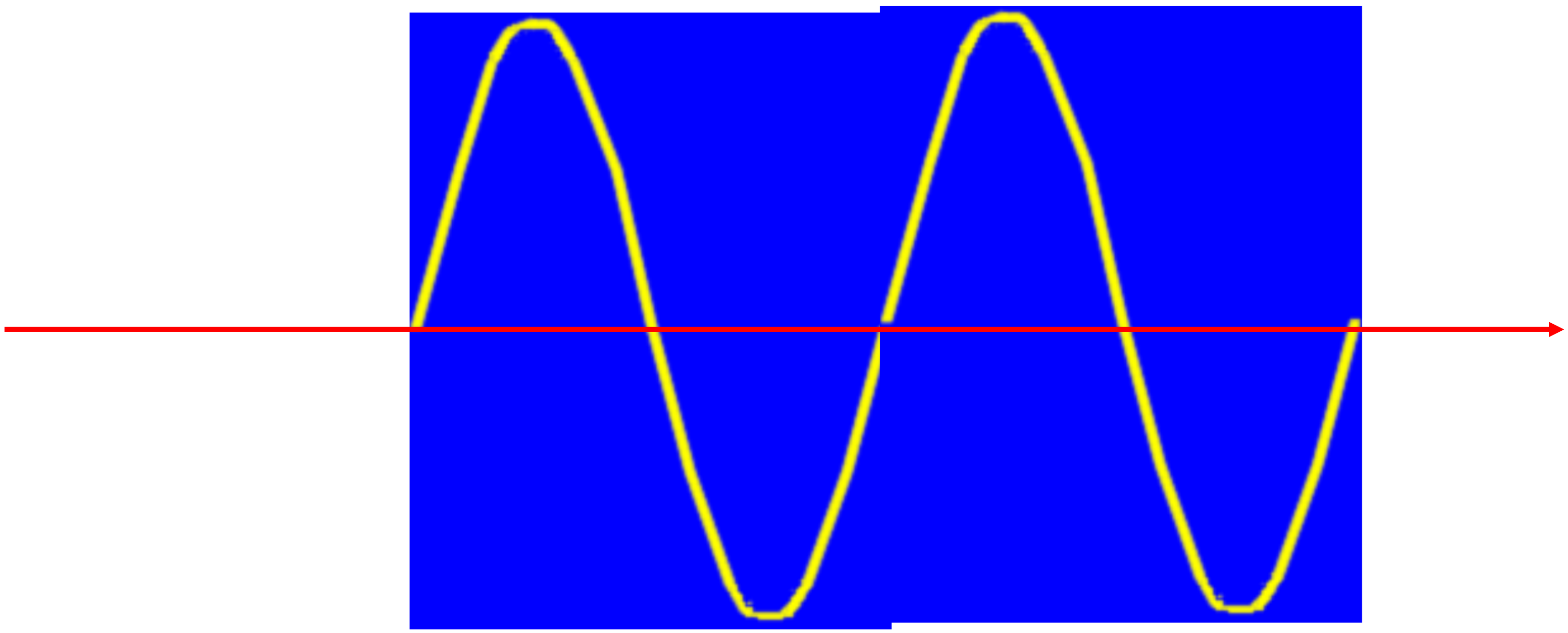
- In 1847, Pasteur performed the first resolution of enantiomers from his racemic mixture of tartaric acid salts Louis Pasteur discovered that sodium ammonium salts of tartaric acid crystallize into right handed and left handed forms



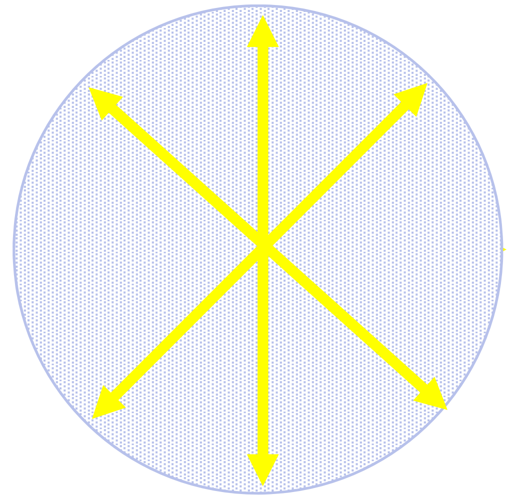


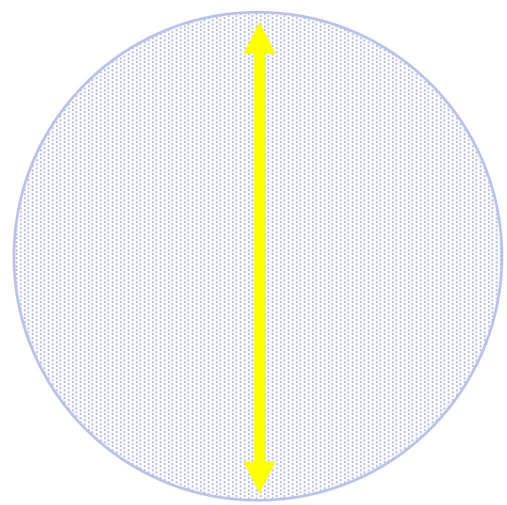
Sodium ammonium tartrate

Light

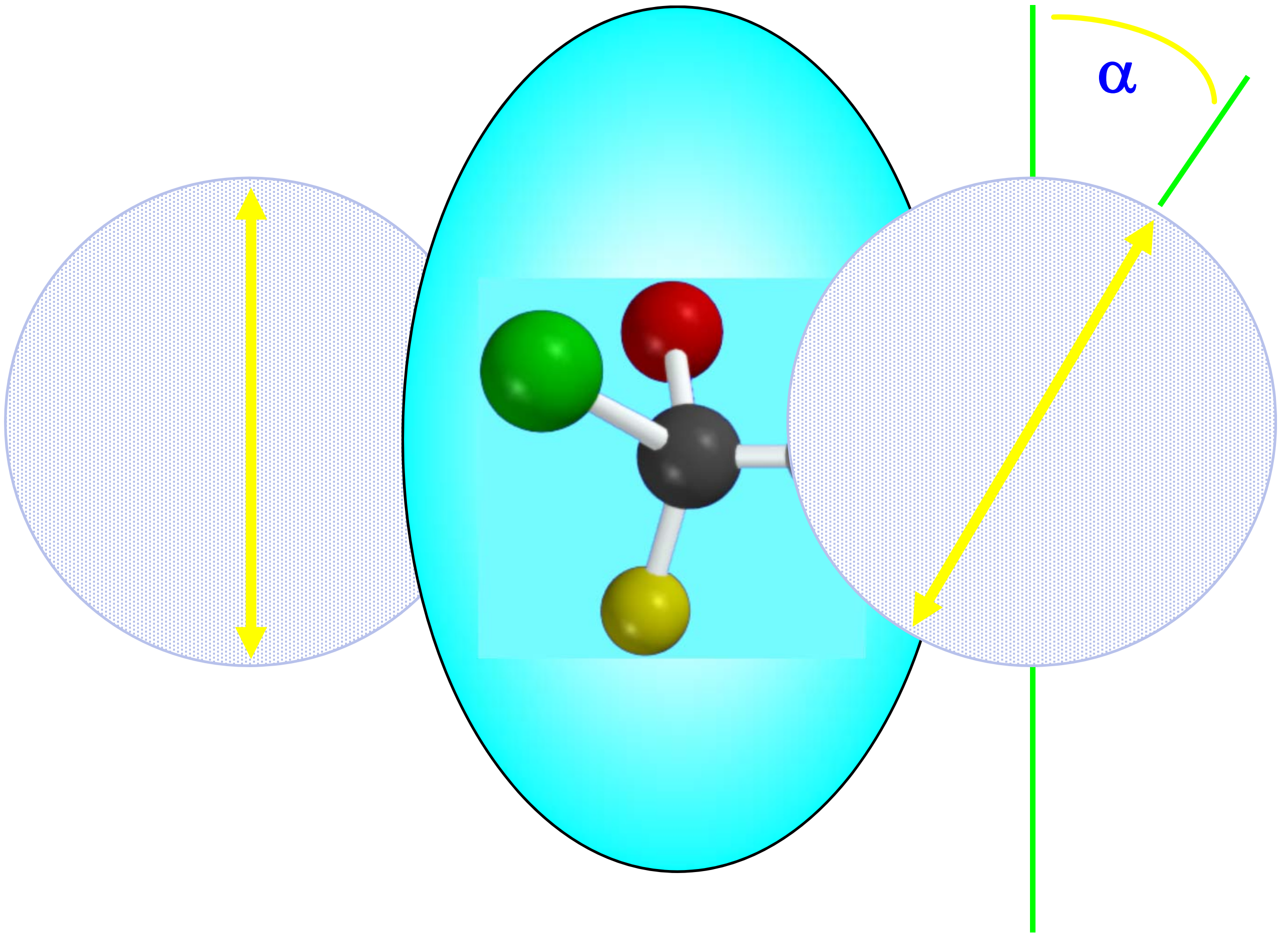


Polarized light





Rotation of plane-polarized light



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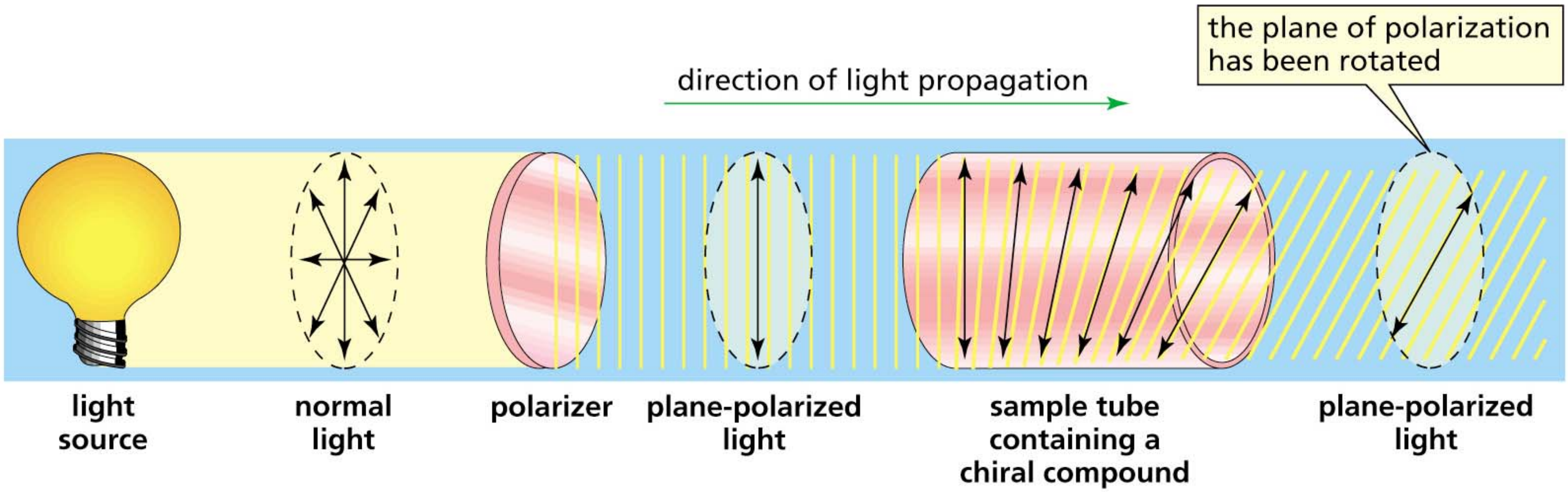


Clockwise (+) Counterclockwise (-)

Different from *R*,*S* configuration

A polarizer measures the degree of optical rotation of a compound

The observed rotation (α)

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l \times c}$$

$[\alpha]_{\lambda}^{T}$ = *specific rotation*

T is the temp in °C

λ is the wavelength

α is the measured rotation in degrees

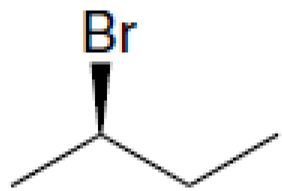
l is the path length in decimeters

c is the concentration in grams per mL

Each optically active compound has a characteristic specific rotation

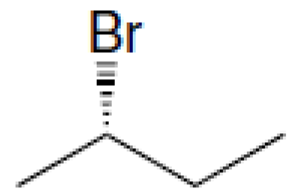
Optical Activity

- Consider the enantiomers of 2-bromobutane.



(*R*)-2-Bromobutane

$$[\alpha]_{D}^{20} = -23.1$$



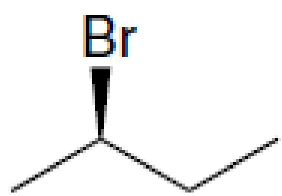
(*S*)-2-Bromobutane

$$[\alpha]_{D}^{20} = +23.1$$

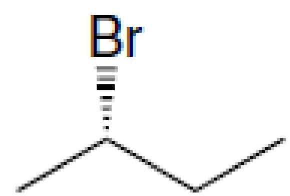
The optical activity was measured at 589 nm, which is the sodium D line wavelength.

Optical Activity

- For unequal amounts of enantiomers, the ENANTIOMERIC EXCESS (% ee) can be determined from the optical rotation.



$[\alpha]_D^{20} = -23.1$

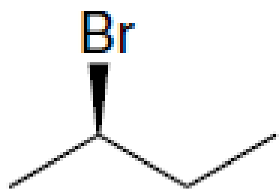


$[\alpha]_D^{20} = +23.1$

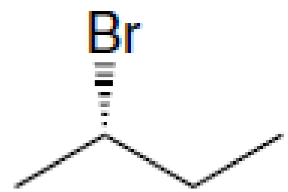
- For a mixture of 70% (*R*) and 30% (*S*), what is the % ee?

Optical Activity

- If the mixture has an optical rotation of +4.6, use the formula to calculate the % ee and the ratio of *R*/*S*.



$[\alpha]_D^{20} = -23.1$



$[\alpha]_D^{20} = +23.1$

$$\text{optical purity} = \frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}}$$

$$\text{enantiomeric excess (e.e.)} = \frac{\text{excess of a single enantiomer}}{\text{entire mixture}}$$

Calculate the enantiomeric excess for a sample in which the Ratio of diastereomers determined is 3.5:1.

Resolution of Enantiomers

- To separate compounds from one another, most methods take advantage of the differences in physical properties of the compounds to be separated:
  - Distillation separates compounds with different boiling points.
  - Recrystallization separates compounds with different solubilities.
  - Can you think of more methods of separation or purification?

Resolution of a Racemic Mixture

(*R*)-acid ((*S*)-acid

enantiomers

(*S*)-base →

(*R*,*S*)-salt (*S*,*S*)-salt

diastereomers

(*R*,*S*)-salt (*S*,*S*)-salt

HCl ↓ ↓ HCl

(*S*)-baseH^+ + (*R*)-acid

(*S*)-baseH^+ + (*S*)-acid

For Next Time….

Wednesday Chapter 6:
Kinetics and Thermodynamics (6.1-6.6)

Friday Chapter 6: Mechanisms (6.7 - 6.10, 6.12)
(We'll come back to 6.11 later.)

Suggested Homework Problems Chapter 5
#4, 9, 19,23,31, 36,38 (a-c), 39 (a-e),45, 55

Suggested Homework Problems Chapter 6
#4, 7, 11, 17, 24, 26, 28, 34-36