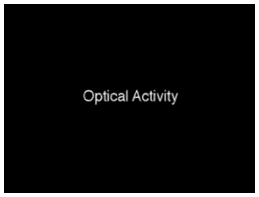
# Optical Activity/ Optical Rotation

## *Optical Activity*



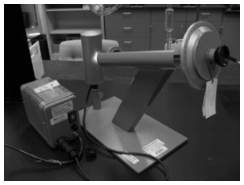

## *Optical Activity*

A substance is optically active if it rotates a plane of polarized light.

In order for a substance to exhibit optical activity, it must be chiral and one enantiomer must be present in excess of the other.

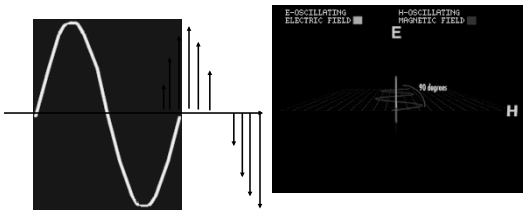
## *Polarimetry*

http://chemconnections.org/organic/chem226/226assign-12.html#polarimetry



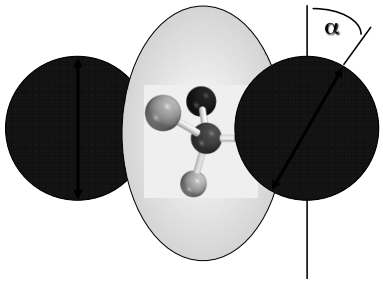
http://chemconnections.org/organic/chem226/Labs/opt-rotation/opt-rot-I.html

## *Light: electromagnetic radiation*

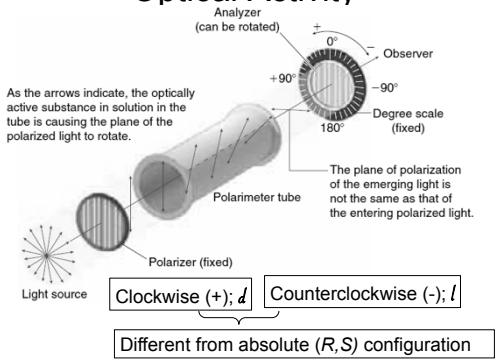



Optical activity is usually measured using light having a wavelength of 589 nm; this is the wavelength of the yellow light from a sodium lamp and is called the D line of sodium.

## *Rotation of plane-polarized light*



# Optical Activity




# Optical Activity/ Rotation

- The angular rotation observed in a polarimeter depends on:
  - the optical activity of the compound
  - the concentration of the sample
  - the path length of the sample cell
- A compound's specific rotation [α] can be used as a characteristic physical property of a compound:
  - the rotation observed using a 10-cm sample cell and a concentration of 1 g/mL.

# Optical Activity

$$[\alpha] = \frac{\alpha\ (observed)}{c * l}$$

**[α] = specific rotation**

**c = concentration in g/mL**

**l = path length in dm**

**α (observed) = rotation observed for a specific sample**

# Optical Activity

Example: A solution of 2.0 g of (+) -glyceraldehyde in 10.0 mL of water was placed in a 100. mm polarimeter tube. Using the sodium D line, a rotation of 1.74° was observed at 25°C. Calculate the specific rotation of (+) -glyceraldehyde.

$$[\alpha] = \frac{\alpha\ (observed)}{c * l}$$

# Optical Activity

**Given: α (obs) = 1.74°**

$$l = 100.\,mm \times \frac{1\,m}{1000\,mm} \times \frac{10\,dm}{1\,m} = 1.00\,dm$$

$$c = \frac{2.0\,g}{10.0\,ml} = 0.20\,g/mL$$

**Find: [α]**

$$[\alpha] = \frac{\alpha\ (observed)}{c * l}$$

## Question: *Calculate* $[\alpha]_D$

- A 1.00-g sample is dissolved in 20.0 mL ethanol. 5.00 mL of this solution is placed in a 20.0-cm polarimeter tube at 25°C. The observed rotation is 1.25° counterclockwise.

$[\alpha]_D$ =

A) -1.25 ° B) -6.125 ° C)-12.5 ° D) +61.25 °

*Racemic mixture*

A 50:50 mixture containing equal quantities of *enantiomers* is called a *racemic mixture*.

*A racemic mixture is optically inactive.*

($\alpha = 0$)

A sample that is optically inactive can be either an achiral substance or a racemic mixture.

*Optical purity*

an optically pure substance consists exclusively of a single enantiomer

enantiomeric excess =
% one enantiomer – % other enantiomer

% optical purity = enantiomeric excess

Some mixtures are neither optically pure (all one enantiomer) nor racemic (equal mixture of both enantiomers). They can be defined by their optical purity which equals enantiomeric excess.

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

$$\text{enantiomeric excess} = \frac{\text{excess of a single enantiomer}}{\text{entire mixture}} \times 100\%$$

## Optical Activity

Example: (-)-2-butanol has a specific rotation of - 13.5° while the specific rotation of (+)-2 -butanol is +13.5°. Calculate the optical purity of a mixture containing (+) and (-)-2-butanol if the mixture has an observed rotation of – 8.55°. Does the mixture contain more (+) or more (-)-2-butanol?

**o.p. = $\frac{-8.55^\circ}{-13.5^\circ}$ x 100% = 63.3%**

## Optical Activity

What is the e.e of a mixture containing 25% (+)-2-butanol and 75% (-)-2-butanol if the specific rotation of (+)-2-butanol is 13.5°.

$$e.e. = \frac{|d - l|}{d + l} x\,100\%$$

$$e.e. = \frac{|25 - 75|}{25 + 75} x\,100\% = \frac{|-50|}{100} x\,100\% = 50.\%$$

## Optical Activity

What is the e.e of a mixture containing 25% (+)-2-butanol and 75% (-)-2-butanol if the specific rotation of (+)-2-butanol is 13.5°.

$$e.e. = \frac{|d - l|}{d + l} x\,100\%$$

$$e.e. = \frac{|25 - 75|}{25 + 75} x\,100\% = \frac{|-50|}{100} x\,100\% = 50.\%$$

## Question

A sample of a pure *R*- enantiomer has a specific rotation of – 40°. A mixture of R-/S- enantiomers has an observed optical rotation of + 22°. What is the % ee of the mixture?

A. 55 % ee *R*
B. 55 % ee *S*
C. 18 % ee *R*
D. 0.55 % ee *R*
E. none of the above

## Question

If a sample is 50 % ee of *R* stereoisomer, what is the % *R* in the mixture?

A. 50
B. 100
C. 25
D. 75

## Question

If a chemical reaction produces a mixture of 80% *R* and 20 % *S*, what is the % ee?

A. 80
B. 60
C. 20
D. 10
E. 4

## Question

If a sample of the pure *R* enantiomer of a molecule has a specific rotation of – 40° what is the specific rotation of pure *S*?

A. –60°
B. +60°
C. –40°
D. +40°
E. cannot be determined

## Question

If the specific rotation of (*R*)-2-methylhexan-2-ol is –35°, what is the specific rotation of (*S*)-hexan-2-ol?

A. +35°
B. –35°
C. It is negative but value cannot be determined.
D. It is positive but value cannot be determined.
E. It cannot be determined.

## Question

If a sample of the pure *R* enantiomer of a molecule has a specific rotation of – 40° and an enantiomeric mixture of that molecule has an 82% ee *S*, what shoulld be the observed specific rotation of the sample?

A. +40°
B. +8.2°
C. +32.8°
D. –48.7°
E. cannot be determined

## Question

Calculate the relative proportions of (+)-2-butanol, $[\alpha]_D = +13.5^o$, and (-)-2-butanol, $[\alpha]_D = -13.5^o$, required to give a specific rotation of $+0.45^o$.

A. 50% R : 50% S
B. 90% R : 10% S
C. 3.3 % R : 92.7% S
D. 52% R : 48% S
E. cannot be determined