



Kinetics of Chemical Reactions – Chem 313

Lecture 7

Rate's Investigation Cont.

Ahmad Alakraa

Chemical methods

- ▶ As titrations where a sample (aliquot) is taken at different intervals and **analyze** it.
- ▶ Slow methods
- ▶ Sampling errors
- ▶ Requires to stop (**quench**) reactions or at least **slow it down** during analysis. This may involve:
 - ▶ a sudden cooling
 - ▶ removing one of the reagent (**e.g.**, in **saponification of ester** an acid can be added to neutralize excess alkali)
 - ▶ adding a large amount of solvent
 - ▶ removing a catalyst
 - ▶ adding a quencher

Exercise



- The catalytic decomposition of hydrogen peroxide, H_2O_2 , is easily followed by titrating 10.0 cm^3 samples with $0.0100 \text{ mol dm}^{-3}$ KMnO_4 at various times. Calculate the $[\text{H}_2\text{O}_2]$ at the various times, and show that these values lie on a smooth curve when plotted against time?

t/min	5	10	20	30	50
V(KMnO_4)/mL	37.1	29.8	19.6	12.3	5.0

Solution

Reduction



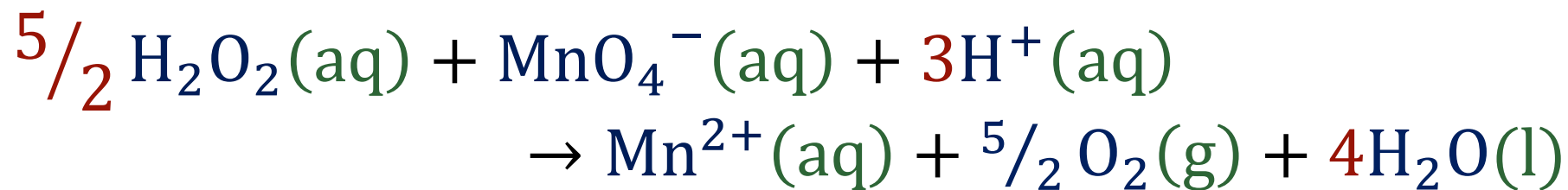


Oxidation



× 5/2

Overall



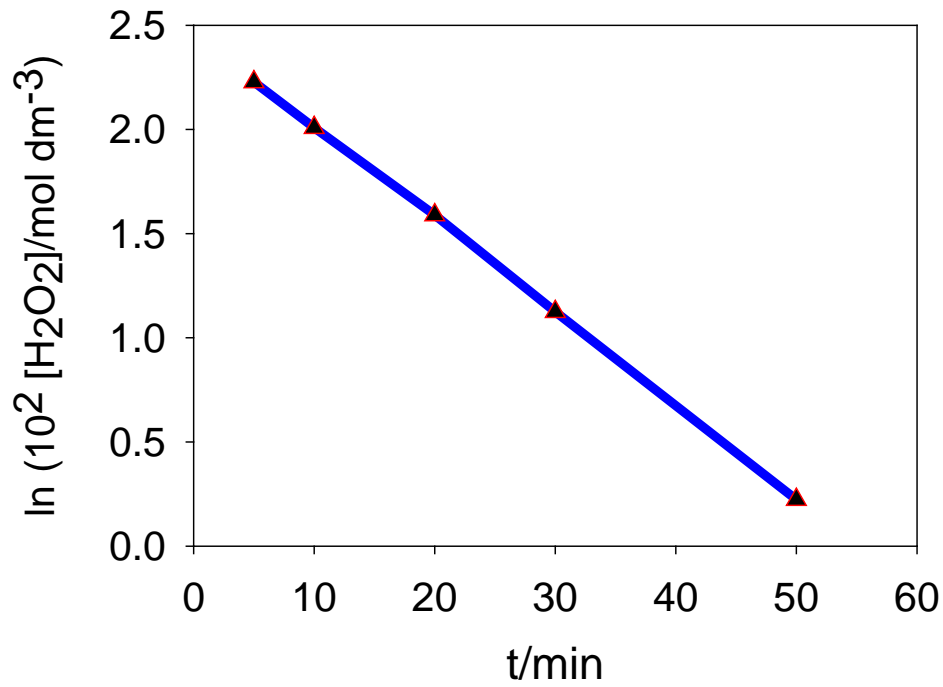
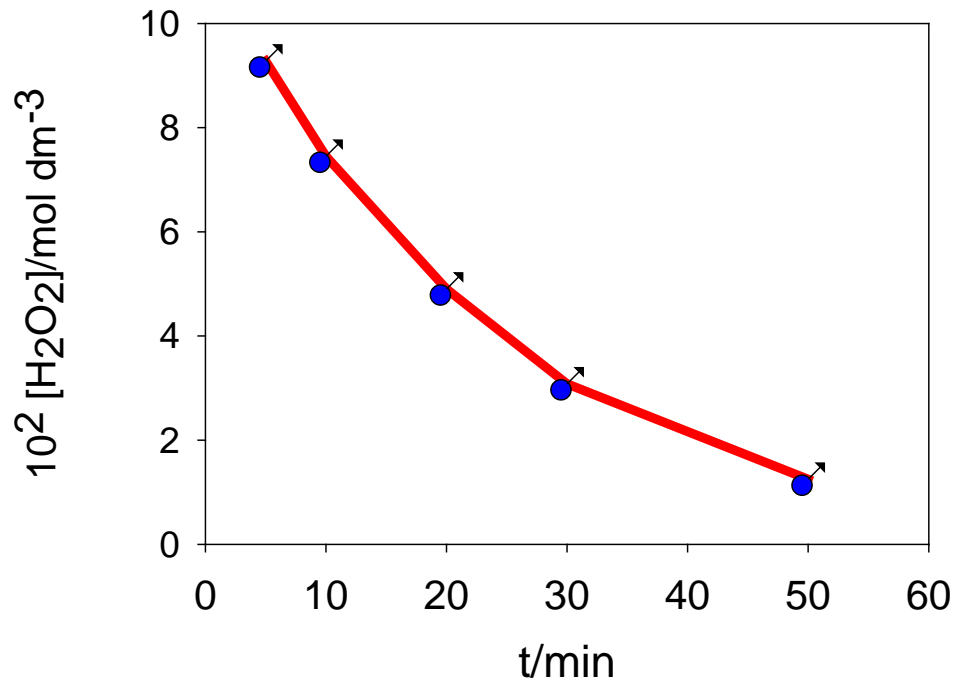
0.0100 mol dm^{-3} KMnO_4

10 mL H_2O_2

t/min	5	10	20	30	50
$V(\text{MnO}_4^-)/\text{mL}$	37.1	29.8	19.6	12.3	5.0
$10^4 \times \text{moles MnO}_4^-$	3.71	2.98	1.96	1.23	0.50
$10^4 \times \text{moles H}_2\text{O}_2$	9.28	7.45	4.90	3.08	1.25
$10^2 \times [\text{H}_2\text{O}_2]/\text{mol dm}^{-3}$	9.28	7.45	4.90	3.08	1.25

1 mol MnO_4^- reacts with $5/2$ mol H_2O_2

A graph of $[\text{H}_2\text{O}_2]$ vs. **time** is a smooth curve showing the progressive decrease in reactant concentration with time.



Changes in Physical Properties



Sometimes, it is not possible to generate kinetic information in terms of common properties (**concentration, total pressure, partial pressure**, etc.).



It might be possible to measure the reaction extent as a function of any physical property of the system, such as



absorbance,



electric conductivity,



refractive index, and



rotation of a plane of polarized light.



These are **additive functions** of the contributions of all chemical species and in general they vary **linearly** with the **concentration**

Refractive index (RI) / n

dimensionless



When a ray of electromagnetic radiation strikes a flat surface at an angle, the ray may be bent upward (**reflected**) or bend downward (**refracted**).



Snell's Law

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

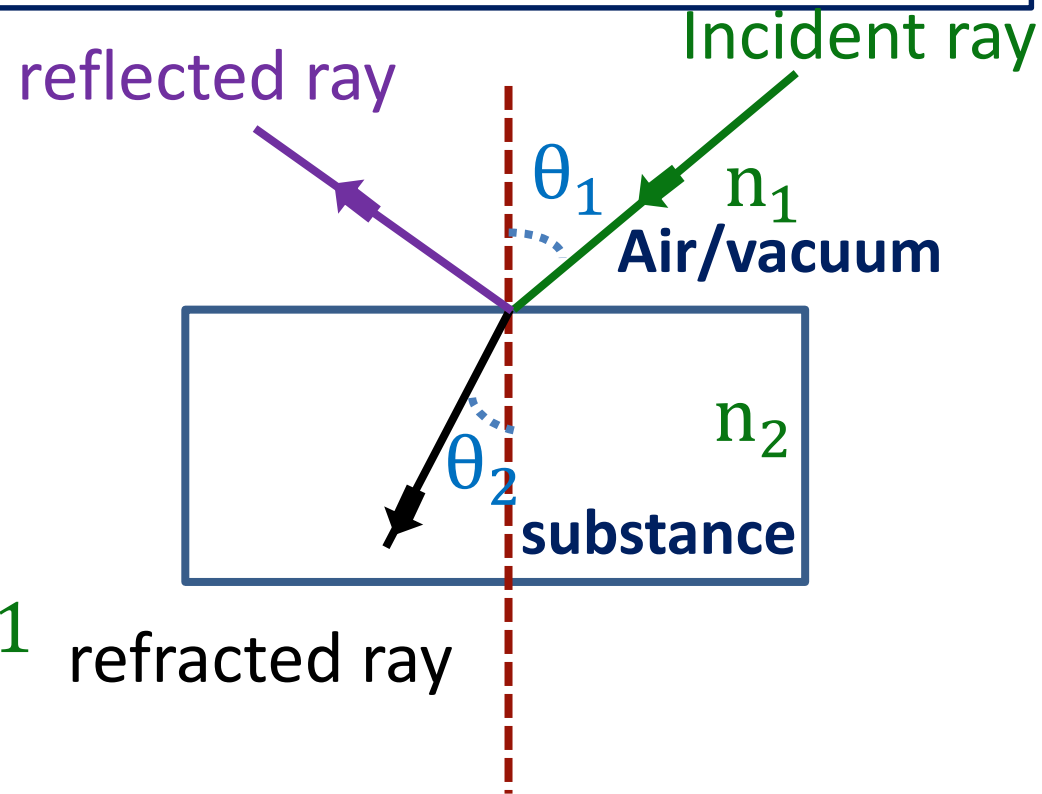
θ_1 : angle of incidence

θ_2 : angle of refraction

For Air & Vacuum, $n_1 \approx 1$

$$n_2 = \frac{\sin \theta_1}{\sin \theta_2} = \frac{V_1}{V_2}$$

V_1 : speed of light in vacuum or air
 V_2 : speed of light in a substance



Refractive index, RI or n



The **lower** the **optical density** of the substance, the **faster** the **movement** of light inside it and the **lower** its **RI**.



depends on **temperature** and **wavelength** of light.



is a **constant quantity** for a pure substance under standard conditions of **temperature** and **pressure**.



If the concentration in a solution is sufficiently **low**, the refractive index is proportional to **concentration**.

Specific & molecular refractivity



For any compound, each **atom**, **bond**, or **group** contributes to the overall RI of the compound.



When these individual contributions (**atomic refractions**) are taken together, the result is the specific refractivity (**r**).

$$r = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{d}$$

d: density of the compound

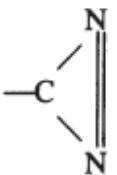
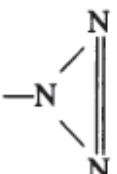
$$R = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{d}$$

Lorentz-Lorenz equation



If the specific refractivity is multiplied by the molecular mass (**M**) of a compound, then the molecular refractivity, **R**, is obtained.

Atomic refractions

Element structural unit	N_{aD}	Element structural unit	N_{aD}
F	1.0	Nitro group in	
C	2.42	aromatic nitro compounds	7.30
H	1.10	nitroamines	7.51
O in OH	1.52	nitroparaffins	6.72
O in ester OR	1.64	alkyl nitrites	7.44
O^{2-}	2.21	alkyl nitrates	7.59
Cl	5.97		
Br	8.86	Nitroso group in	
I	13.90	nitrates	5.91
S in SH	7.69	nitrosoamines	5.37
S in R_2S	7.97		
S in RCNS	7.91	Double bond	
S in R_2S_2	8.11	no radicals	1.51
O in ether	1.64	$RCH=CH_2$	1.60
N		$RCH=CHR$	1.75
in I° aliphatic amines	2.32	$R_2C=CHR$	1.88
in II° aliphatic amines	2.49	$R_2C=CR_2$	2.00
in III° aliphatic amines	2.84		
in I° aromatic amines	3.21	Triple bond	2.40
in II° aromatic amines	3.59	3-membered ring	0.71
in III° aromatic amines	4.36	4-membered ring	0.48
in hydroxylamines	2.48		
in hydrazines	2.47	Diazo group	
in aliphatic cyanides	3.05		
in aromatic cyanides	3.79		8.43
in aliphatic oximes	3.93		
in amides	2.65		7.47
in II° amides	2.27		
in III° amides	2.71		

N_{aD} : Standard refractive index measurements are taken at the "yellow doublet" [sodium D line](#), $\lambda = 589 \text{ nm}$.

Example

Using the table of atomic refractions, calculate the RI of dimethoxymethane ($\text{CH}_3\text{OCH}_2\text{OCH}_3$; $M = 76.10 \text{ g/mol}$, $d = 0.8560 \text{ g/mL}$)?

Solution

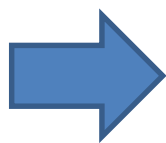
$$3\text{C:} \quad 3 \times 2.42 = 7.26$$

$$8\text{H:} \quad 8 \times 1.10 = 8.80$$

$$2 \text{ ether O:} \quad 2 \times 1.64 = 3.28$$

$$R = 19.34 \text{ mL/mol}$$

$$R = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{d}$$



$$19.34 = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{76.10}{0.8560}$$



The value reported in literature is **1.3534**, i.e, **matching**

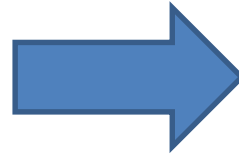
$$n = 1.354$$

Refractive index of mixtures, r_m



The RI of mixtures ($a + b$) varies linearly with the mole fraction of the components.

$$r_m = \frac{Xr_a}{Z} + \frac{Yr_b}{Z}$$



$$Zr_m = Xr_a + Yr_b$$

X : mass of compound a

Y : mass of compound b

r_a : specific refractivity of compound a

r_b : specific refractivity of compound b

Z : the total mass of the mixture

r_m : specific refractivity of the mixture



The **mixture composition** can be assessed as in the following example.

Example

20 mL of a mixture of xylene and carbon tetrachloride had a density of 1.2156 g/mL and $n_D^{25} = 1.4338$. Pure xylene has a density of 0.8570 g/mL and $n_D^{25} = 1.4915$; pure carbon tetrachloride has a density of 1.5816 g/mL and $n_D^{25} = 1.4562$. Calculate the mass % of this mixture.

Solution

$$Zr_m = Xr_a + Yr_b$$

$$r = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{d}$$



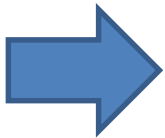
Data provided can calculate Z , r_m , r_a , and r_b .

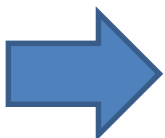
Z →

$$\begin{aligned} Z &= \text{Volume} \times \text{density} \\ &= 20 \text{ mL} \times 1.2156 \text{ g mL}^{-1} = 24.31 \text{ g} \end{aligned}$$

r_m →

$$r_m = \left(\frac{1.4338^2 - 1}{1.4338^2 + 2} \right) \frac{1}{1.2156} = 0.2311 \text{ mL g}^{-1}$$

r_a  $r_a = \left(\frac{1.4915^2 - 1}{1.4915^2 + 2} \right) \frac{1}{0.8570} = 0.3382 \text{ mL g}^{-1}$
X: xylene

r_b  $r_b = \left(\frac{1.4562^2 - 1}{1.4562^2 + 2} \right) \frac{1}{1.5816} = 0.1719 \text{ mL g}^{-1}$

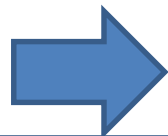
Y: carbon tetrachloride

Substitute in

$$Zr_m = Xr_a + Yr_b$$

$$(24.31)(0.2311) = 5.618 = 0.3382 X + 0.1719 Y$$

However



$$X + Y = 24.31 \text{ g}$$

Solve 2 equations in 2 unknowns

$$X = 8.65 \text{ g}$$

$$Y = 15.66 \text{ g}$$

Mixture is 64.4% by mass carbon tetrachloride and 35.6% by mass xylene.

Refractometry Limitations



To measure RI, the reaction mixture should be an **optical element** of the refractometer (**limitation**).



Suitable only for slow reactions (reaction times in the **order of an hour**).



A severe limitation is that refraction can only measure the **total concentration** of mixtures.

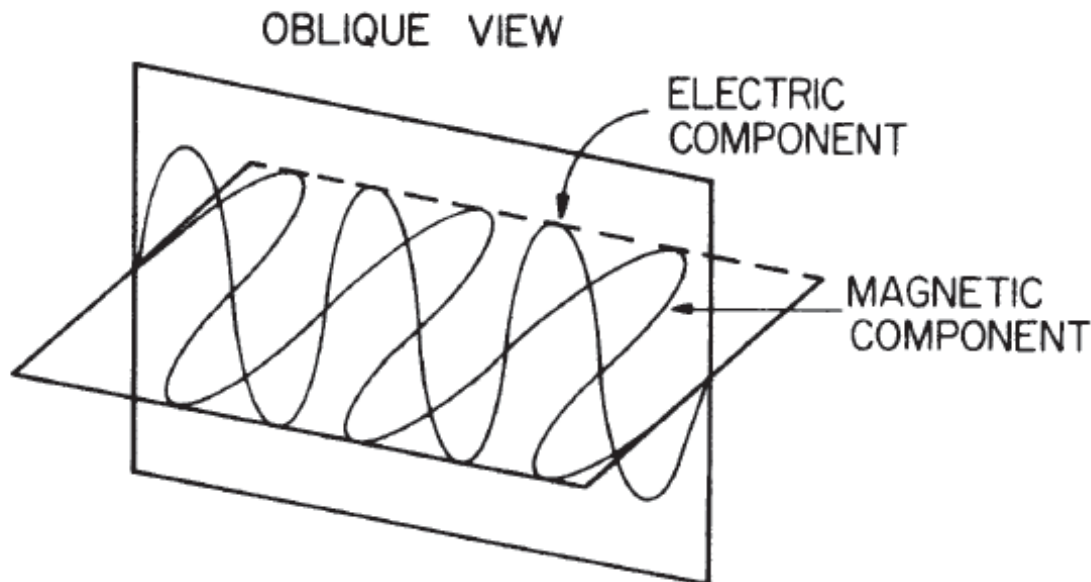
Polarimetry: Polarized radiation



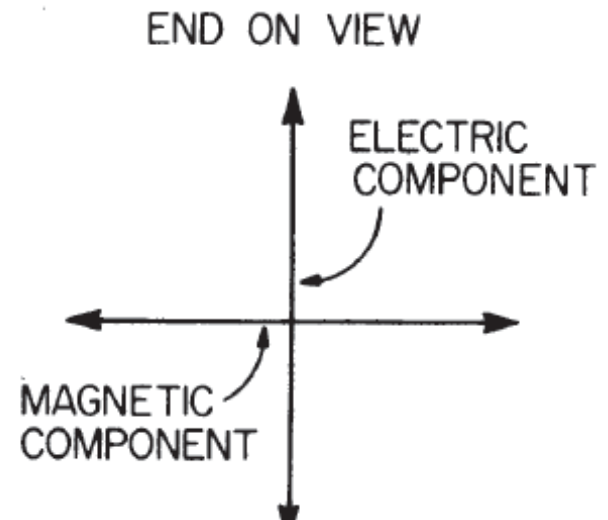
Radiation from normal lamps (**unpolarized**) propagates in all directions with **perpendicular** electric and magnetic components).



If, by some means, all of the rays had their **electric** and **magnetic** components all in the same direction, then the radiation is **plane polarized**.



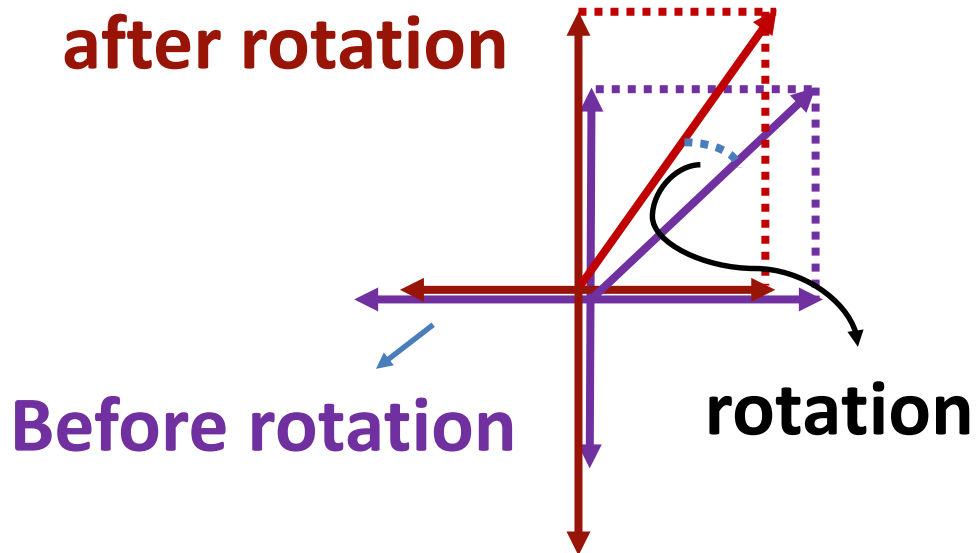
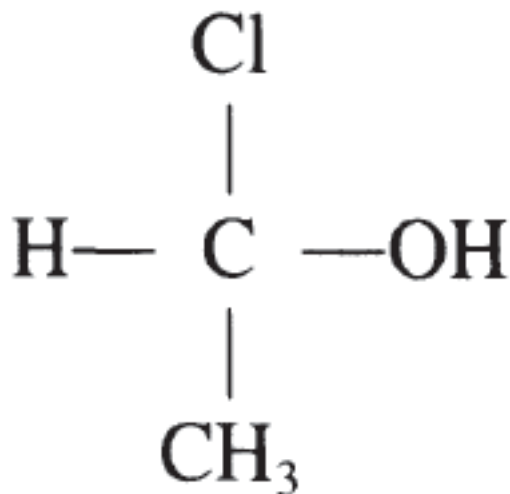
Unpolarized radiation



Plane polarized radiation

Optically active materials for rotation

1-chloro-1-ethanol



It is **unsymmetrical**, no matter where we placed a mirror in this molecule, we could not get an exact mirror image.



If **unpolarized radiation** strikes this molecule, and the electric component of one ray interacts more with one side than the other, we might notice an effect.



However, since the radiation is **unpolarized**, there are always some rays oriented opposite to the first ray that react in just the opposite manner and cancel out any initial effect we might have seen.



On the other hand, if **polarized radiation** strikes the molecule, there is no way for an opposite effect to take place, and the radiation is "**rotated**."



Compounds that can rotate polarized light are said to be **optically active**

Nomenclature for optical rotation



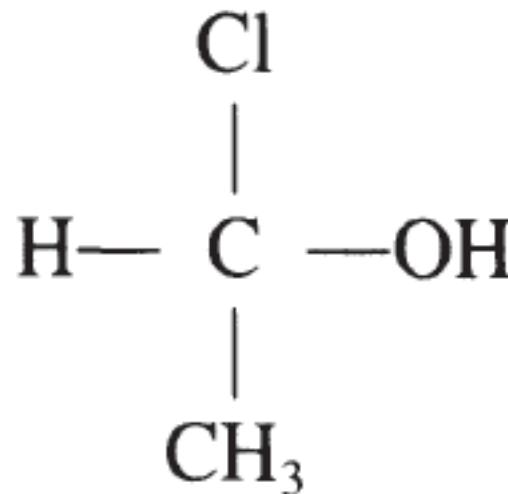
Old system: if you were looking toward the light source and the rotation was clockwise, then the compound was said to be **dextro** (+, **right**); if rotation was counterclockwise, then the compound was **levo** (–, **left**).



Cahn-Ingold-Prelog system (Currently): is not based on rotation but on molecular configuration. e.g., for **1-chloro-1-ethanol**,



Select the "**center**" of the asymmetric atom to be examined. In this case, it is the **C** with the **H**, **Cl**, **OH**, and **CH₃** groups attached.





Assign the groups in their **order of importance**.



The atom directly bonded to the center atom with the highest atomic number is most important.



In this case, $\text{Cl} > \text{O} > \text{C} > \text{H}$.



In cases of a tie, mass is the tie breaker (e.g., ethyl > methyl).



Hold the molecule so that the **lowest priority atom** is directly **away** from you and behind the central atom.



Start at the **next lowest priority number** and go around to the highest.



If you go to the right, then the compound is designated R;



If to the left, then it is designated S.



In this case, we would go C to O to Cl in a **counterclockwise direction**; therefore this is an **S configuration**.

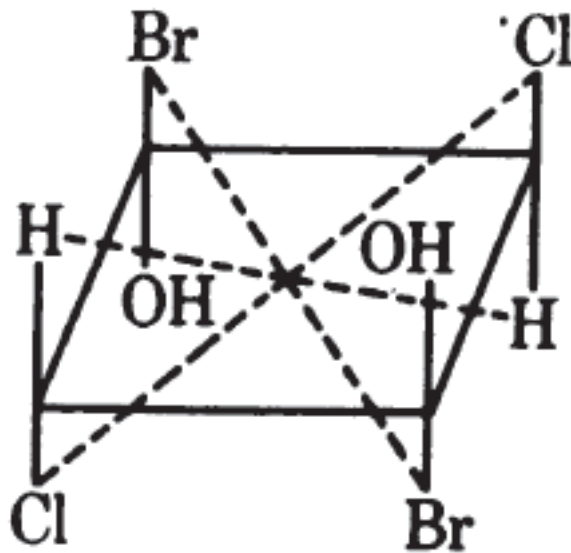
Asymmetric centers



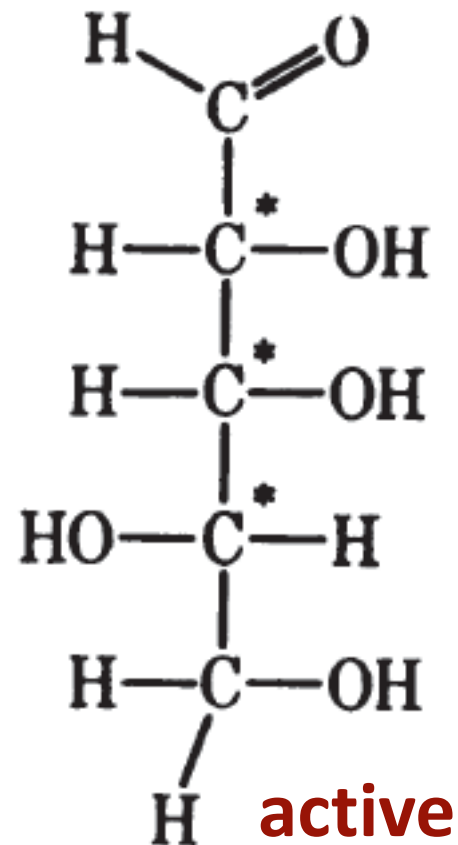
If a compound has a **plane of symmetry**, it cannot rotate polarized radiation, because what effect occurs on one side of the molecule is canceled out by an opposite effect on the other side of the molecule.



When we have an optically active atom in a molecule, it is generally **starred** and is called an **asymmetric center**.



inactive



active

Polarimetry



Optical rotation can be measured using a **polarimeter**. The reactor can be placed between the **polarizer** and the **analyzer** of the polarimeter.



This method can only be used to determine the concentration of **optically active components**.



The **angle** of rotation of the plane-polarized light is usually proportional to the **concentration** of the optically active component.

Exercise



Sugar inversion or the acid-catalyzed hydrolysis of saccharose (common table sugar).



Saccharose is dextrorotatory (rotates the plane of polarized light right), while the products of hydrolysis – glucose and fructose – laevorotatory (rotate it left). (This is the reason to call this process sugar inversion.)

Equation for analytical polarimetry

$$[\alpha]_{\lambda}^t = \frac{\alpha}{lc}$$



$[\alpha]_{\lambda}^t$: is the specific rotation in **degrees**,



t: the temperature in **°C**,



λ : the wavelength of radiation employed,



α : observed angle of rotation in **degrees** (function of **c**)



l: the length of the tube in **decimeters**,



c: the concentration in **g/mL** (for a pure liquid, density d replaces **c**).



$[\alpha]_{\lambda}^t$ varies with **temperature**, **wavelength** and sometimes with **concentration**.



Typically, $[\alpha]_{\lambda}^t$ does not change with **c** as it is normalized to it.

Example

A solution of an organic compound is placed in a 20-cm tube and produces a rotation of 38.73° . A tube containing only solvent has a rotation of 1.46° . If the specific rotation is 62.12° , what is the concentration of the solute?

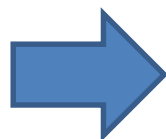
Solution

$$[\alpha]_{\lambda}^t = 62.12^\circ \quad l = 2 \text{ dm}$$

Correction for solvent

$$\alpha = 38.73^\circ - 1.46^\circ = 37.27^\circ$$

$$[\alpha]_{\lambda}^t = \frac{\alpha}{lc}$$



$$c = \frac{\alpha}{l[\alpha]_{\lambda}^t} = \frac{37.27^\circ}{2 \times 62.12^\circ} = 0.30 \text{ g mL}^{-1}$$

Effect of T on specific rotation

$$[\alpha]_{\lambda}^{t_1} - nt_1 = [\alpha]_{\lambda}^{t_2} - nt_2 = \text{constant}$$

$$[\alpha]_{\lambda}^{t_1} = [\alpha]_{\lambda}^{t_2} + n(t_1 - t_2)$$



$[\alpha]_{\lambda}^{t_1}$: is the specific rotation in degrees at t_1 ($^{\circ}\text{C}$),



$[\alpha]_{\lambda}^{t_2}$: is the specific rotation in degrees at t_2 ($^{\circ}\text{C}$)



n : is a constant

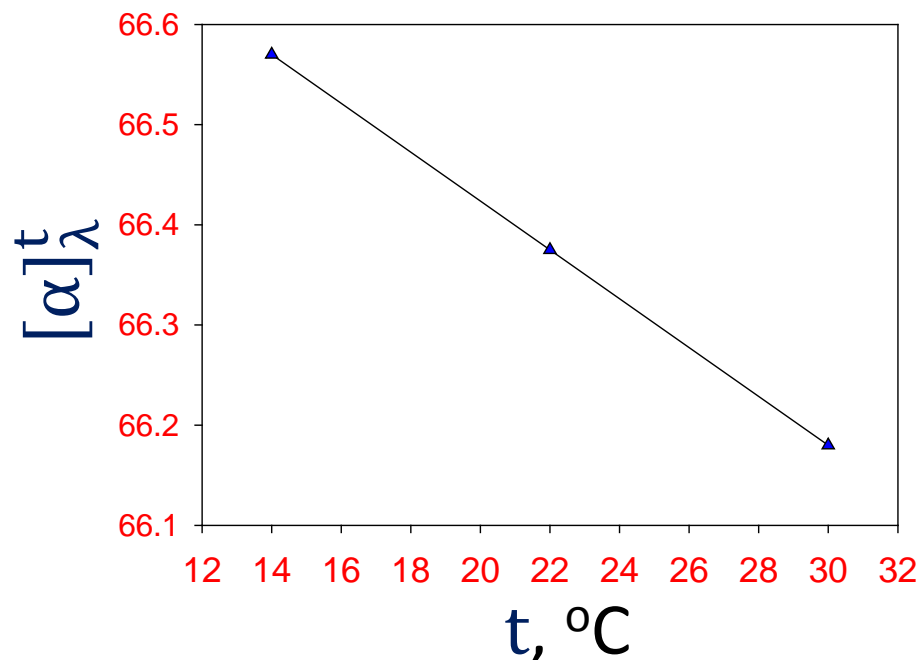
Example

A solution of sucrose was placed in a polarimeter and the specific rotation of sucrose was determined at three different temperatures. From the following data, determine the constant n and the value of $[\alpha]_D^{20}$:

Solution

$$[\alpha]_{\lambda}^t - nt = \text{constant}$$

$$[\alpha]_{\lambda}^t = nt + \text{constant}$$



t/°C	$[\alpha]_D^t$
14.0	66.57
22.0	66.375
30.0	66.18

$$\text{slope} = n = -0.0244$$

$$[\alpha]_{\lambda}^{20} = [\alpha]_{\lambda}^{22} - n(22 - 20)$$

$$\begin{aligned} [\alpha]_{\lambda}^{20} &= 66.375 + 0.0244(22 - 20) \\ &= 66.42 \end{aligned}$$

Effect of concentration on specific rotation



If $[\alpha]_{\lambda}^t$ changed with c , a second correction must be applied (Biot's equations)

$$[\alpha] = \begin{cases} A + Bq \\ A + Bq + Cq^2 \\ A \left[\frac{Bq}{C + q} \right] \end{cases}$$

linear

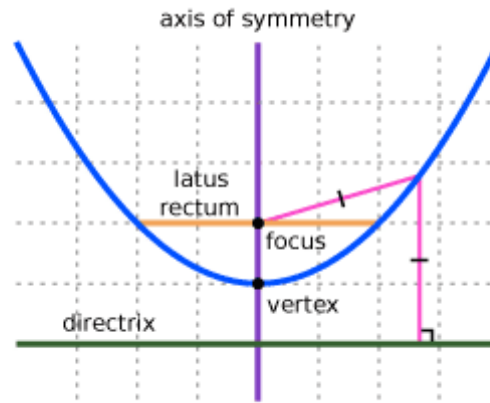
parabolic

hyperbolic

A, B, and C are constants and q the mass fraction of solvent in the solution.

$$[\alpha] = \frac{\alpha}{lpd}$$

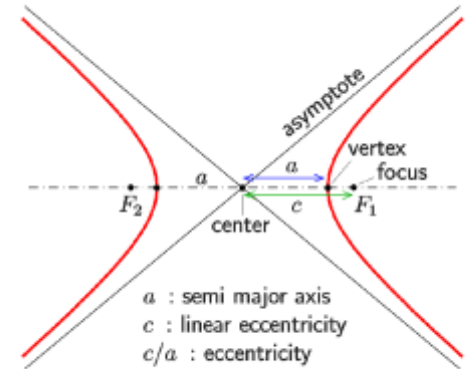
p : mass fraction of solute



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PARABOLA

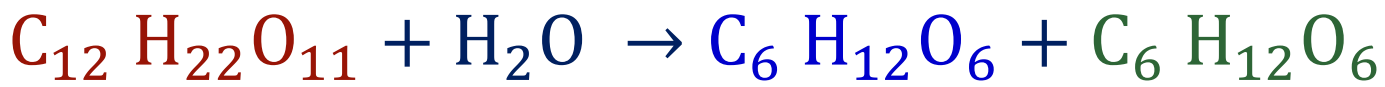
- When a set of points in a plane are equidistant from a given directrix or a straight line and from the focus then it is called a parabola.



HYPERBOLA

- When the difference of distances between a set of points present in a plane to two fixed points is a positive constant, it is called a hyperbola.

Inversion of Sucrose (cane sugar)



Sucrose

Glucose

Fructose

Sugar	$[\alpha]$ (°)
Sucrose	+66.5
Glucose	+52.7
Fructose	-92.0



The reaction is pseudo-first order and **rate** \propto **[Sucrose]**.



The reaction progress can be measured by the change in $[\alpha]$ by sucrose. α & $[\alpha]$ **increase** with $[\text{Sucrose}]_{\text{reacted}}$



If $[\alpha]_0$, $[\alpha]_t$ and $[\alpha]_\infty$ corresponded to rotations by sucrose at zero time, time t and by the end, respectively.



$$[\text{Sucrose}]_0 \propto [\alpha]_0 - [\alpha]_\infty$$



$$[\text{Sucrose}]_{\text{reacted}} \propto [\alpha]_0 - [\alpha]_t$$



$$[\text{Sucrose}] = [\text{Sucrose}]_0 - [\text{Sucrose}]_{\text{reacted}} \propto [\alpha]_t - [\alpha]_\infty$$

$$k = \frac{2.303}{t} \log \frac{[\text{Sucrose}]_0}{[\text{Sucrose}]} = \frac{2.303}{t} \log \frac{[\alpha]_0 - [\alpha]_\infty}{[\alpha]_t - [\alpha]_\infty}$$