

# Spectroscopy and its applications

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Principles, Electronic Spectroscopy of Conjugated Molecules, Woodward-Fieser Rule

Infrared Spectroscopy, Group Frequencies

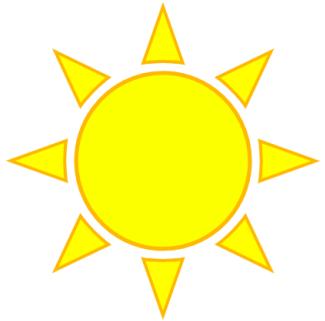
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## Reference Books

- Fundamental of Molecular Spectroscopy By **C B Banwell & E M McCash**
- Organic Spectroscopy By **William Kemp**
- Spectroscopy Of Organic Compounds By **P S Kalsi**
- Elementary Organic Spectroscopy By **Y R Sharma**

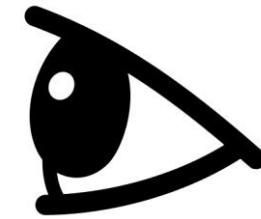




**Light Source**



**Interaction  
with matter**

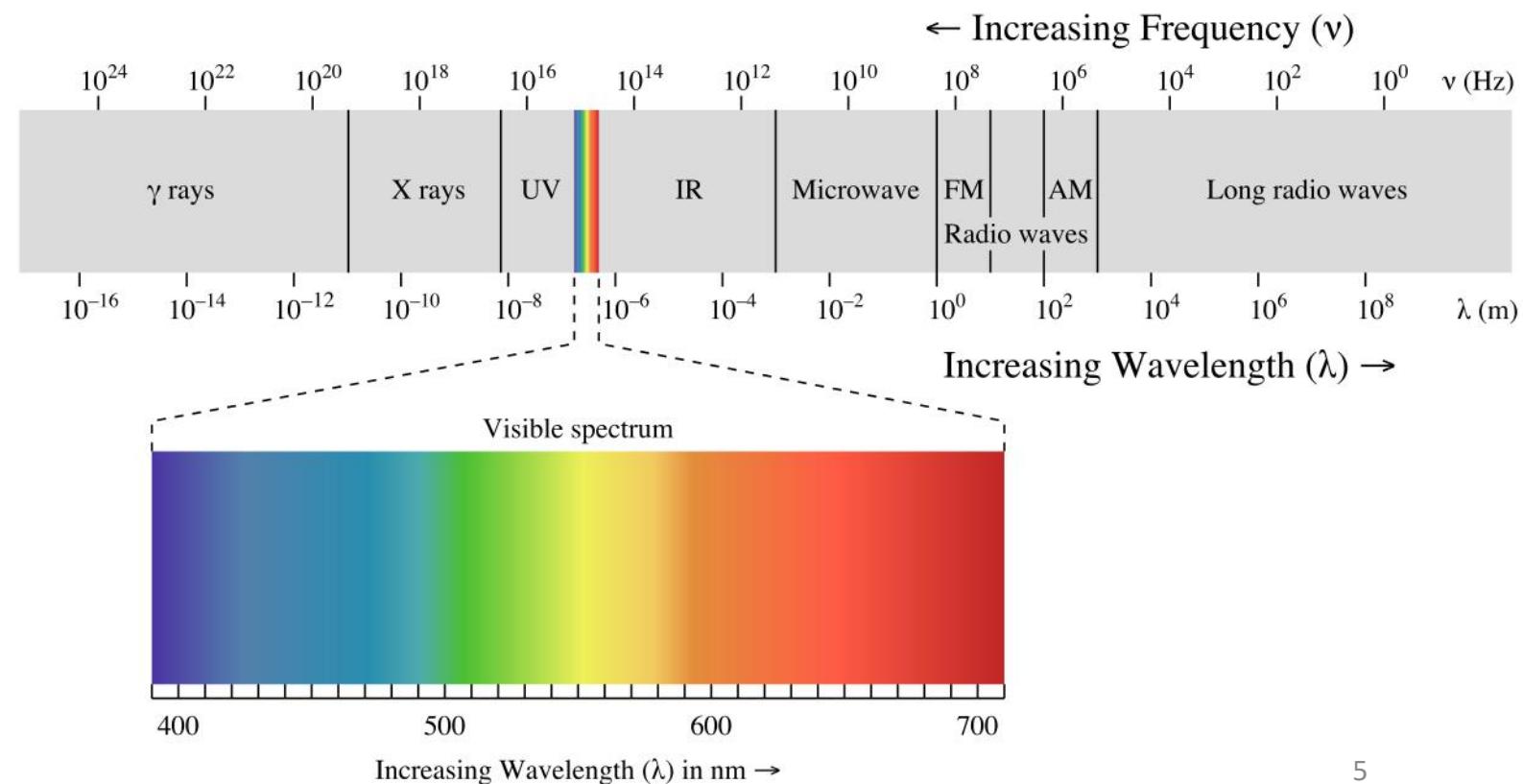


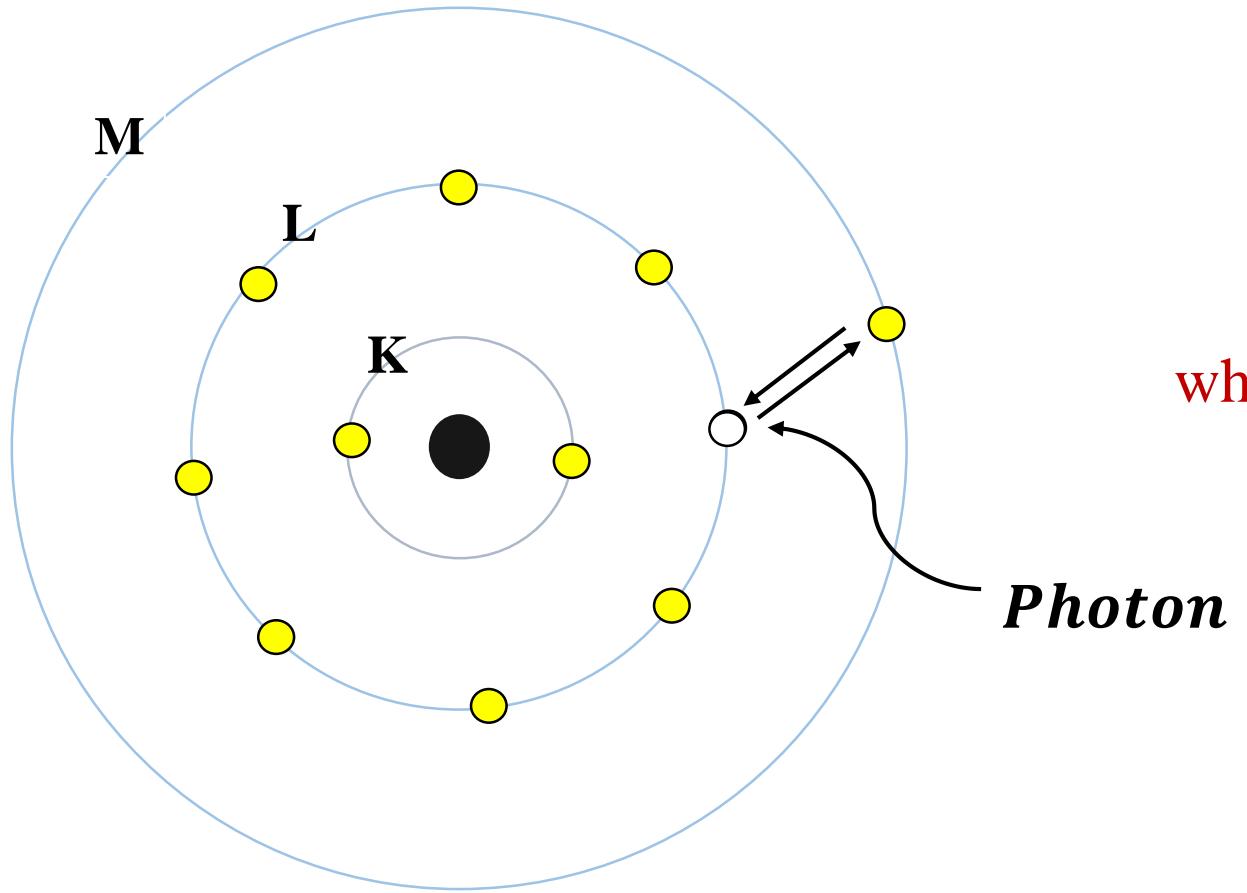
**Detector**

## ❑ Matter



## ❑ Radiation





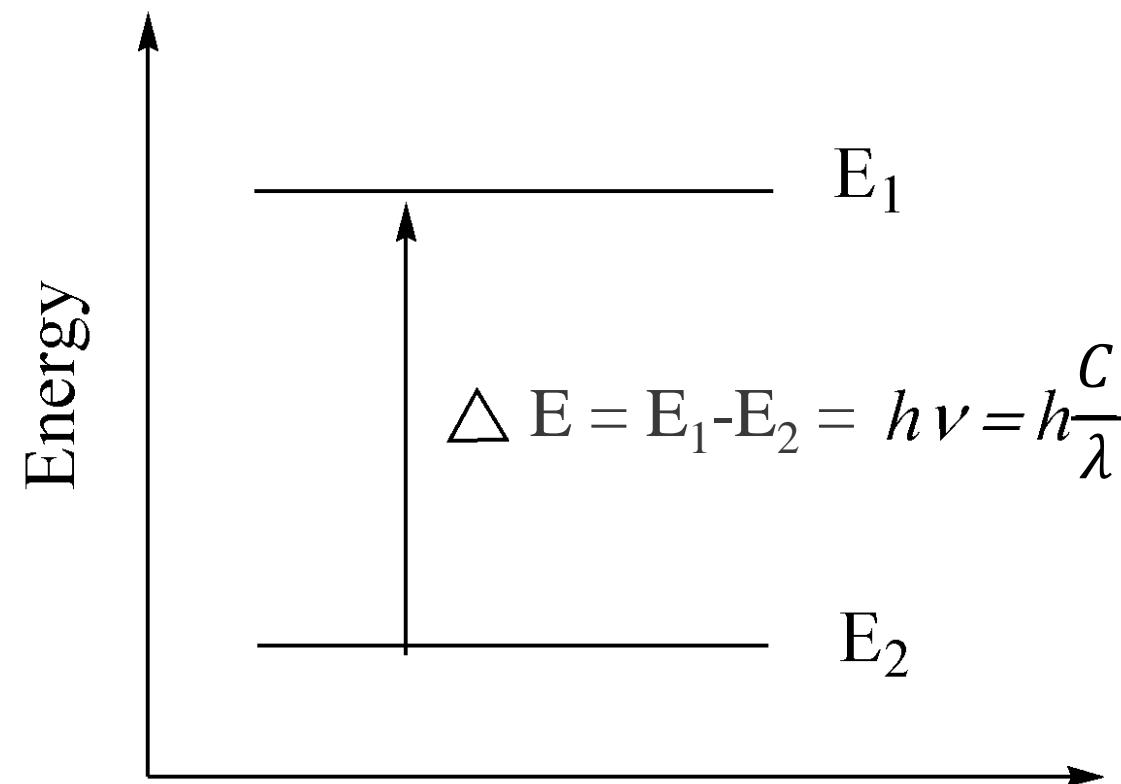
$$E = h\vartheta = h \frac{c}{\lambda}$$

where  $\vartheta$  = frequency &  $\lambda$  = wavelength

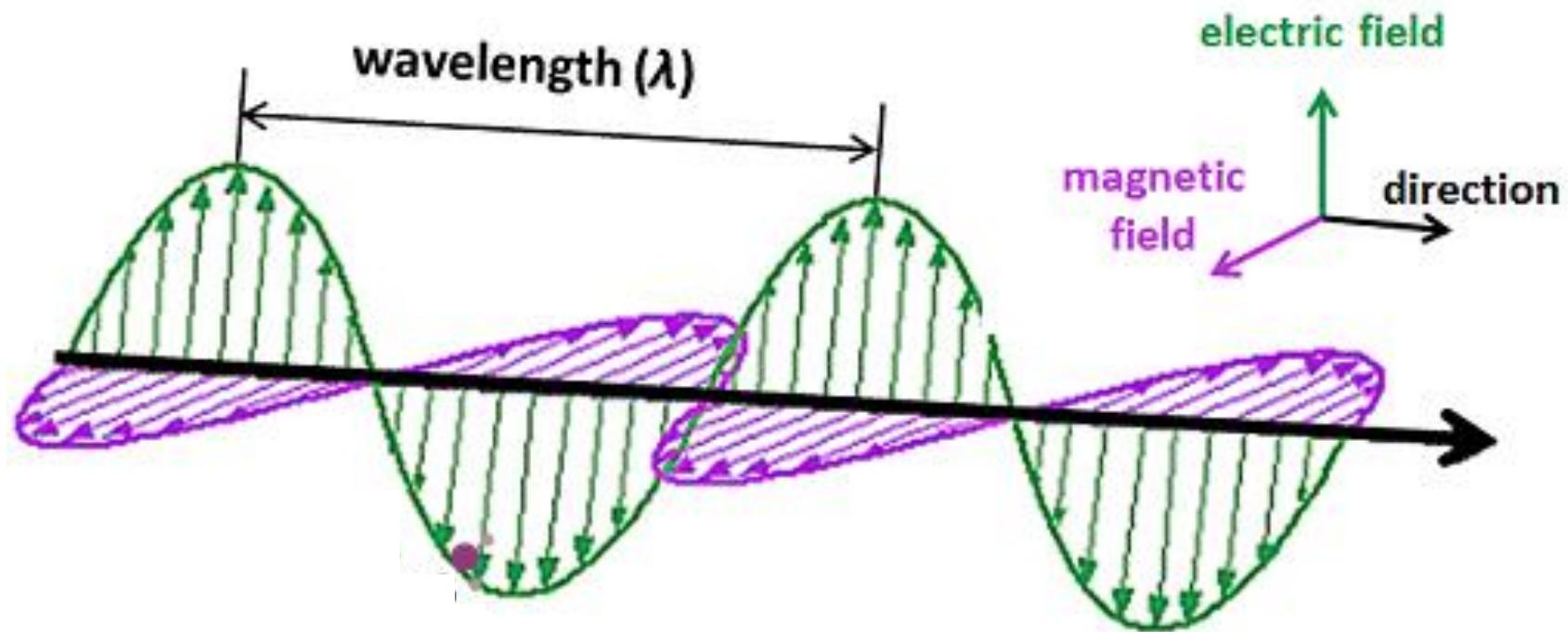
**Photon**

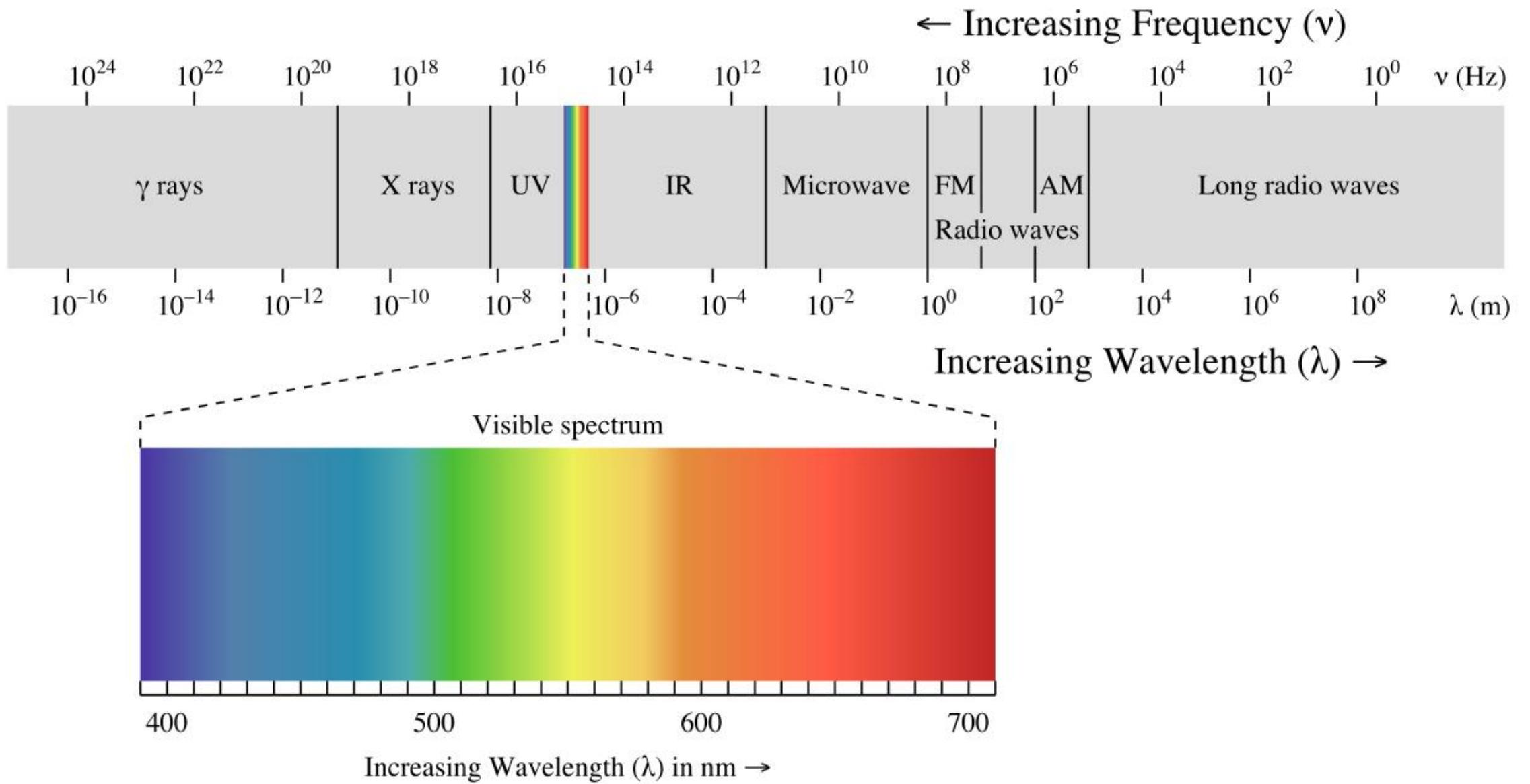
$$\text{Energy, } E = h\nu = h\frac{c}{\lambda}$$

where  $\nu = \text{frequency}$  &  $\lambda = \text{wavelength}$



# Electromagnetic Radiation





□ Various forms of EM radiations are

Ultra Violet (UV)

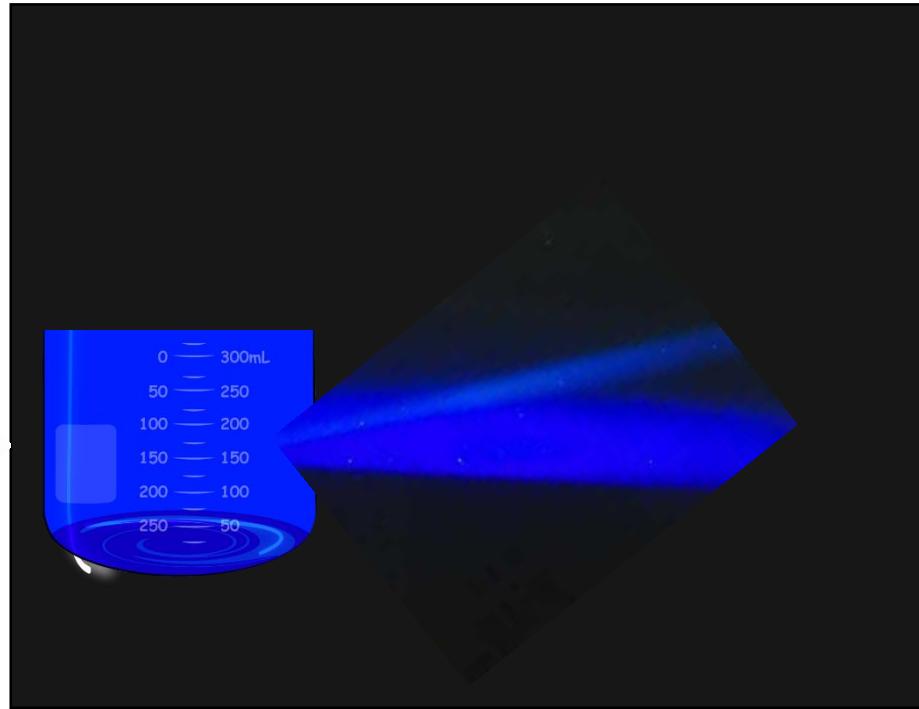
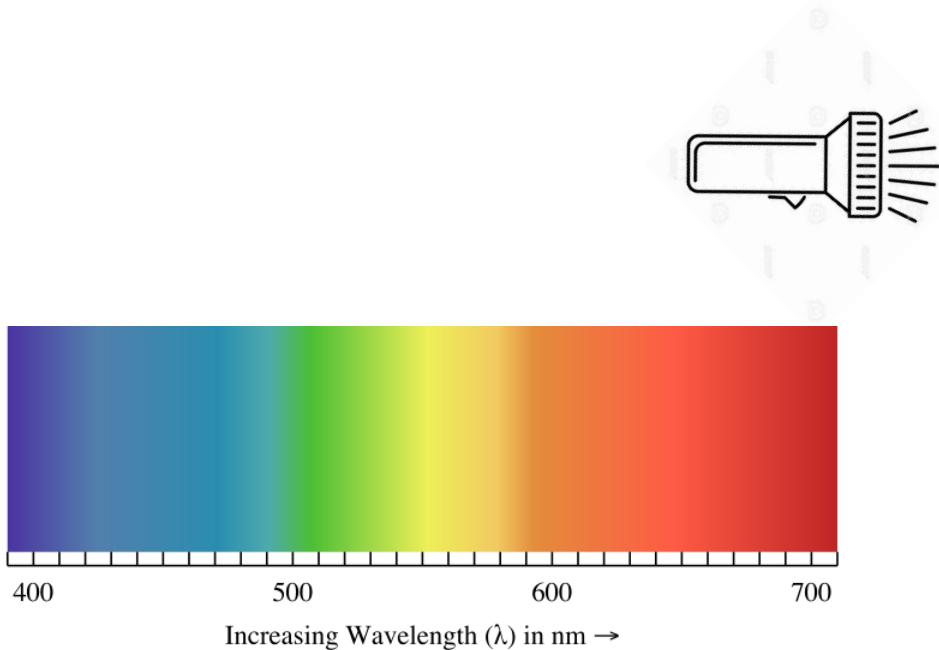
Visible

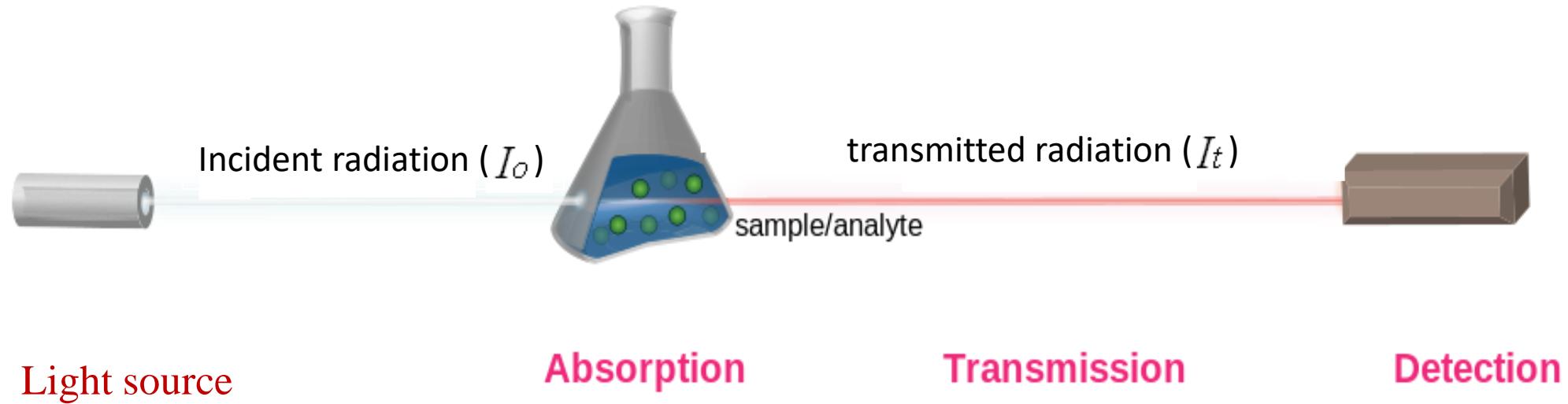
Infra-red (IR)

Radio frequency *etc.*

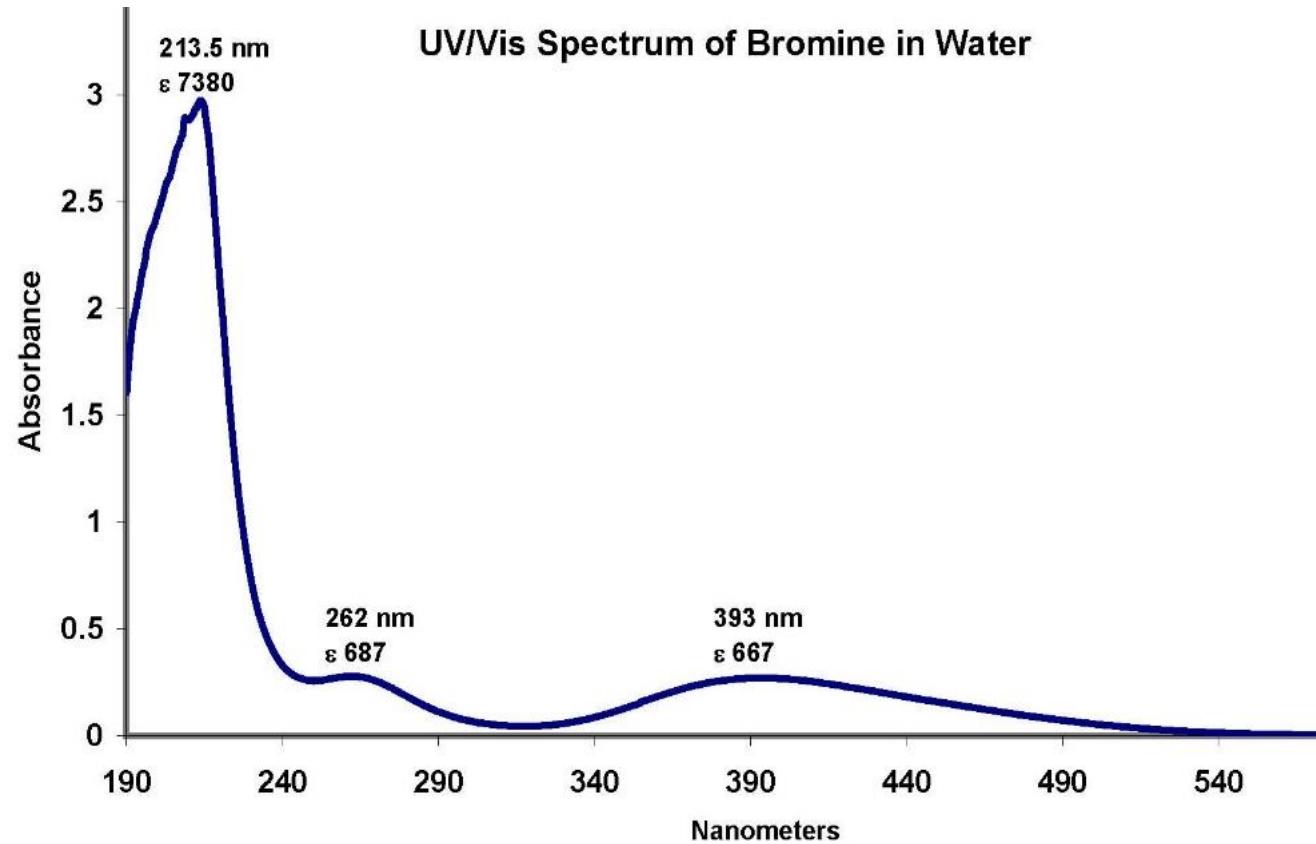
□ The study of Spectroscopy deals with absorption as well as emission of EM of different wavelength

- When EM radiation is passed through the substance then radiations of certain wavelength are absorbed by the substance depending on the structure of the compound

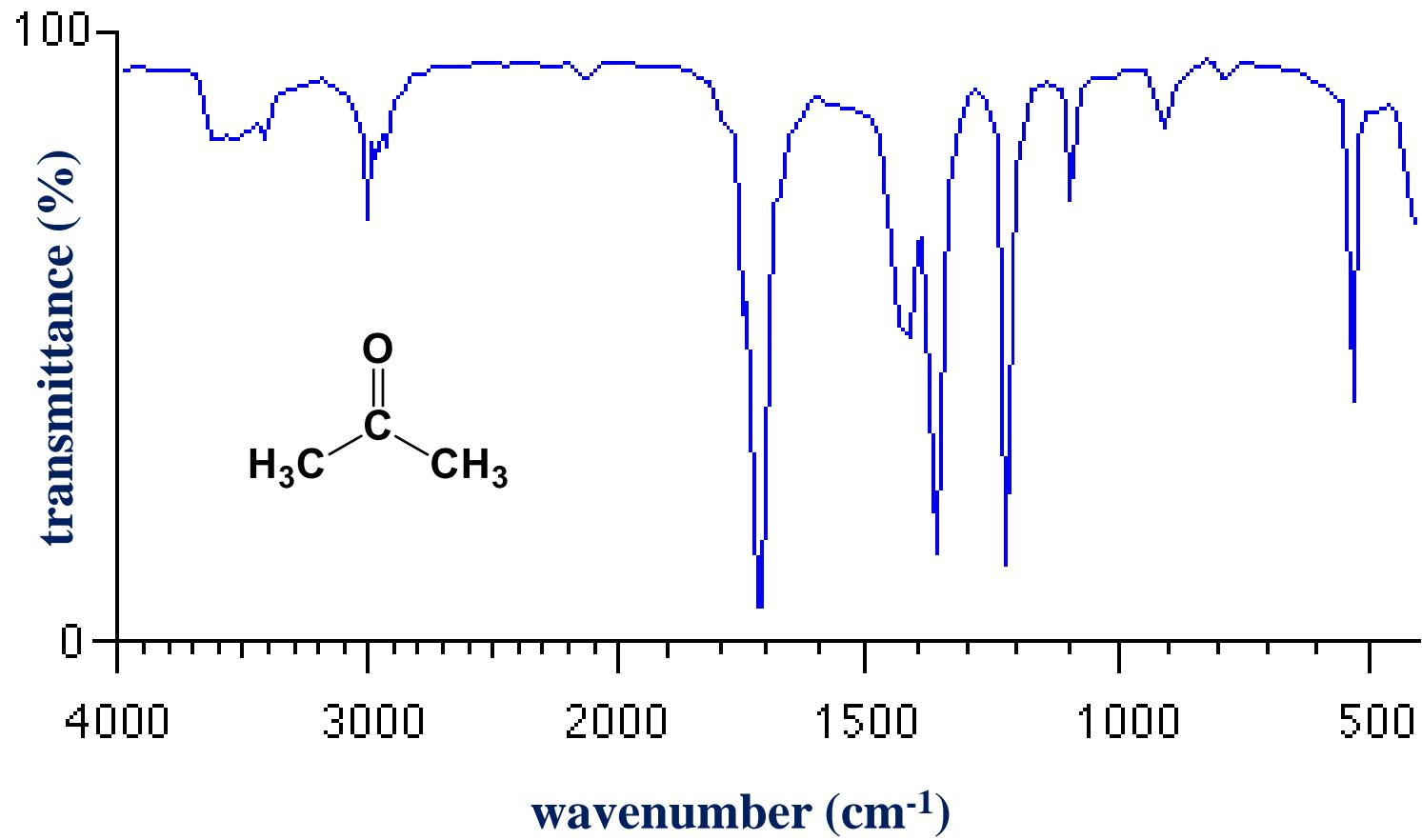




# UV-Visible Spectrum



# Infra-Red Spectrum



# **UV-Visible Spectroscopy**



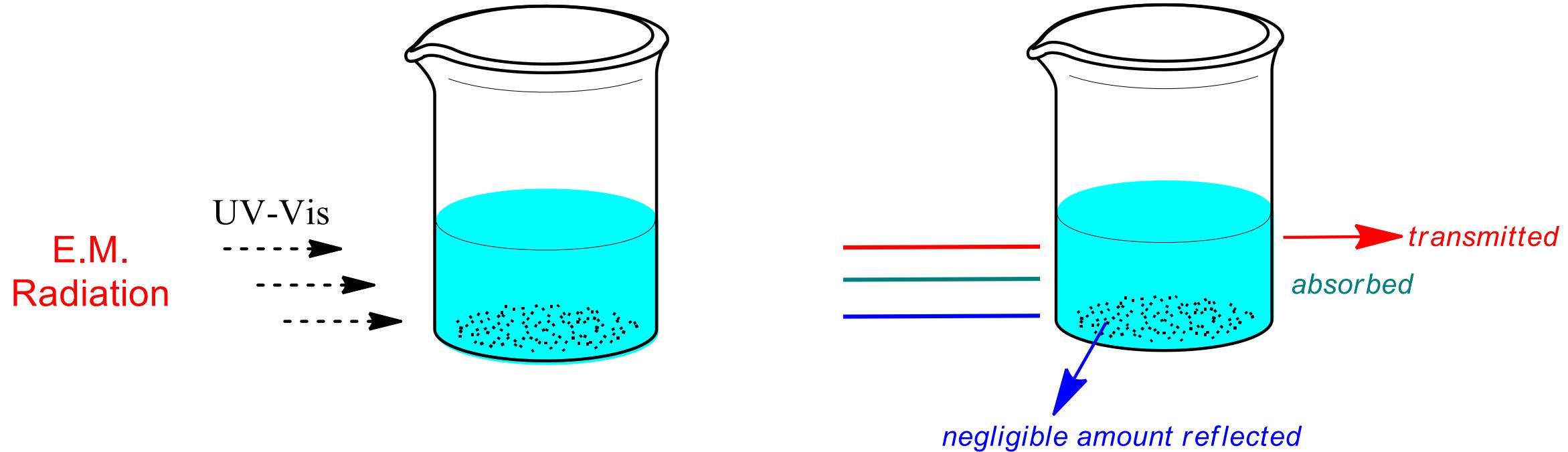
## UV-Visible Spectrometer

□ Visible Range: **400-800 nm**

□ UV Range: **200-400 nm**

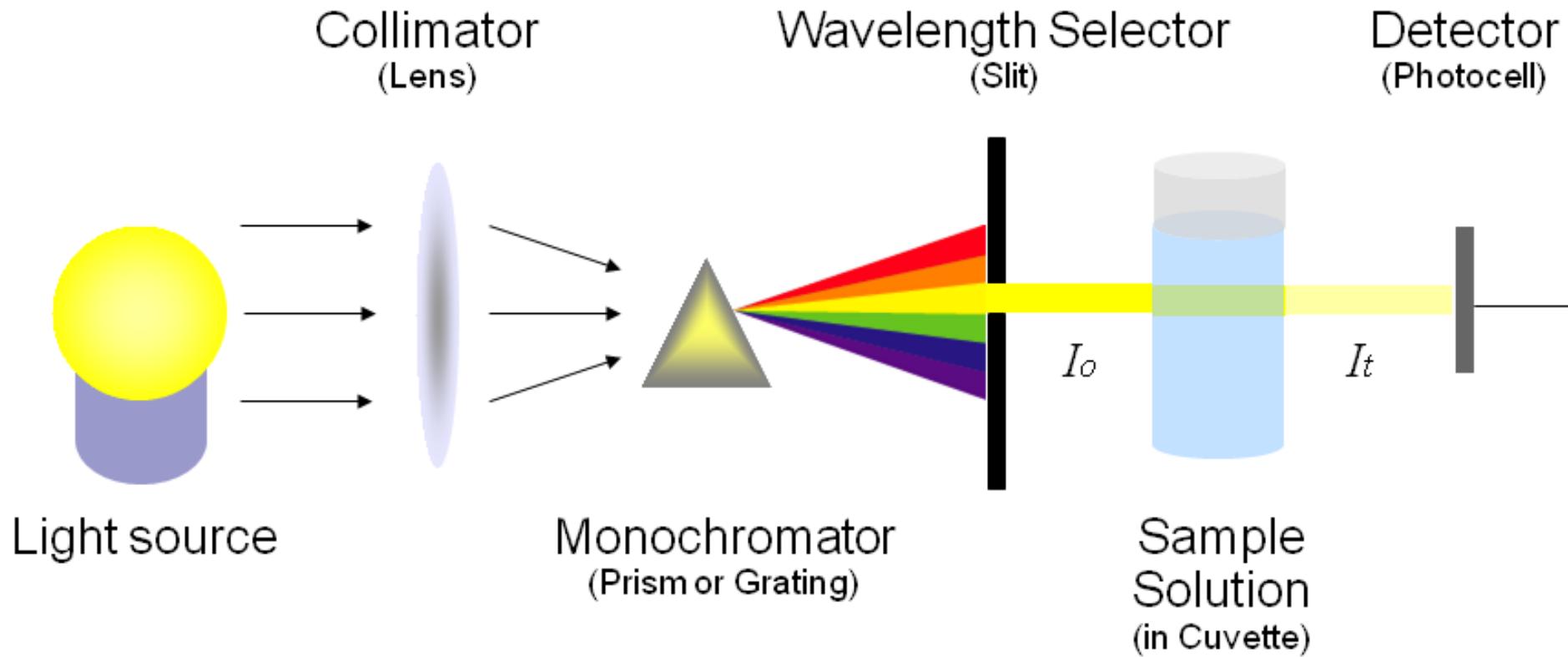
□ Far UV Range: **Below 200 nm**

Far UV spectra is also known as **Vacuum UV Spectroscopy** since it is performed in vacuum to avoid the absorption of gases e.g. O<sub>2</sub>, N<sub>2</sub>



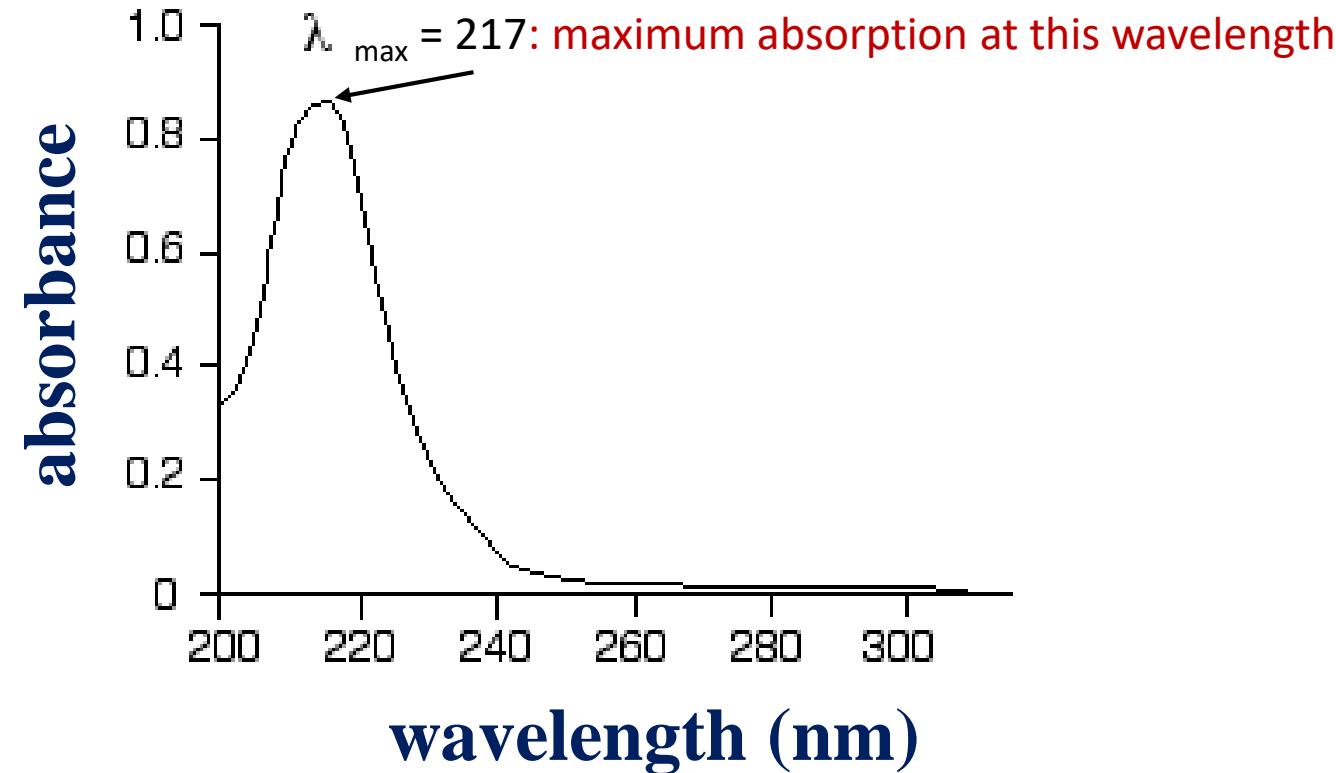
When UV-Visible radiation (monochromatic\*) is passed through homogenous absorbing medium:  
A portion of radiation is absorbed by the compound and rest is transmitted.

\*Radiations of very narrow range of wavelength or frequency



Function of monochromator is to separate desired set of wavelength from the band of spectrum

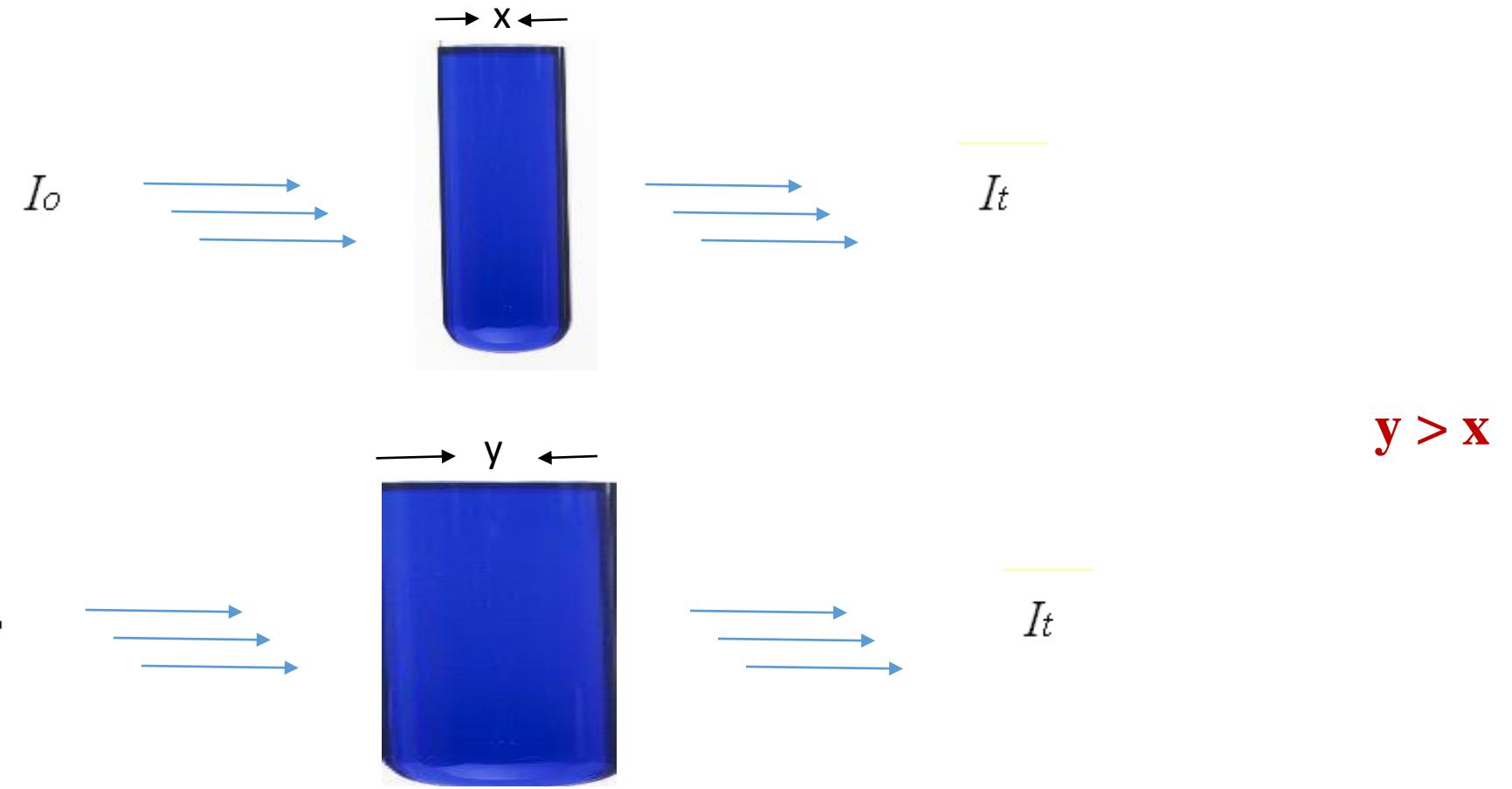
**Plot of Electronic Spectra:** The UV-Vis spectra is observed as a plot of **intensity of absorbed(or absorbance)** radiation against the **wavelength** of the absorbed radiation.



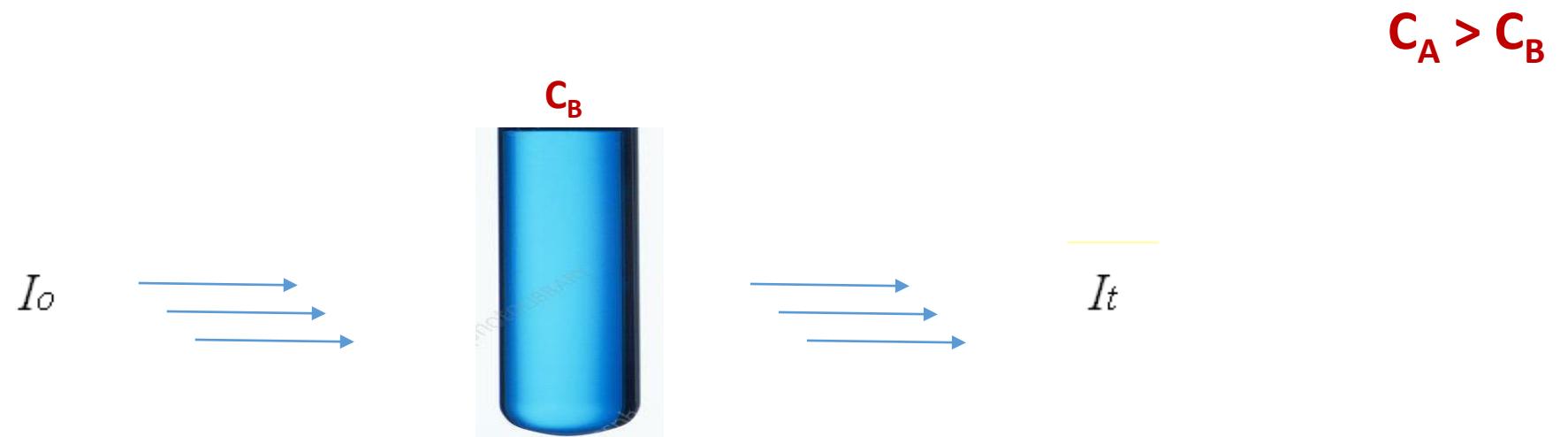
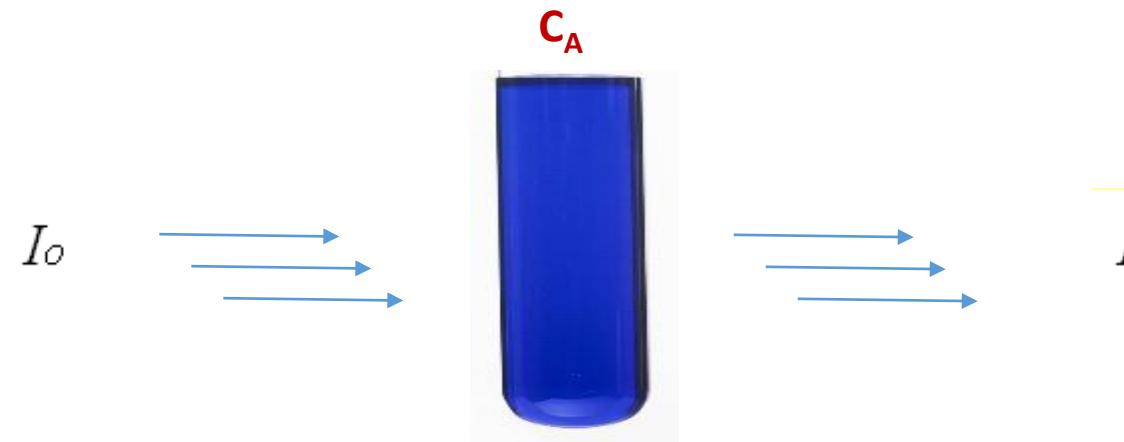
# The Absorption Law

Lambert's Law : Solid Sample

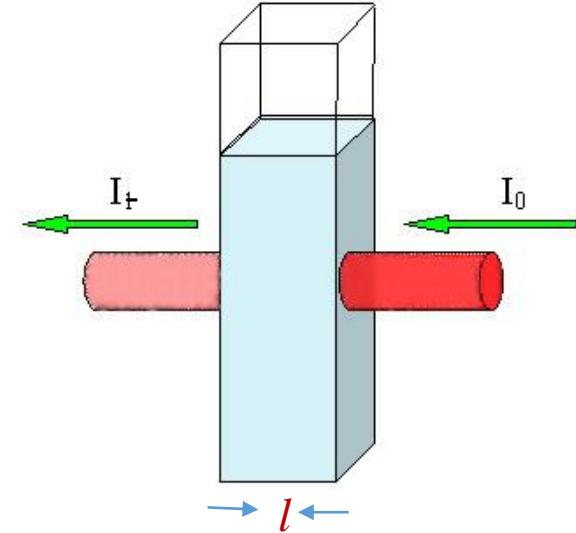
Beer's Law : Solution



Sample of same concentration but different path length



Sample of same path length but different concentration



## The Beer-Lambert's law

- The amount of light absorbed is directly proportional to the concentration ( $c$ ) of the solution of the sample       $A \propto c$
- The absorbance is directly proportional to the length of the light path ( $l$ ), which is equal to the width of the cuvette.     $A \propto l$

$$A \propto cl$$

$$A = \epsilon cl$$

## Derivation

Mathematically, the law is expressed as,

$$-\frac{dI}{dx} \propto Ic$$

$$\Rightarrow -\frac{dI}{dx} = kIc$$

$$\Rightarrow \int_{I_o}^{I_t} \frac{dI}{I} = - \int_{x=0}^{x=l} kc \, dx$$

$$\Rightarrow \ln \frac{I_t}{I_o} = -kcl \quad \text{or} \quad \log \frac{I_t}{I_o} = -\frac{k}{2.303} cl$$

$$\Rightarrow I_t = I_o 10^{-\varepsilon cl}$$

Where,

c = concentration of the solution.

k=Proportionality constant

l = path length

Since,  $\ln \frac{I_t}{I_o} = 2.303 \log \frac{I_t}{I_o}$

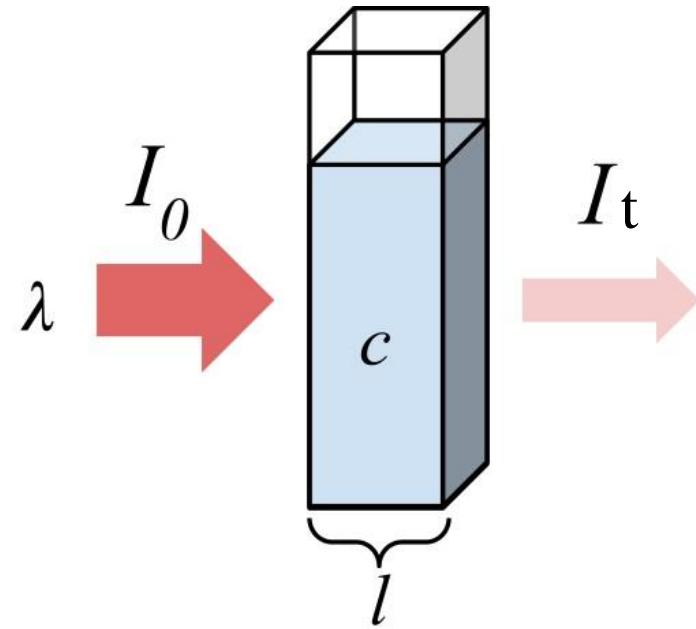
$$\Rightarrow I_t = I_o 10^{-\varepsilon cl}$$

Here,  $\varepsilon = \frac{k}{2.303}$  where  $\varepsilon$  is known as **molar extinction coefficient** or **molar absorptivity** of the absorbing medium.

$$\frac{I_t}{I_o} = 10^{-A} \quad \text{or} \quad \log \frac{I_o}{I_t} = A$$

$$A = \log \frac{1}{T}$$

Here, **A** is known as **Absorbance** And **T** is called **Transmittance** which is equal to  $\frac{I_t}{I_o}$ .

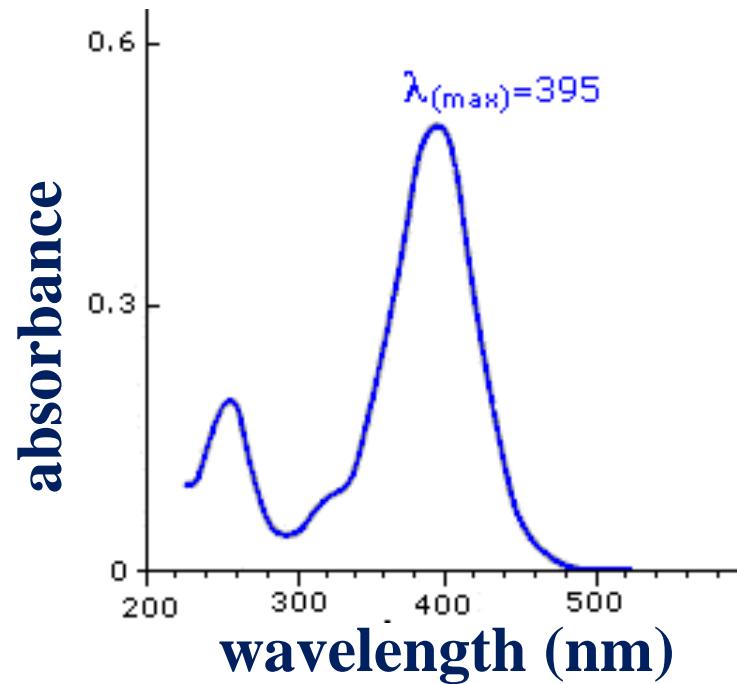
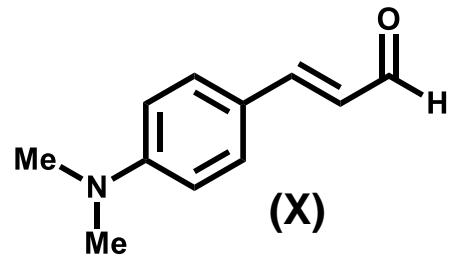


$$A = \epsilon cl = \log \frac{I_0}{I_t} = \log \frac{1}{T} = 2 - \log T\%$$

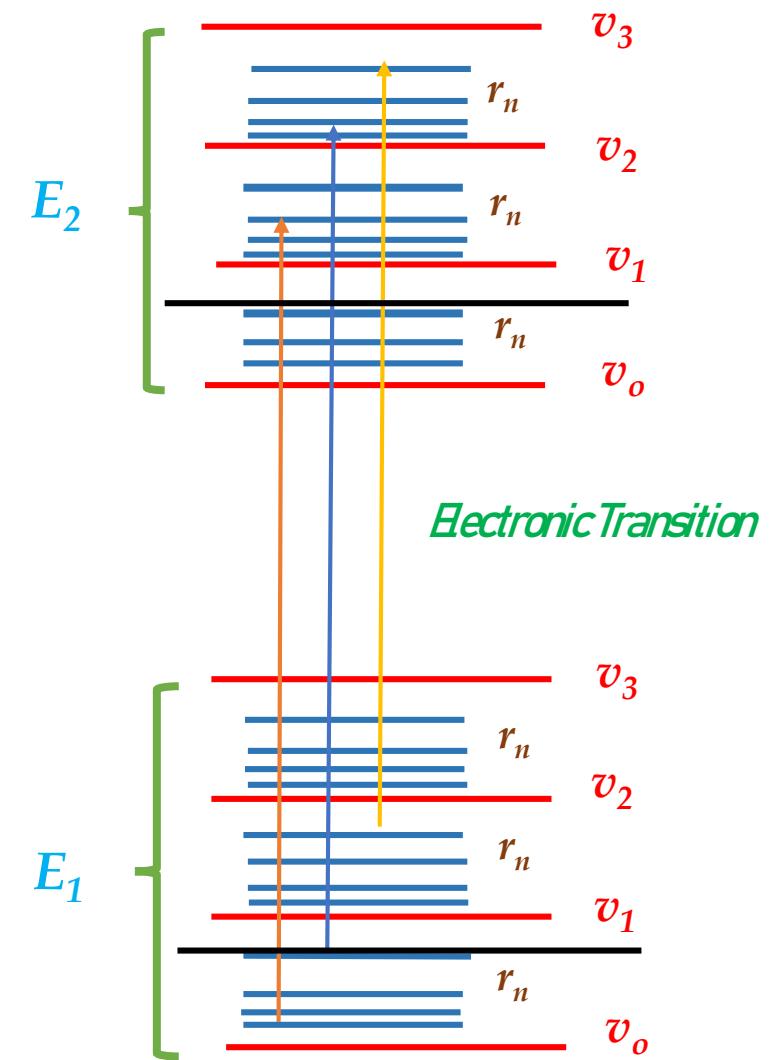
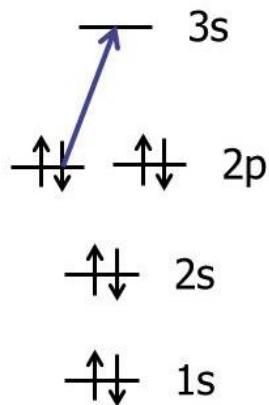
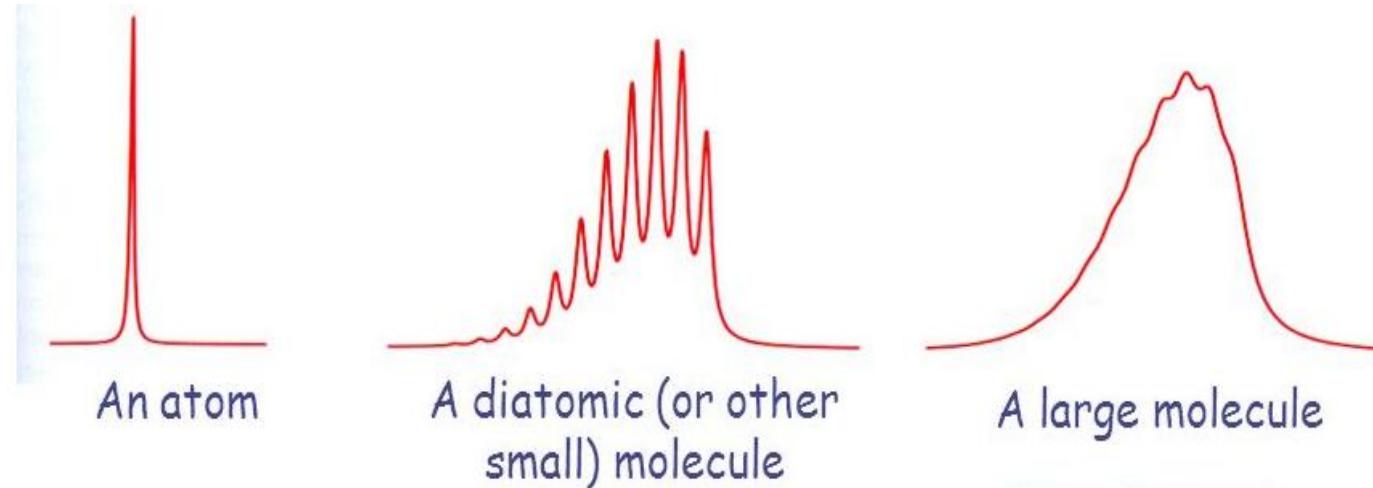
**1. Problem:** The molar absorption coefficient of tyrosine in water is  $1280 \text{ M}^{-1} \text{ cm}^{-1}$  at 280 nm. Calculate the concentration of a tyrosine solution in water if the absorbance of the solution is 0.34 in a 1 cm path length cell. (**Hint:**  $\lambda = 280 \text{ nm}, \epsilon = 1280 \text{ M}^{-1} \text{ cm}^{-1}, l = 1 \text{ cm}, A = 0.34, c = ?$ )

**2. Problem:** Calculate absorbance of a radiation in a photo-absorption technique if 60% of it has been absorbed by the sample. (**Hint:**  $T=0.4$  since absorption is 60%,  $A=?$ )

## Representative UV spectra for compound ‘X’



# Absorption peaks broadens from atom to polyatomic molecules



- Excitation of electrons are also accompanied by the constant vibratory and rotatory motion of the molecules.
- Electronic levels are comprised of band of vibrational and rotational levels.

# Born-Oppenheimer Approximation, vibrational and rotational energies are quantised and treated separately

Total energy of a molecule

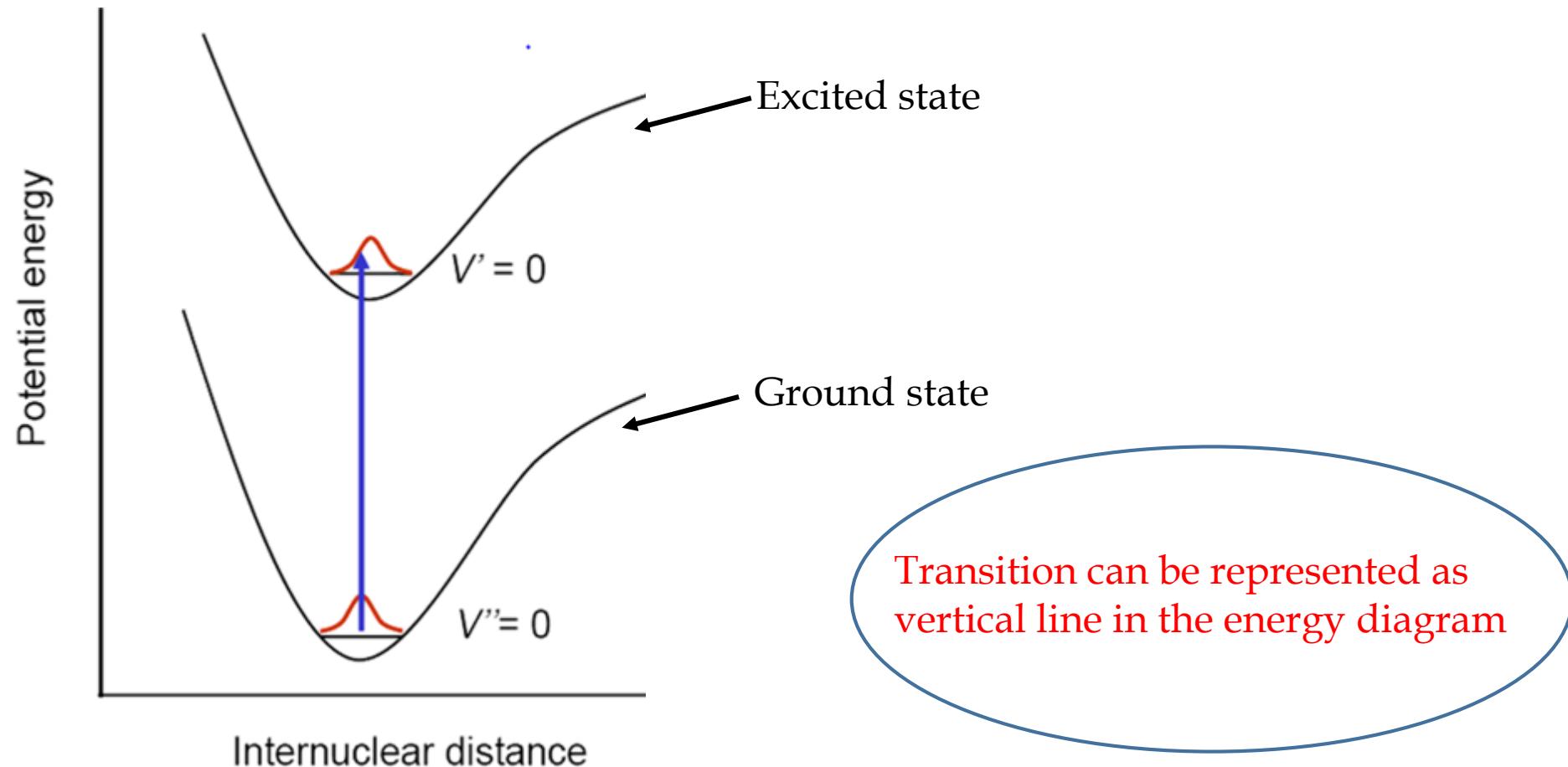
$$E_{\text{tot}} = E_{\text{ele}} + E_{\text{vib}} + E_{\text{rot}} + \dots$$

$E_{\text{ele}}$ : Electronic Energy  
 $E_{\text{vib}}$ : Vibrational Energy  
 $E_{\text{rot}}$ : Rotational Energy

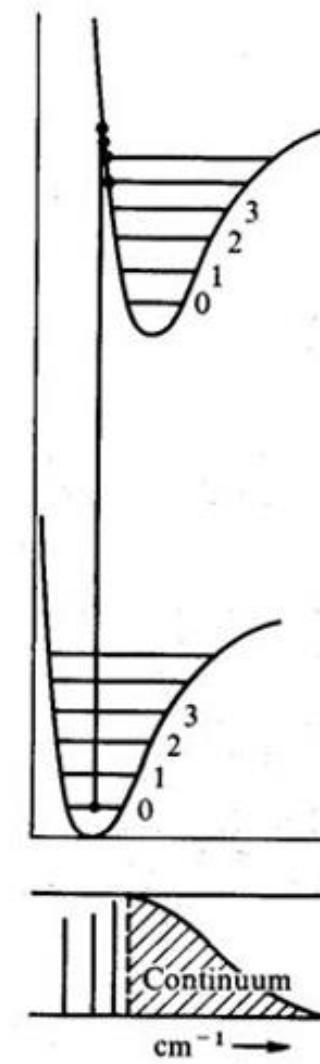
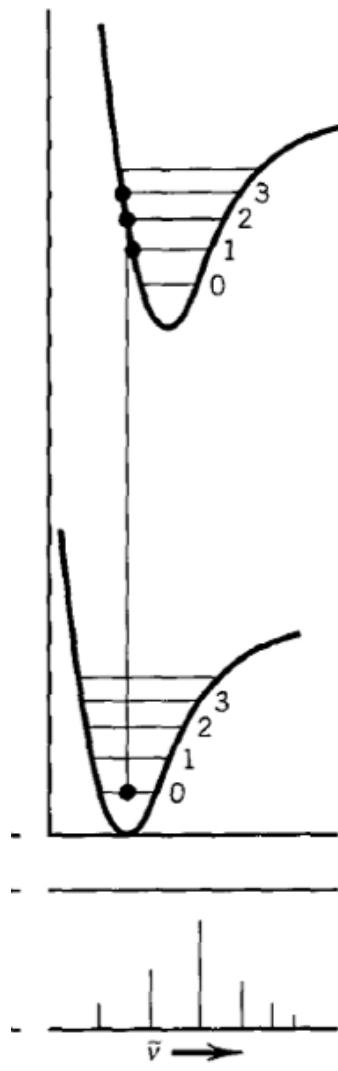
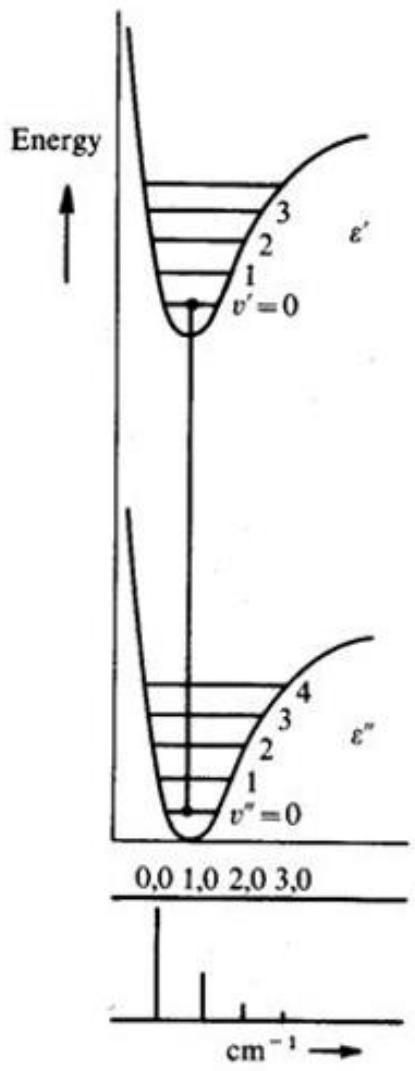
$$E_{\text{ele}} (10^{5-6} \text{ cm}^{-1}) \ggg E_{\text{vib}} (10^3 \text{ cm}^{-1}) > E_{\text{rot}} (1-10 \text{ cm}^{-1})$$

## Frank-Condon Principle assumed

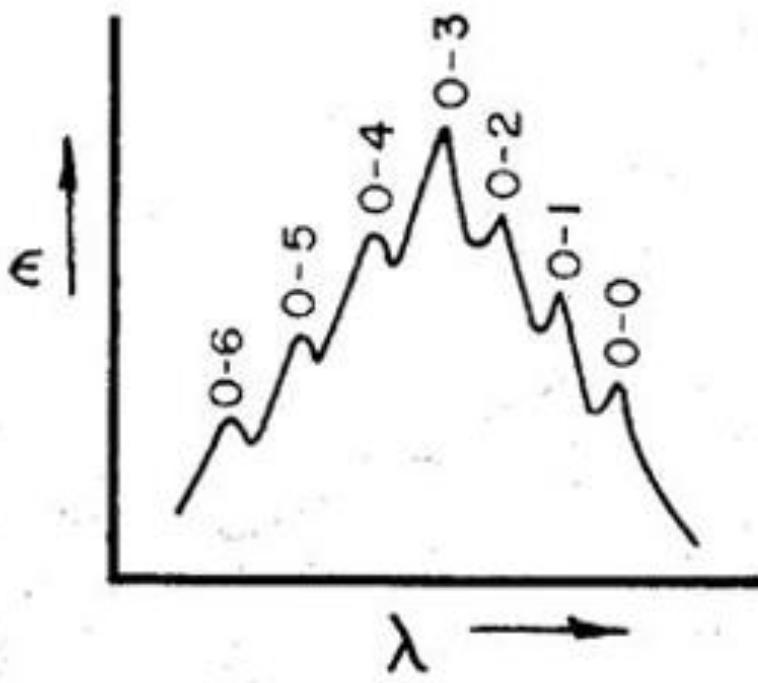
*'an electronic transition takes place so rapidly that the nuclei of the vibrating molecule can be assumed to fixed during the transition'*



Transition can be represented as  
vertical line in the energy diagram



As the optical transition becomes less vertical, the absorption spectra shift due to the change in the Frank-Condon principle.



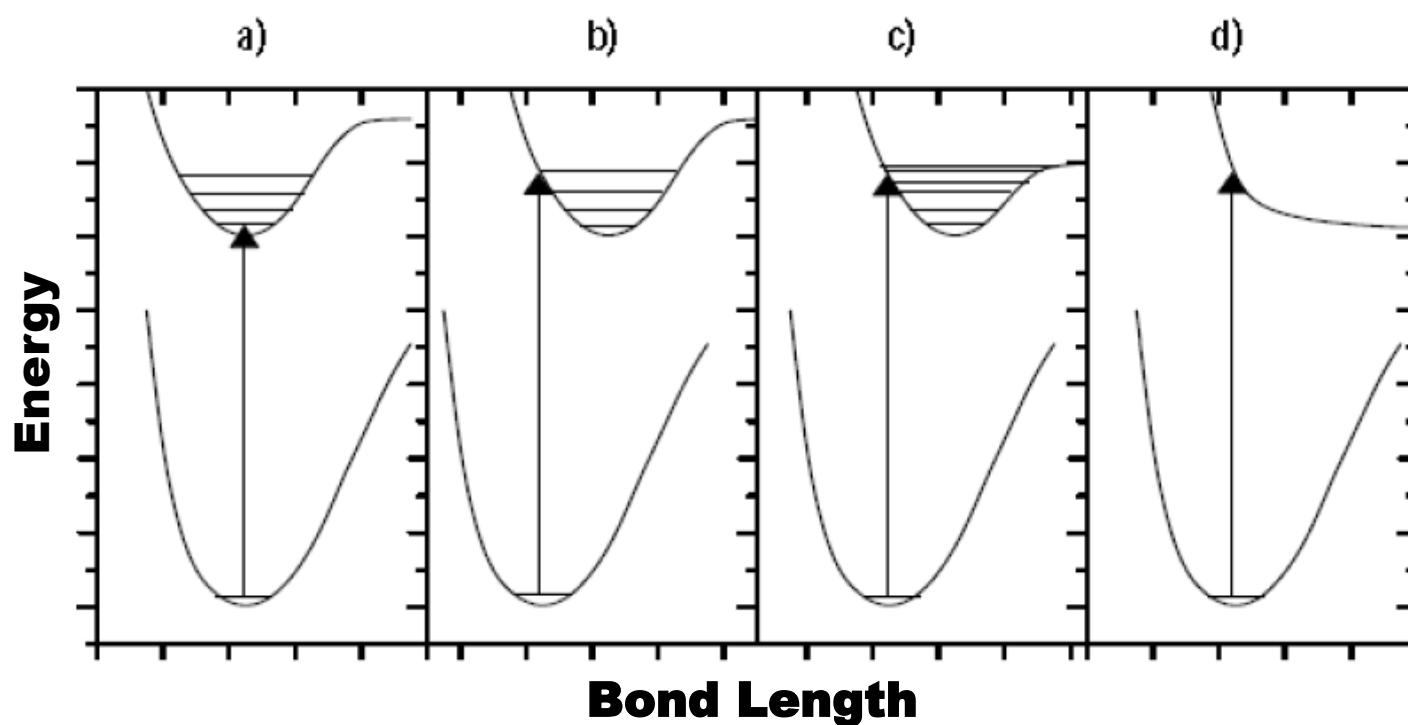
As the optical transition becomes less vertical, the absorption spectra shift due to the change in the Frank-Condon principle.

# Broadening of Spectral Lines

- The electronic excitation is superimposed upon rotational and vibrational levels.
- There will be a large number of possible transitions corresponding to electronic, vibrational and rotational levels.
- Large number of wave length which are close to each other will be absorbed, resulting in the formation of band.

# Other Factors of Spectral Line Broadening

- ❖ **Collision broadening** – Molecular interactions are more severe in liquids than in gas (Gas phase spectra are sharper than those of the corresponding liquids). In case of solids, the spectral lines are sharper but show evidence of interactions by splitting of lines.
  
- ❖ **Doppler effect** – Atoms or molecules in gases and liquids are in continuous motions with different velocities in different directions from the detector which causes Doppler effect (More in gases than in liquids).



**Which depicts a transition to a dissociative state?**

**Which depicts a transition in a molecule that has a larger bond length in the excited state?**

**Which represents the states of a molecule for which the  $v''=0 \rightarrow v'=3$  transition is strongest?**

**Which represents molecules that can dissociate after electronic excitation?**

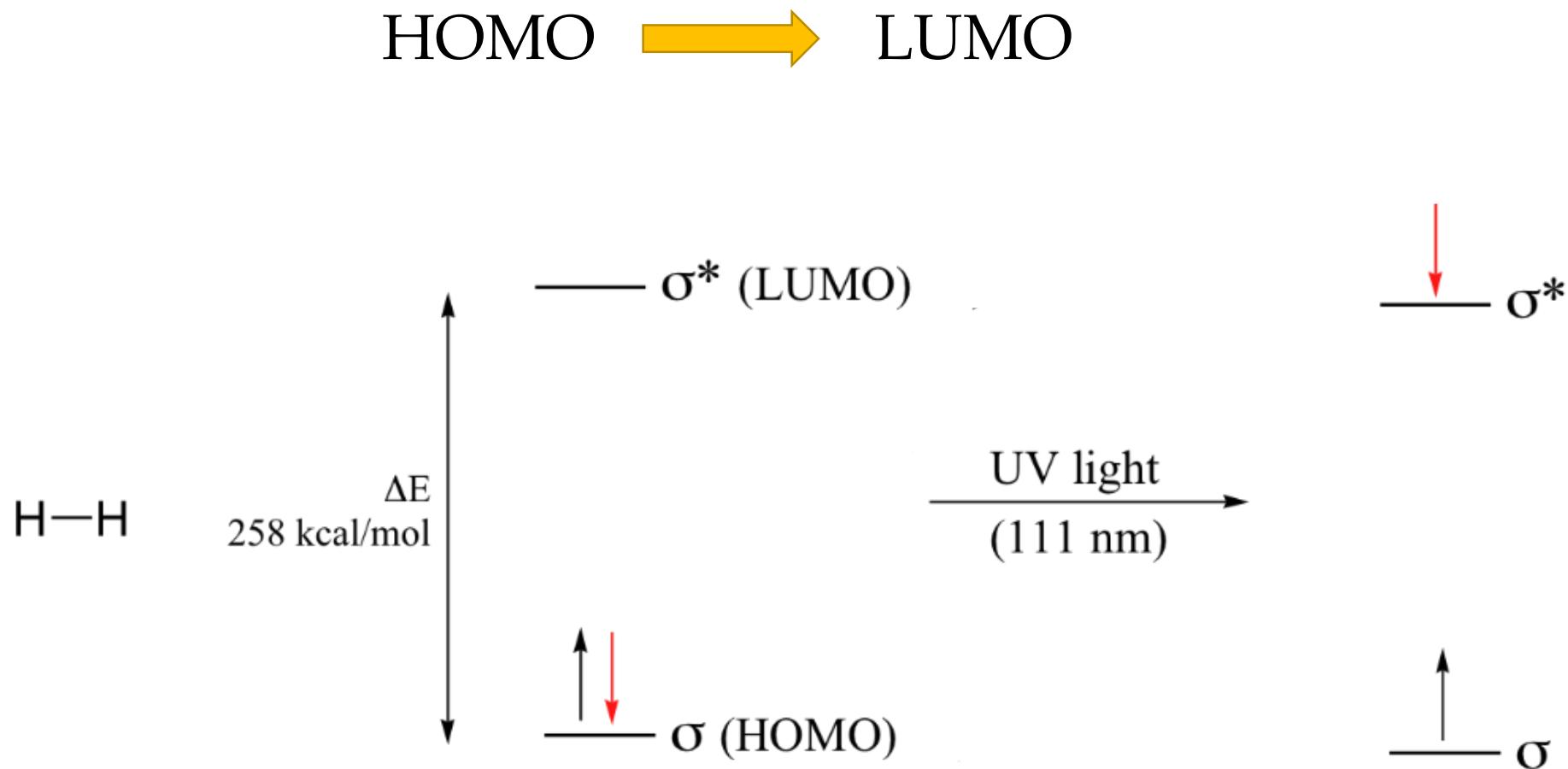
**Which would show the largest intensity in the 0-0 transition?**

❑ Number of Transitions

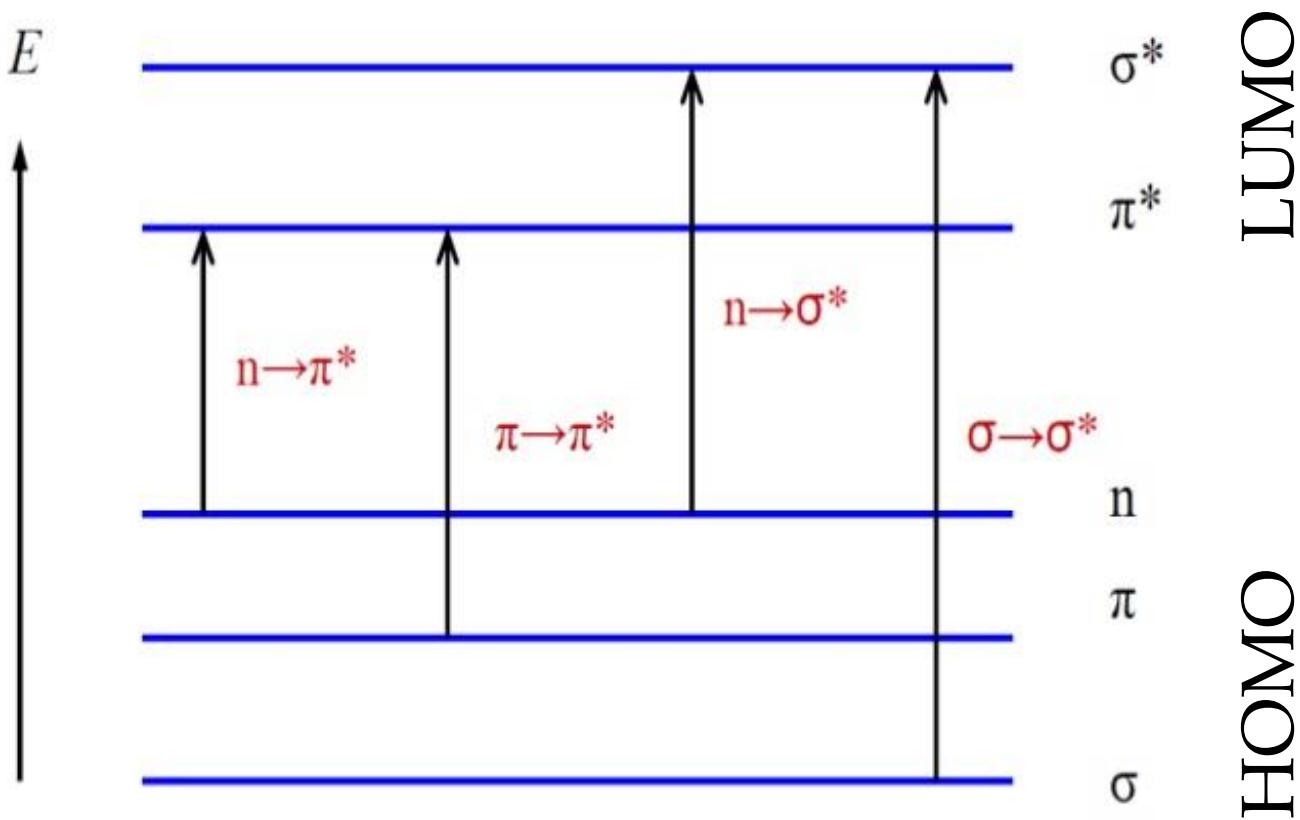
❑ Energy of Transitions

❑ Intensity of Transitions

# Electronic Transitions



# Electronic Transitions



# Types of Electronic Transitions

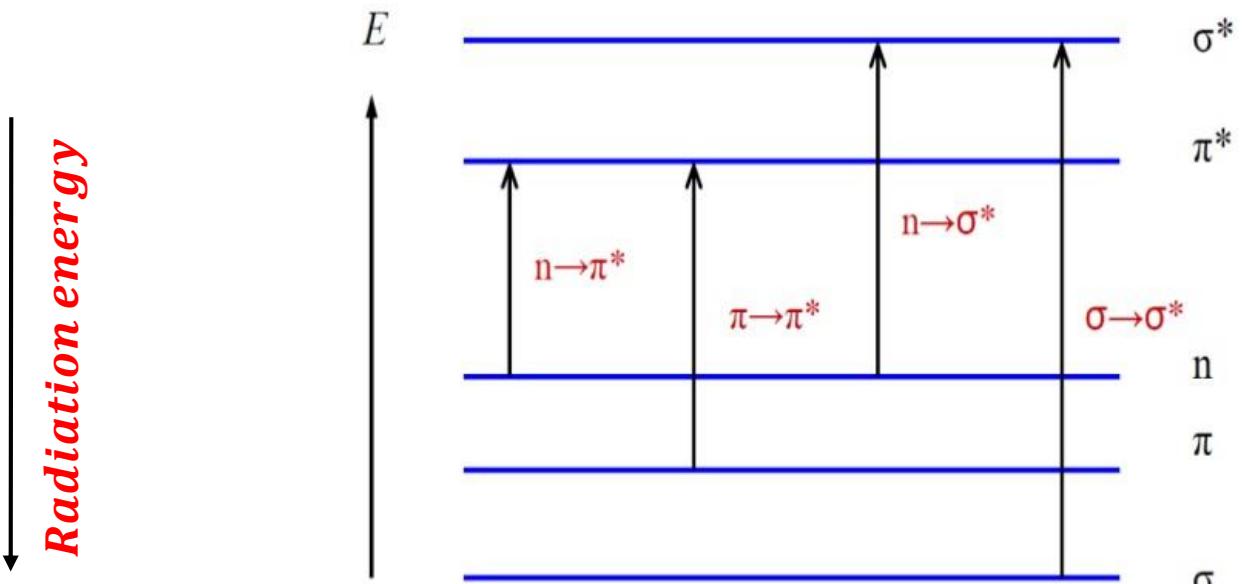
Four types of Electronic transitions are possible

$\sigma \rightarrow \sigma^*$  Transition

$n \rightarrow \sigma^*$  Transition

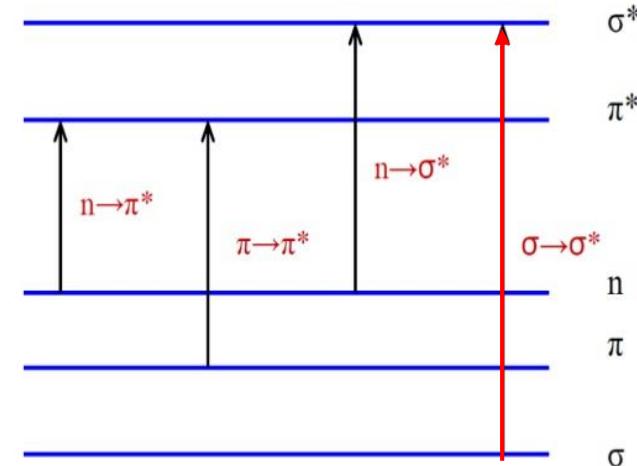
$\pi \rightarrow \pi^*$  Transition

$n \rightarrow \pi^*$  Transition



## $\sigma \rightarrow \sigma^*$ Transition

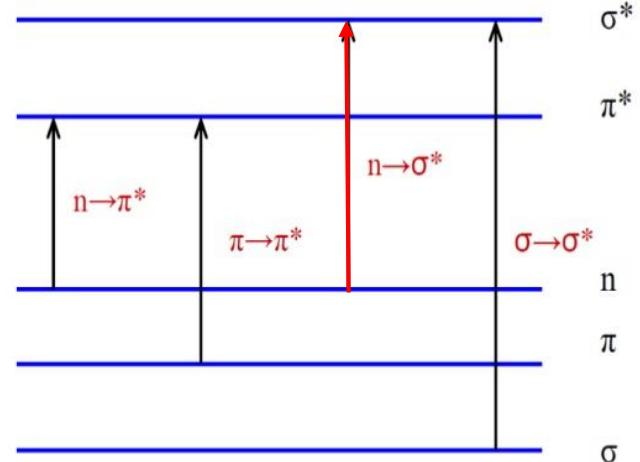
- High energy transition (<<200nm)
- Compounds with single bond show  $\sigma \rightarrow \sigma^*$  Transition
  - e.g. Cyclopropane,  $\lambda_{\max}$  190 nm.
  - Cyclohexane,  $\lambda_{\max}$  153 nm (vacuum UV)
- Colourless, since not absorbed light in visible region.



## $n \rightarrow \sigma^*$ Transition

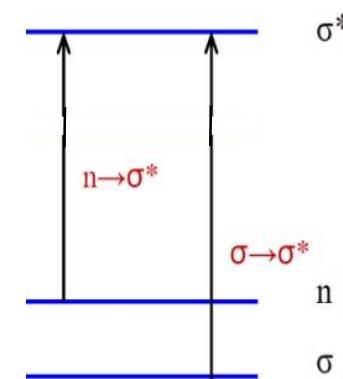
- Appear in the near UV or visible region
- Compounds containing non-bonding electrons or lone-pair electrons show this type of transition

E.g. H<sub>2</sub>O       $\lambda_{max}$  167 nm  
MeOH       $\lambda_{max}$  174 nm  
MeCl       $\lambda_{max}$  169 nm  
NEt<sub>3</sub>       $\lambda_{max}$  227 nm



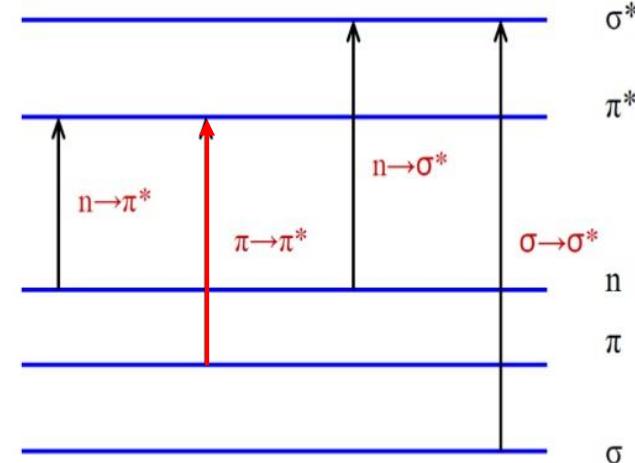
Q. Give an explanation for the difference in  $\lambda_{max}$  value

Compounds	$\lambda_{max}$
MeCl	169 nm
MeI	258 nm



In case of saturated alkyl halides, as the electronegativity increases  $\lambda_{max}$  values decrease. Since, nonbonding electrons are more difficult to excite in case of more electronegative atom.

## $\pi \rightarrow \pi^*$ Transition

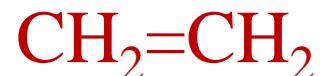


For compounds containing double, triple bonds or aromatic rings show this type of transition.

e.g. Alkenes, Alkynes, Carbonyls, Cyanides, Azo compounds etc.

This is usually a symmetry allowed and high intensity transition.

Q. Why extended conjugation lowers the  $\Delta E$ , and increase the  $\lambda_{max}$ .



$\lambda_{max} 171 \text{ nm}$

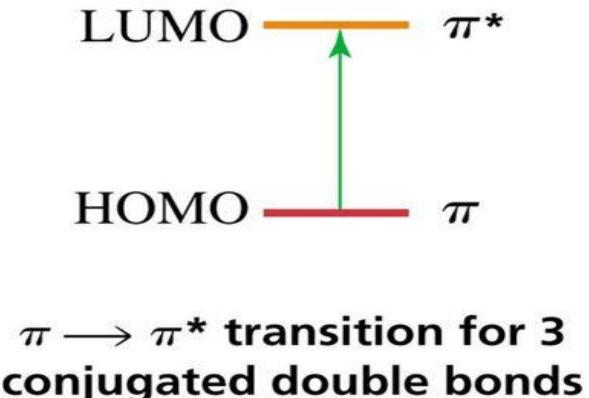
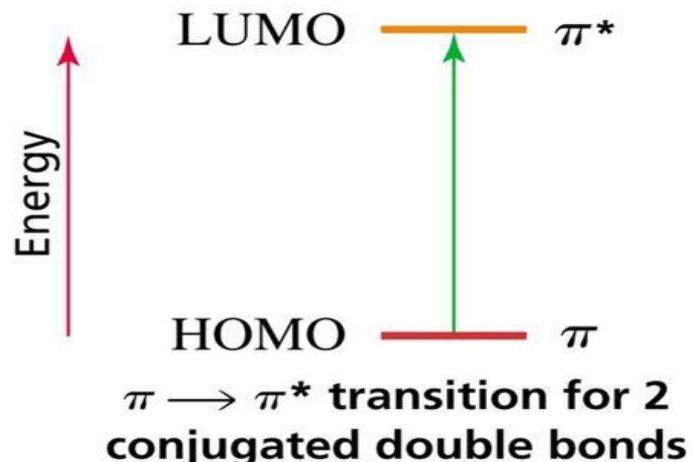


$\lambda_{max} 217 \text{ nm}$



$\lambda_{max} 256 \text{ nm}$

## Conjugation Makes the Electronic Transition Easier



Q. Why introduction of an alkyl group to the double bond shift the  $\lambda_{max}$  value to longer wavelength.

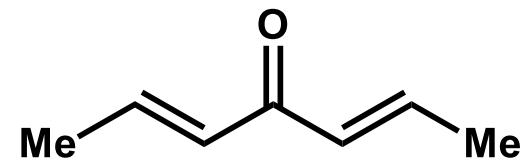
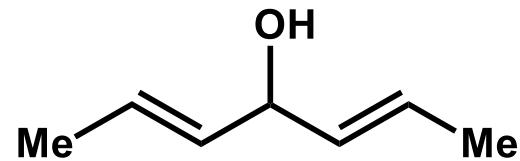
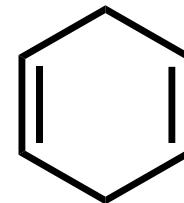
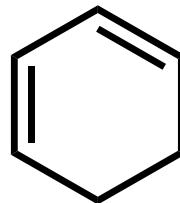
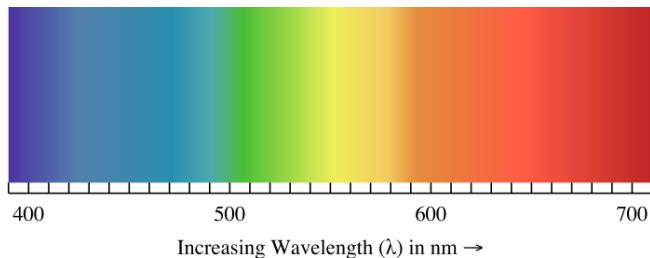


$\lambda_{max} 171 \text{ nm}$



$\lambda_{max} 184 \text{ nm}$

Q. Out of the given set of compounds, find out the one which absorbs at the longest wavelength?



## **$n \rightarrow \pi^*$ transition**

The excitation of an electron on a nonbonding (lone pairs) orbital, such as unshared pair electrons on O, N, S to an antibonding,  $\pi^*$  orbital.

Usually in a double bond with hetero atoms, such as C=O, C=S, N=O  
*etc* show this transition.

A symmetry forbidden and low intensity transition.

e.g. saturated aldehydes and ketones :  $\lambda_{max}$  at 185-300 nm

In carbonyl compounds, two types of transitions take place which are

High energy transitions

$n \rightarrow \sigma^*$  Transition (Intense)

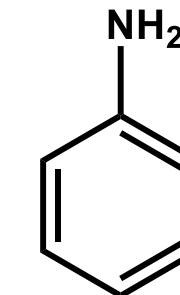
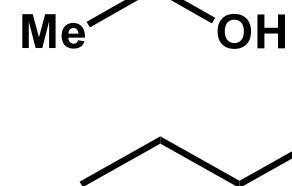
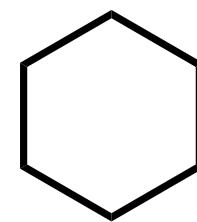
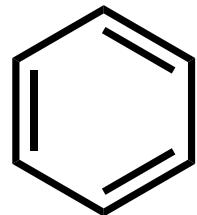
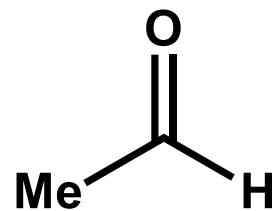
$\pi \rightarrow \pi^*$  Transition (Intense)

Low Energy Transition

$n \rightarrow \pi^*$  Transition (Weak)

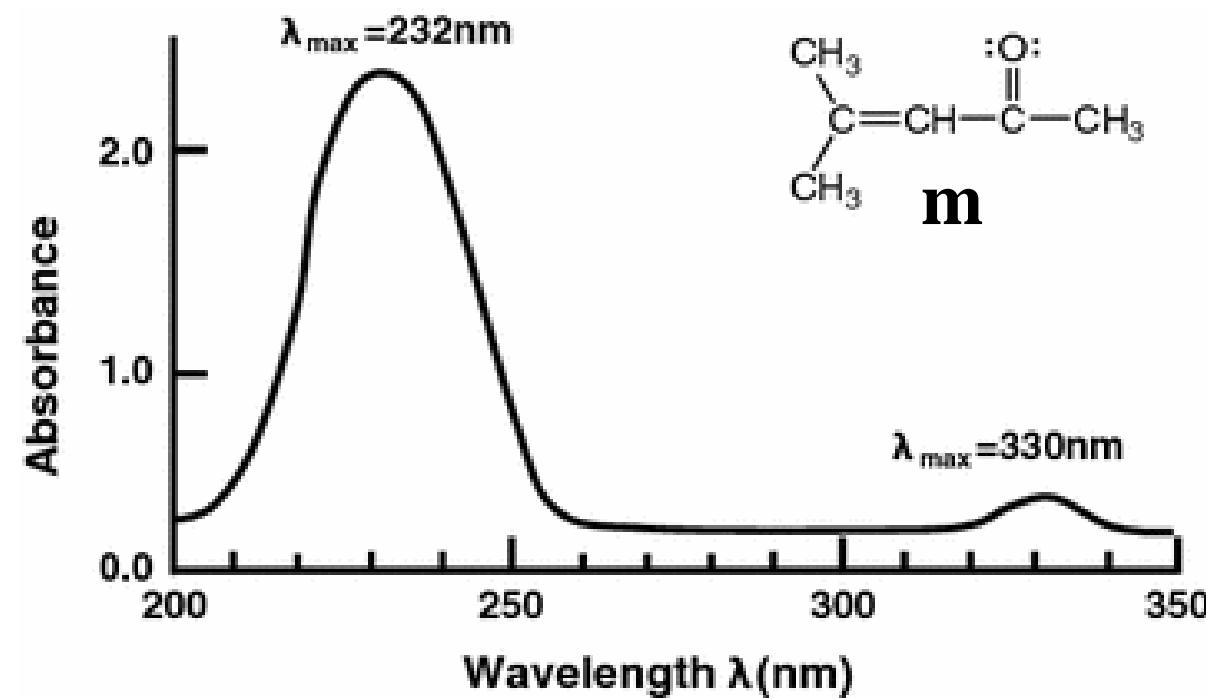
Q. Assign electronic transitions for the following compounds.

Acetaldehyde, Benzene, Cyclohexane, Ethanol, Heptane, Aniline, Butadiene



Q. Acetaldehyde is having absorption peak at 160 nm, 180 nm and 292 nm.  
What type of transition is responsible for each of these absorption?

Q. UV spectra for the compound ‘m’ has given below assign electronic transitions and justify your answer



# Transition Probability

The probability of a particular transition taking place.

As transition probability increases  
intensity of transition increase (high  $\varepsilon_{max}$  value)

- i. Energy of the transition/incident light.
- ii. Orientation of the molecule/material.
- iii. Symmetry of the initial and final states.
- iv. Angular momentum (spin).

## Allowed transitions

The transition with values of  $\varepsilon_{max}$  value more than  $10^4$  are allowed transitions.

$\pi \rightarrow \pi^*$  Transition is allowed.

$n \rightarrow \pi^*$  Transition is forbidden.

In benzophenone, there are two transitions.

252 nm                     $\varepsilon_{max}$  20000 (allowed)

325 nm                     $\varepsilon_{max}$  180 (forbidden)

## **Chromophore :**

Any functional group which absorb in UV-Visible range are Chromophores

Can induce color in the molecule

Chromophore are groups containing either  **$\pi$  electrons** or both  **$\pi$  &  $n$  electrons**

e.g. C=O, C=C, NO<sub>2</sub>, -COOH, -N=N-, C≡C etc.

## Auxochromes:

Shift the  $\lambda_{max}$  value to longer wavelength if attached to chromophores

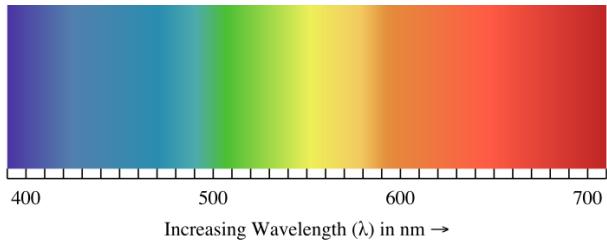
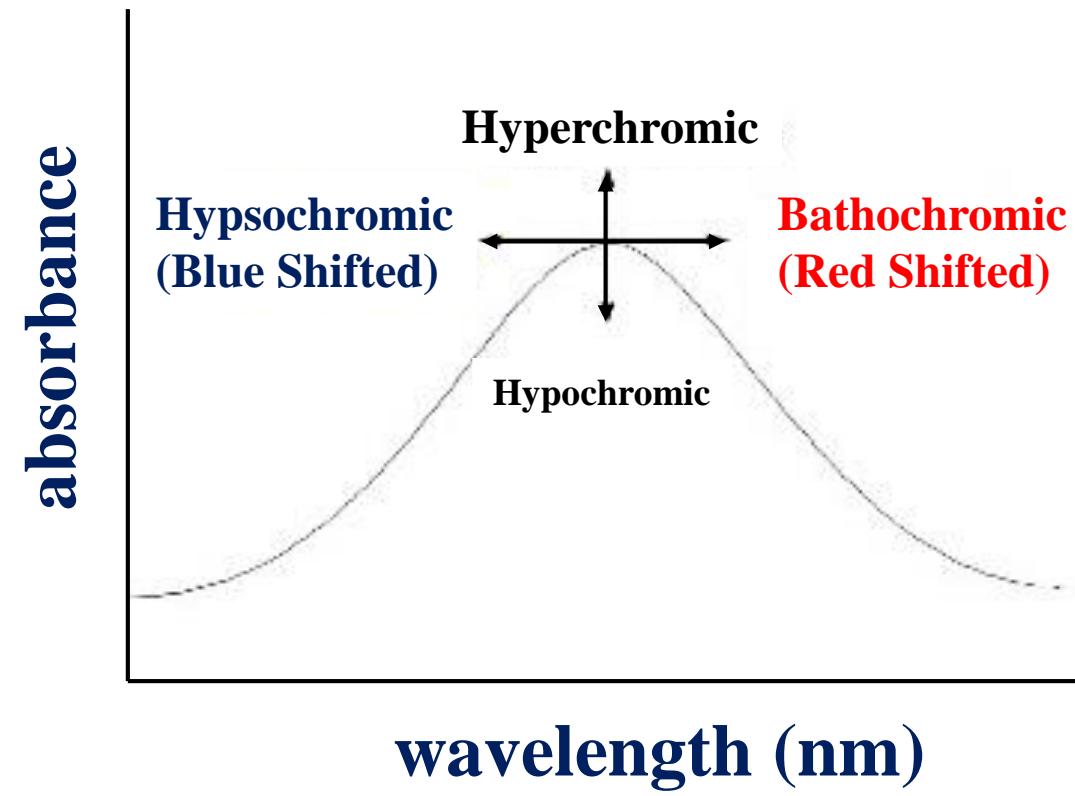
Changes both intensity and  $\lambda_{max}$

e.g. OH, NH<sub>2</sub>, -SH, -Cl, OR, NHR<sub>2</sub> etc.

Auxochromes has ability to extend conjugation of chromophores by sharing its nonbonding electrons

e.g. **Benzene** absorbs at **255 nm** but **Aniline** absorbs at **280 nm**.

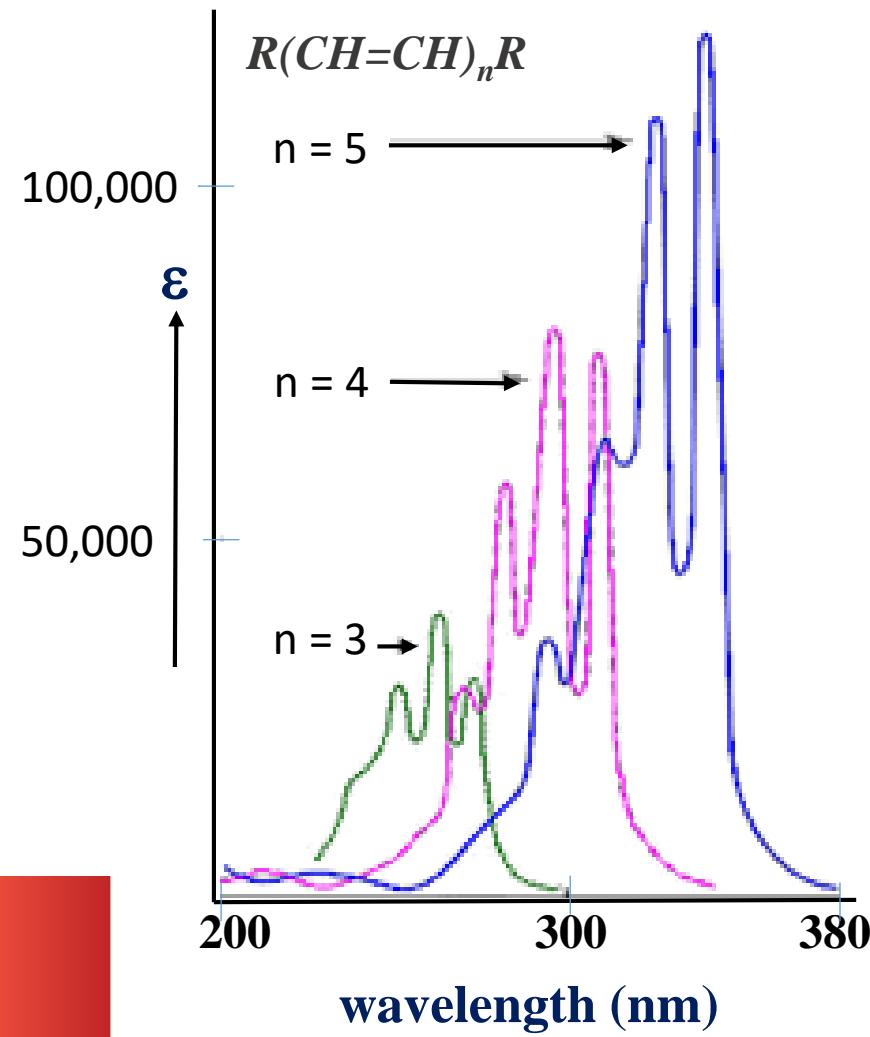
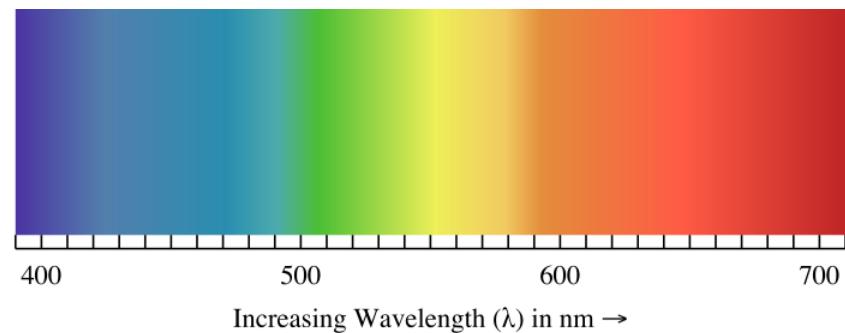
# Absorption and intensity shift

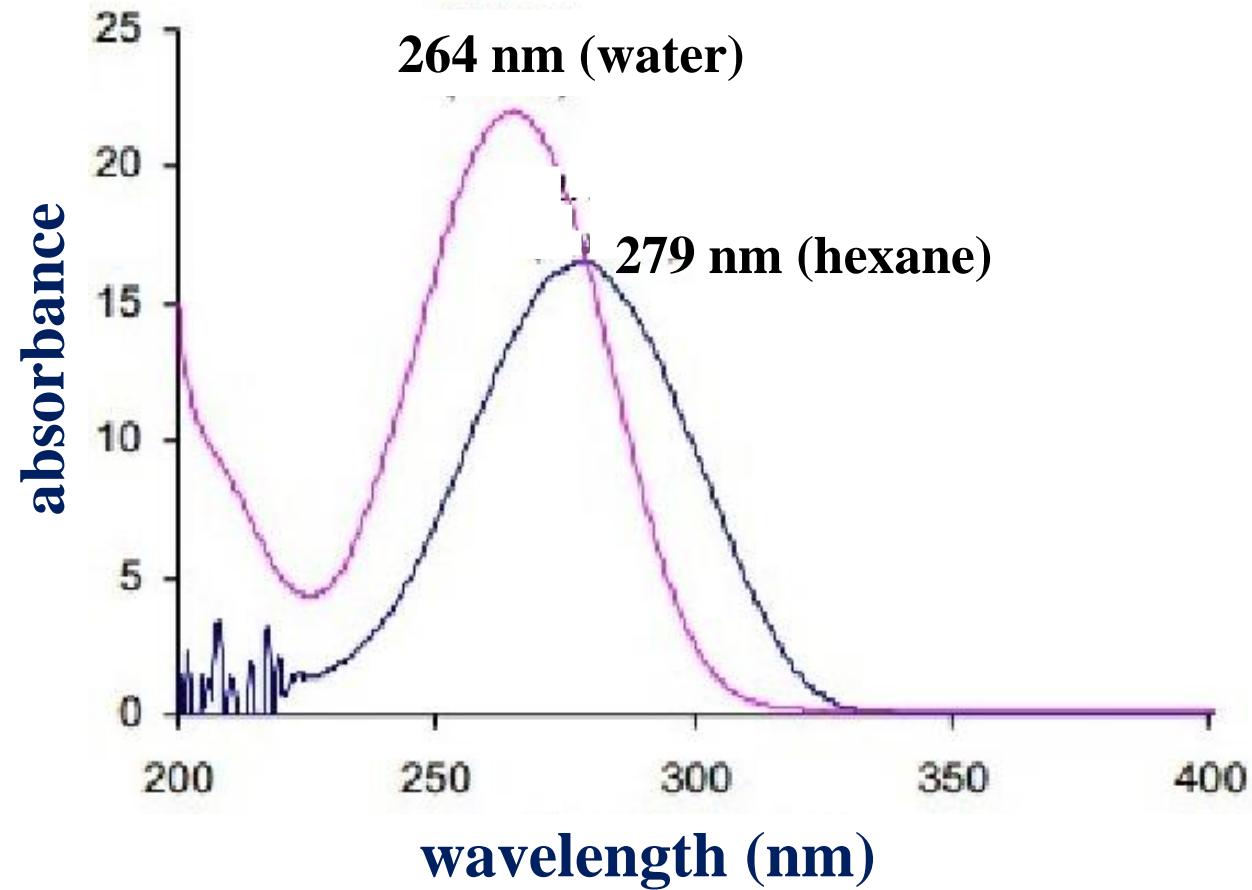


## Bathochromic shift:

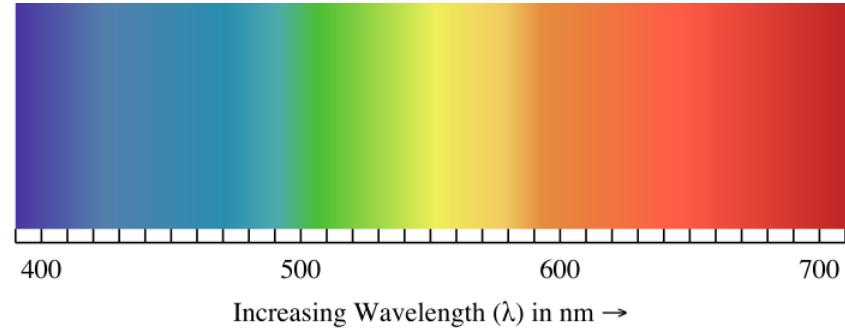
$\lambda_{max}$  value shifted to longer wavelength due to the presence of an Auxochromes or by the change of solvent.

$n \rightarrow \pi^*$  transition for carbonyl compounds experiences red shift when polarity of the solvent is decreased.

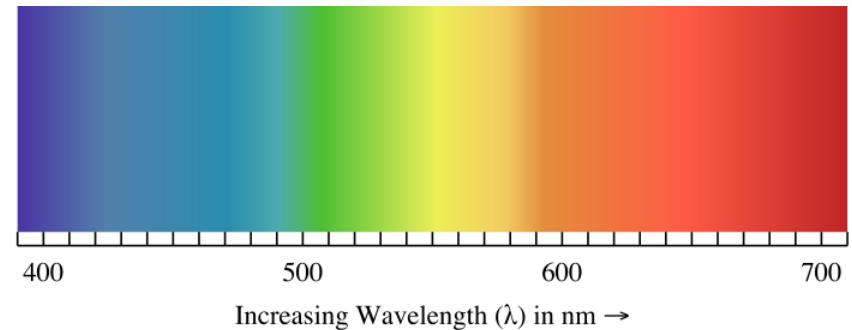
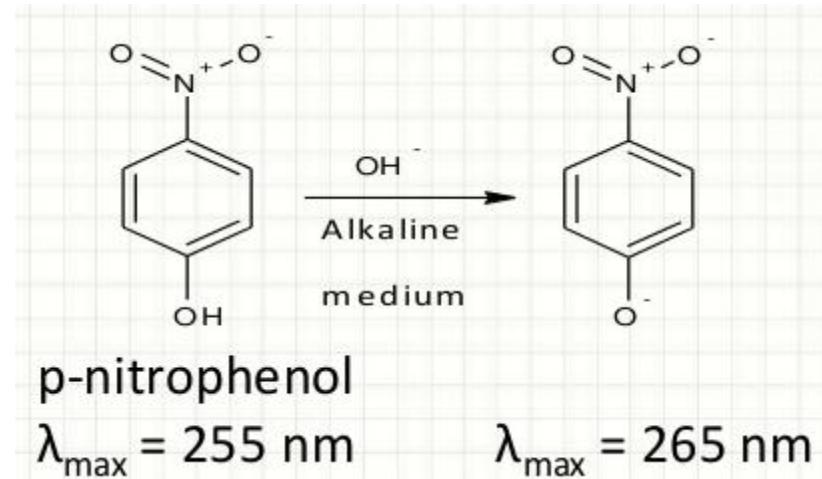




UV-spectra of acetone in hexane and in water



Q. In alkaline medium, p-nitrophenol shows red shift



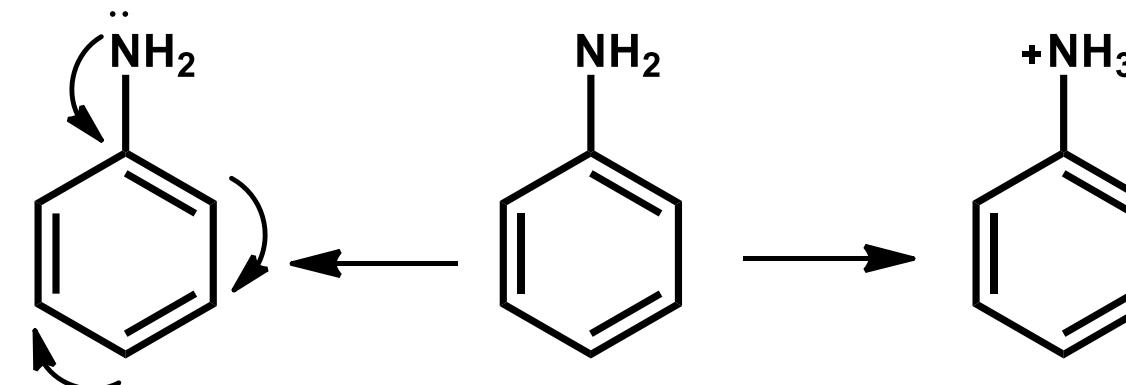
Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron

## Hypsochromic Shift (Blue Shift):

$\lambda_{max}$  value shifted to shorter wavelength Also known as.

e.g. Aniline  $\lambda_{max}$  280 nm

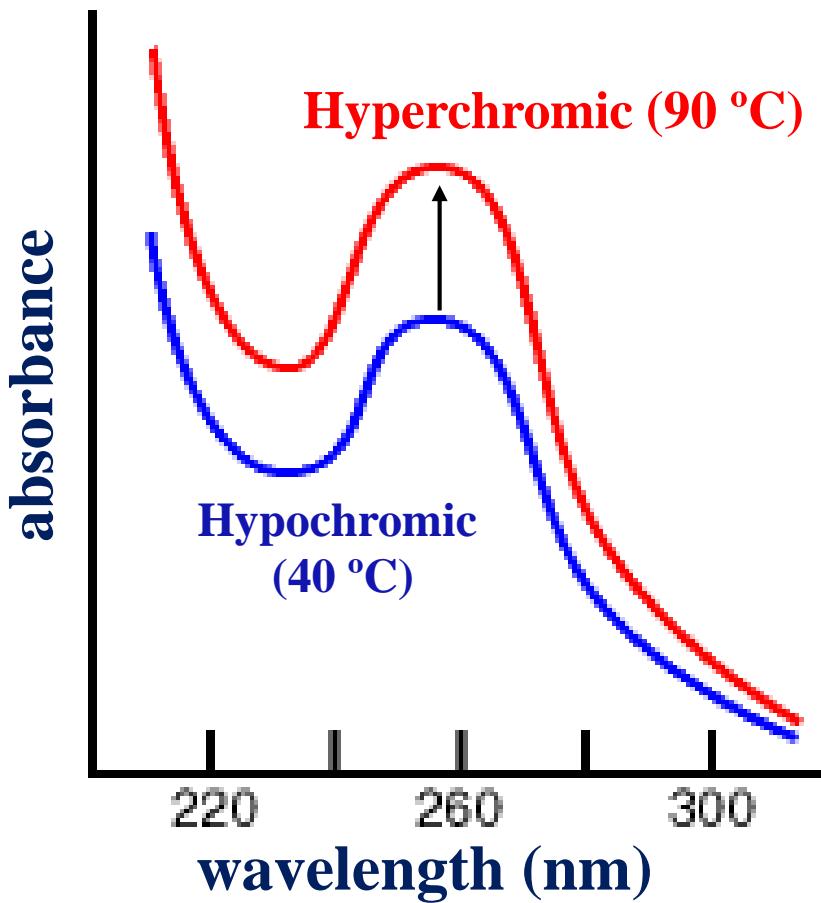
Acidic Aniline  $\lambda_{max}$  203 nm



Lone pair of electron involve  
in conjugation (280 nm)

No conjugation (203 nm)

# Hyperchromic and hypochromic shift



Double strand DNA absorbed less strongly than denatured DNA due to the stacking interactions between the bases. On denaturation, the bases are exposed thereby showing increased interaction.

## Other Examples:

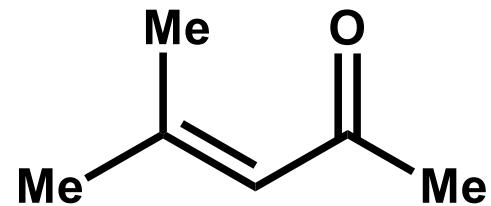
**Pyridine:**  $\lambda_{\max} = 257 \text{ nm}$ ,  $\varepsilon_{\max} : 2750$

**2-Methylpyridine:**  $\lambda_{\max} = 260 \text{ nm}$ ,  $\varepsilon_{\max} : 3560$

**Biphenyl:**  $\lambda_{\max} = 250 \text{ nm}$   $\varepsilon_{\max} : 19000$

**2-Methylbiphenyl:**  $\lambda_{\max} = 237 \text{ nm}$ ,  $\varepsilon_{\max} : 10250$

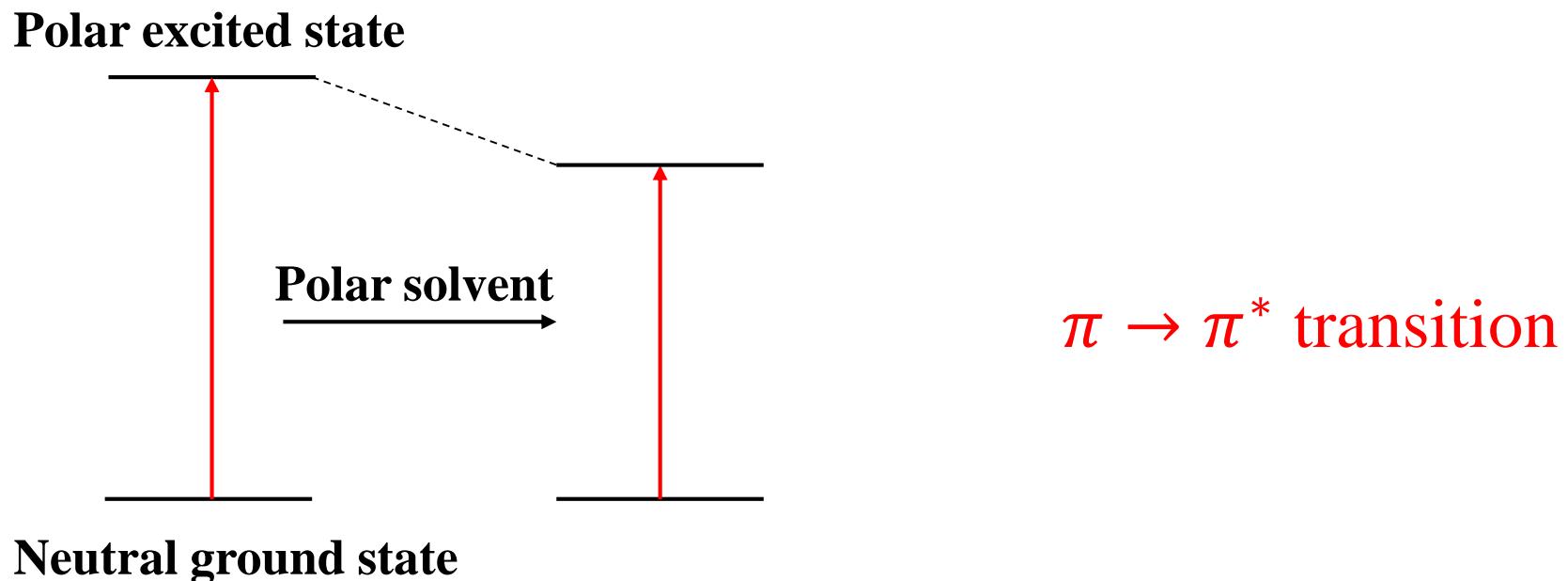
# Influence of solvent on the UV $\lambda_{\max}$ and $\varepsilon_{\max}$ of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation of 4-methylpent-3-en-2-one



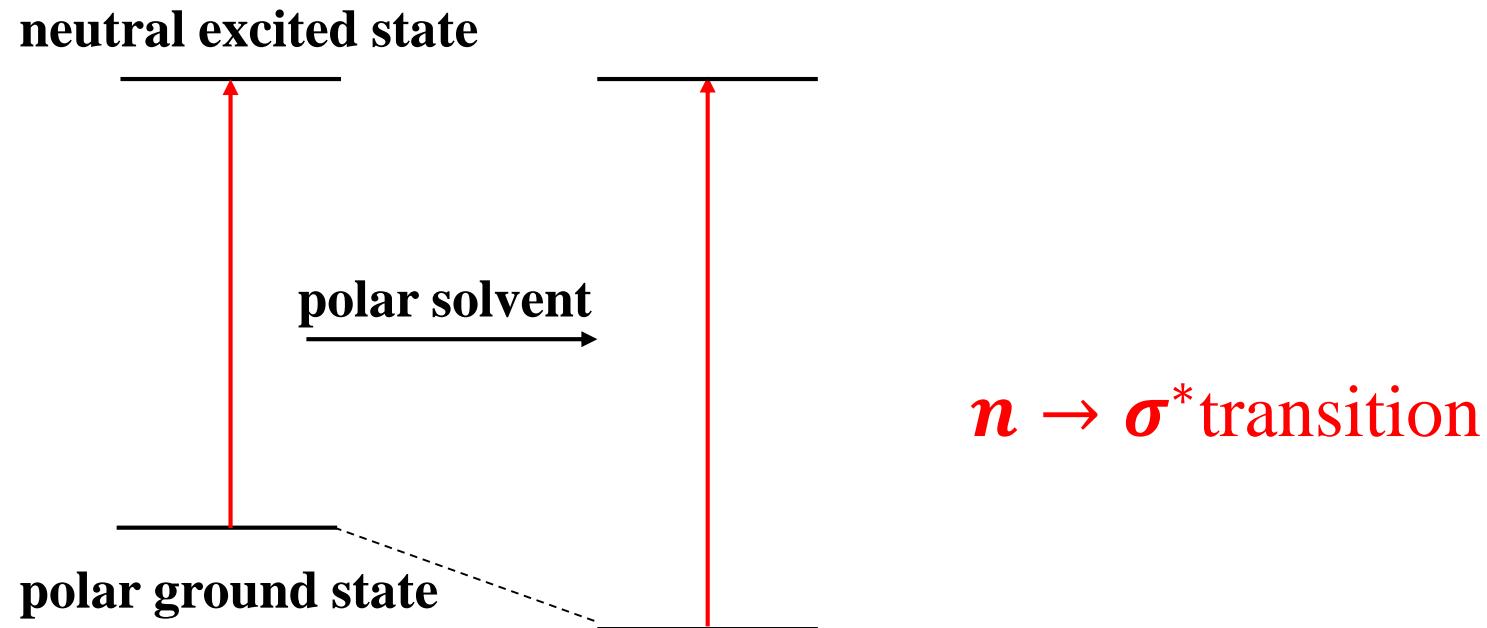
Solvent	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
n-hexane	230(12,600)	327(98)
ether	230(12,600)	326(96)
ethanol	237(12,600)	315(78)
water	245(10,000)	305(60)

# Solvent Effect

- If the excited state is polar, but the ground state is neutral
- Polar solvent will only interact with the excited state and stabilize it
- Hence, absorption shifts to **longer wavelength.**



- ❑ If excited state is neutral and ground states are polar
- ❑ Polar solvent will solvate the ground state
- ❑ The ground state lower its energy due to solvation
- ❑ Hence, absorption shifts to **shorter wavelength**

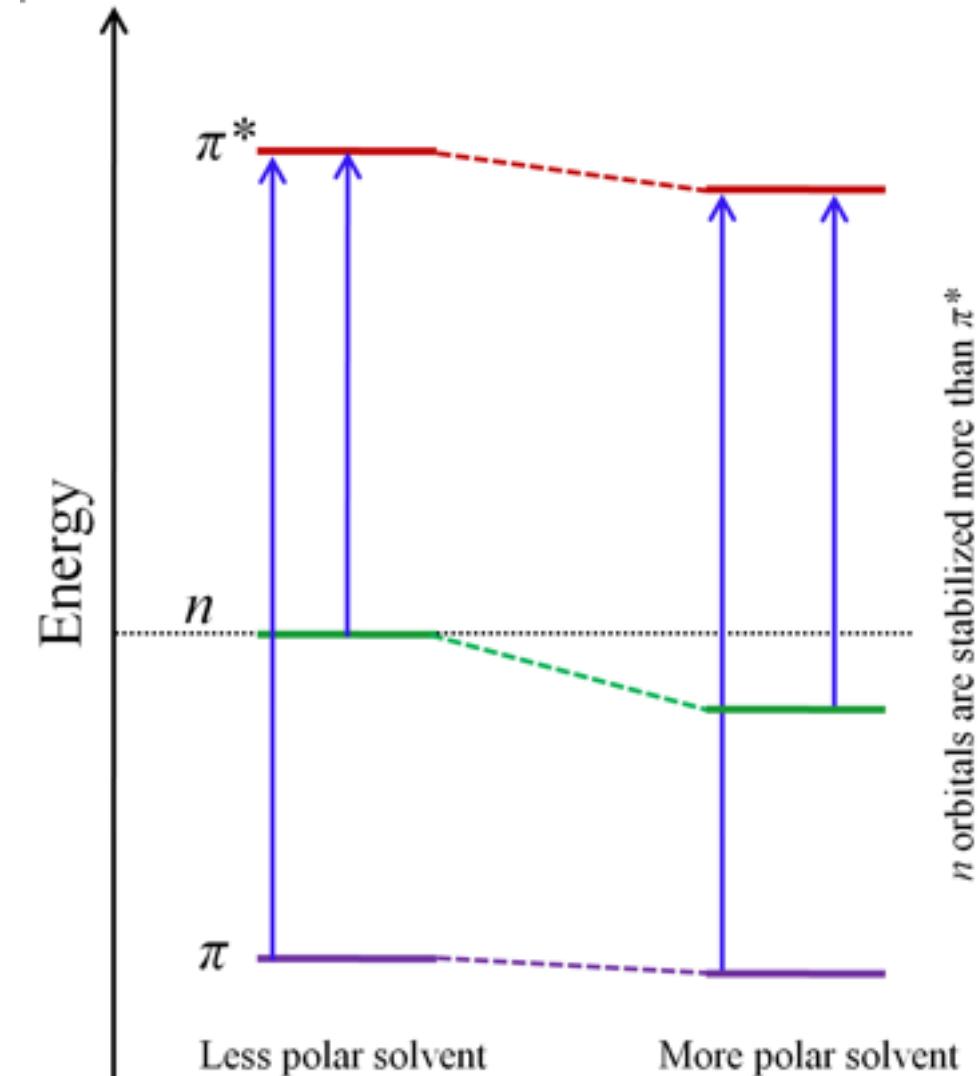


As solvent polarity increases:

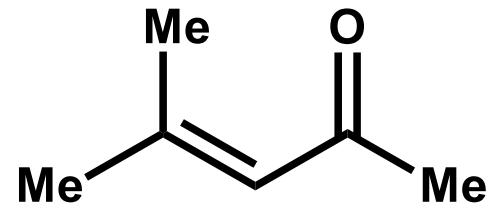
$\pi \rightarrow \pi^*$  band shifts to Longer  $\lambda_{max}$

$n \rightarrow \sigma^*$  band shifts to Shorter  $\lambda_{max}$

$n \rightarrow \pi^*$  band shifts to Shorter  $\lambda_{max}$



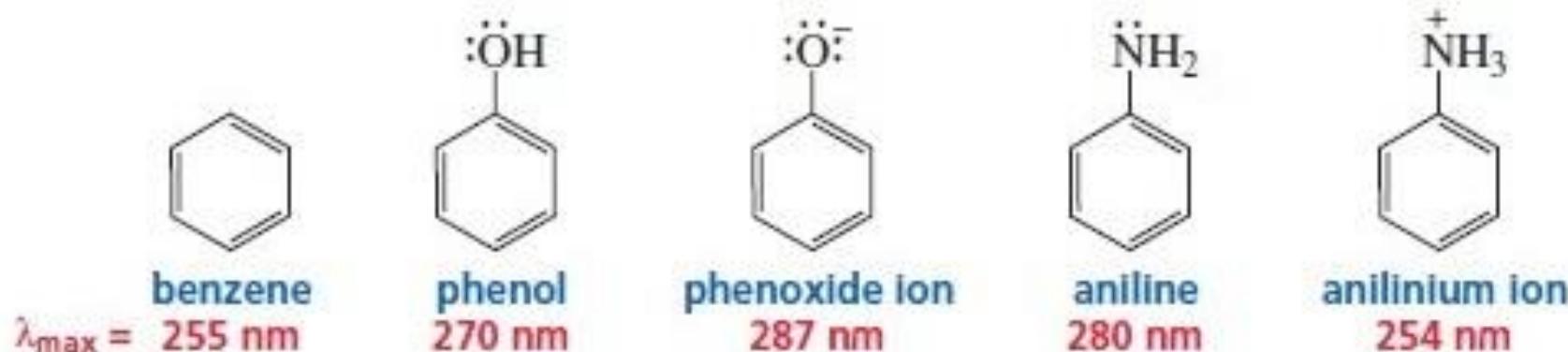
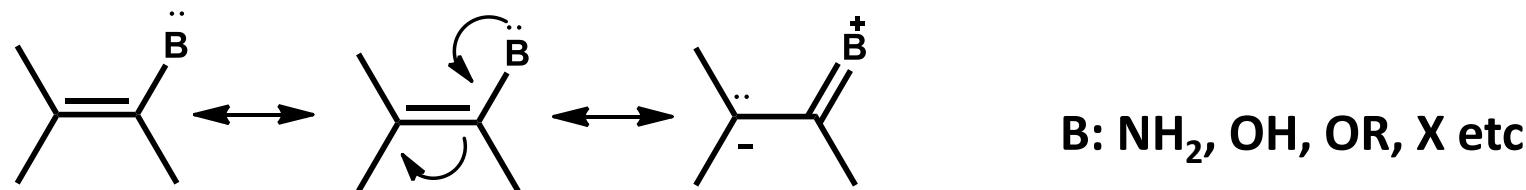
# Influence of solvent on the UV $\lambda_{\max}$ and $e_{\max}$ of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation of 4-methylpent-3-en-2-one



Solvent	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
n-hexane	230(12,600)	327(98)
ether	230(12,600)	326(96)
ethanol	237(12,600)	315(78)
water	245(10,000)	305(60)

## Substituent effect on $\lambda_{max}$ value

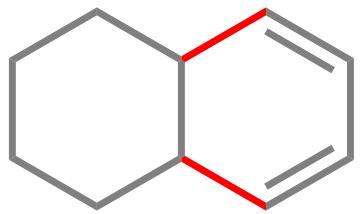
Auxochromes exert their bathochromic shifts by extension of the length of the conjugated system



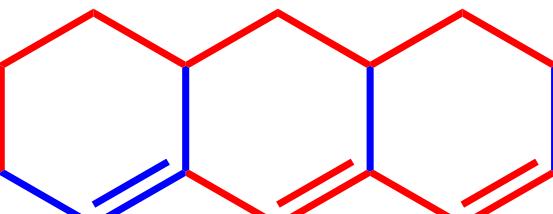
# Calculation of $\lambda_{max}$

## Woodward-Feiser rule

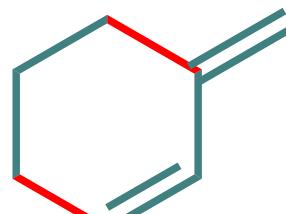
Applicable for the low energy transition ( $\pi \rightarrow \pi^*$ ) from HOMO to LUMO



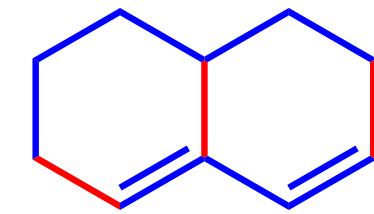
253 nm



214 nm



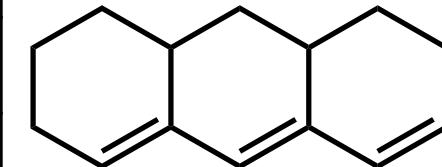
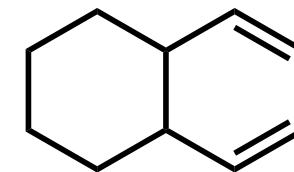
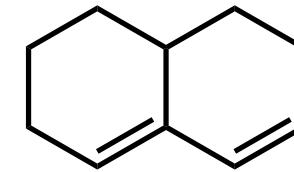
214 nm



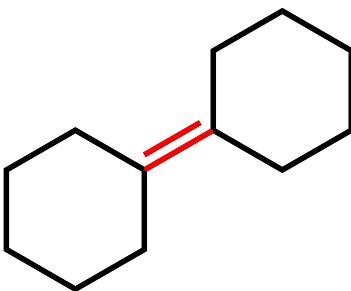
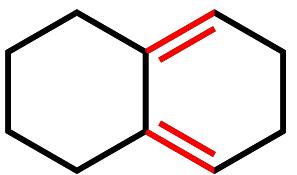
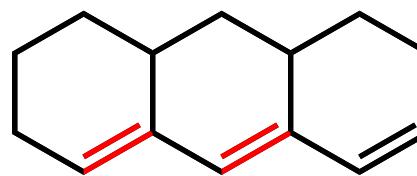
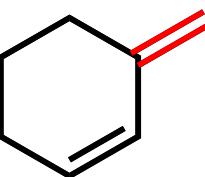
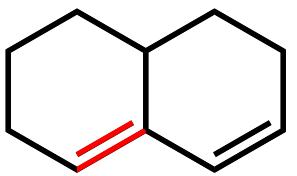
214 nm

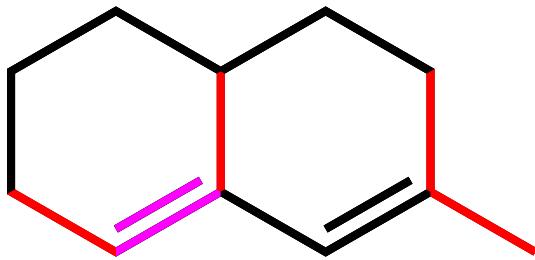
# Calculation of $\lambda_{max}$ in conjugated diene and polyene

<b>Parent values</b>	
Heteroannular Conjugated Diene(transoid)	214 nm
Homoannular Conjugated Diene(cisoid)	253 nm
<b>Increments</b>	
Each Alkyl Residue or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm



## Exocyclic Double bond





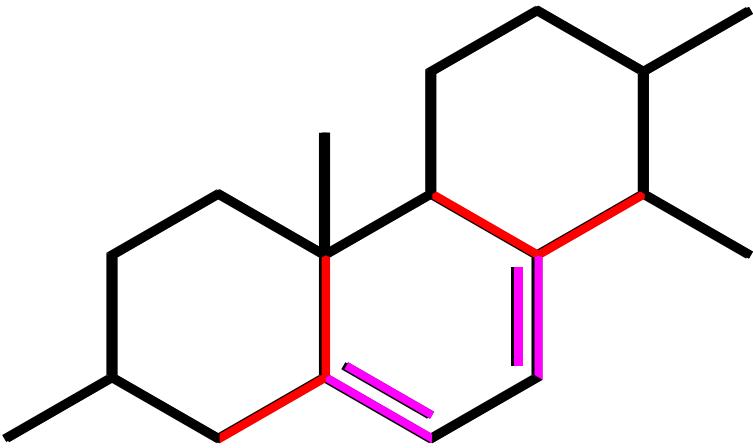
**Heteroannular diene : 214**

**Alkyl substituents : (4x5) : 20**

**Exocyclic double bond : 5**

---

**Absorption maximum : 239 nm**



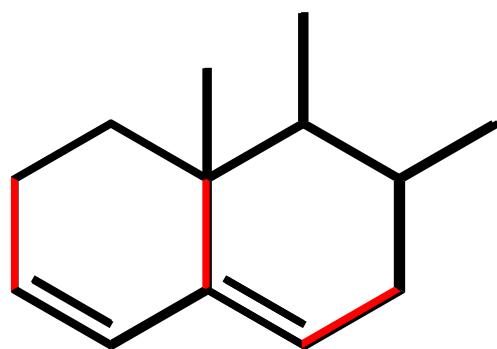
**Homoannular diene : 253**

**Alkyl substituents : (4x5) : 20**

**Exocyclic double bond : (2x5) : 10**

---

**Absorption maximum : 283 nm**



**Transoid (base) :** **214 nm**

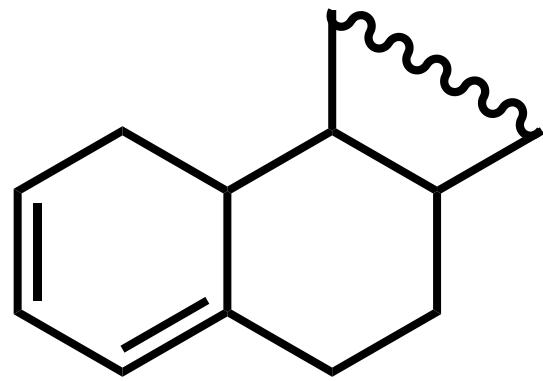
**3 ring residues :** **+ 15 nm**

**1 exocyclic C=C :** **+ 5 nm**

---

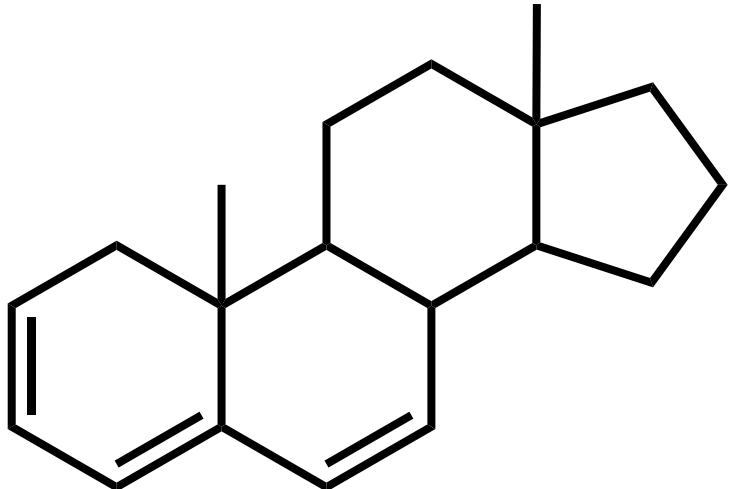
**Total :** **234 nm**

Observed  $\lambda_{\max}$  235 nm



<b>Cisoid(base)</b>		<b>253</b>
<b>3 ring residues</b>		<b>+15</b>
<b>1 exocyclic C=C</b>		<b>+5</b>
	<b>Total</b>	<b>273</b>

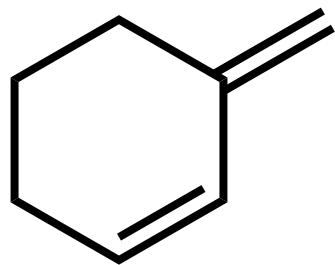
**Observed = 275 nm**



<b>Cisoid(base)</b>	253
<b>3 ring residues</b>	+15
<b>1 exocyclic C=C</b>	+5
<b>1 extra conjugation</b>	+30

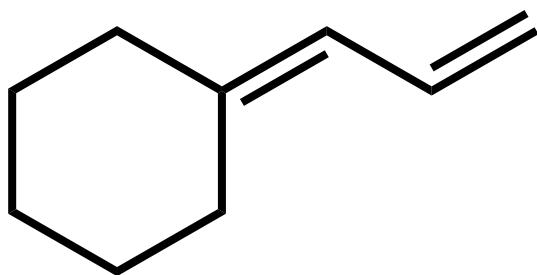
**Total : 303 nm**

**Observed : 304 nm**



<b>Transoid(base)</b>		<b>214</b>
<b>2 ring residues</b>		<b>+10</b>
<b>1 exocyclic C=C</b>		<b>+5</b>
	<b>Total</b>	<b>229</b>

**Observed = 230 nm**

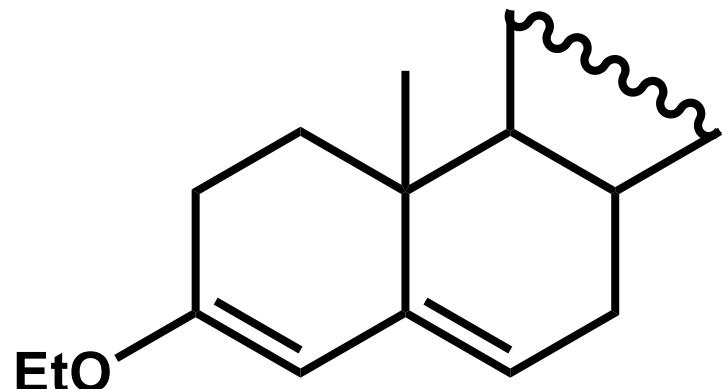


<b>Transoid(base)</b>		<b>214</b>
<b>2 ring residues</b>		<b>+10</b>
<b>1 exocyclic C=C</b>		<b>+5</b>
	<b>Total</b>	<b>229</b>

**Observed = 236 nm**

## Calculation of $\lambda_{max}$

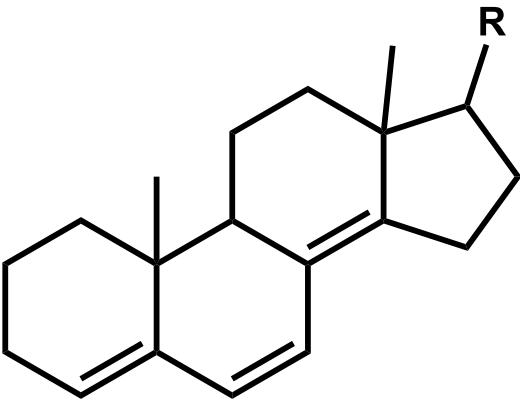
<b>Parent values</b>	
Heteroannular Conjugated Diene	214 nm
Homoannular Conjugated Diene	253 nm
<b>Increments</b>	
Each Alkyl Residue or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
<b>Auxochrome</b>	
-OR	6 nm
-SR	30 nm
-Cl, -Br	5 nm
-NR <sub>2</sub>	60 nm
-OCOCH <sub>3</sub>	0 nm



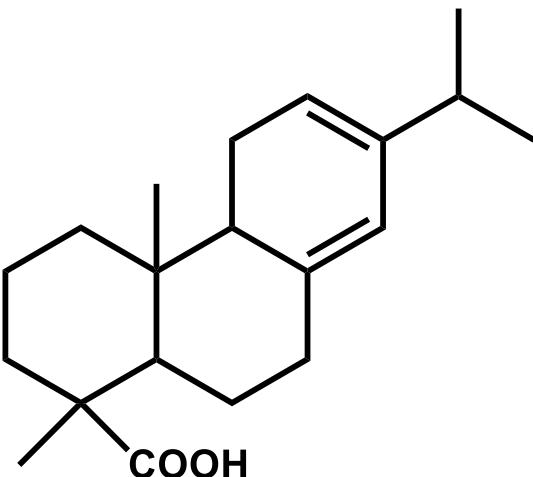
<b>Transoid(base)</b>		214
<b>3 ring residues</b>		+15
<b>1 exocyclic C=C</b>		+5
<b>-OR</b>		+6

**Total** : 240 nm

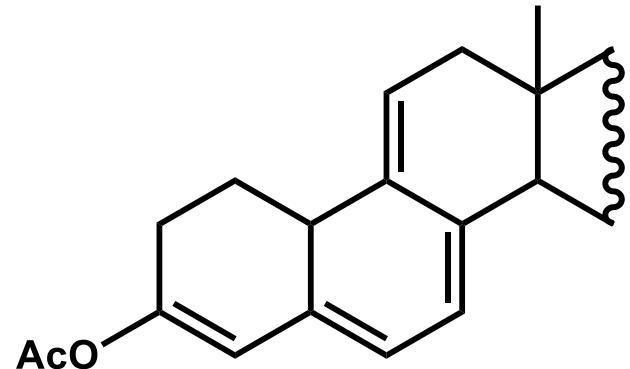
**Observed** : 241 nm



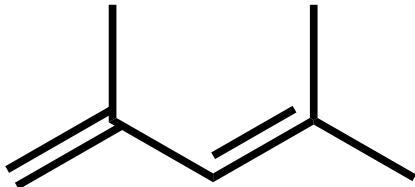
<b>Transoid (base)</b>	<b>214</b>
<b>5 ring residues</b>	<b>+25</b>
<b>3 exocyclic C=C</b>	<b>+15</b>
<b>1 extra conjugation</b>	<b>+30</b>
<hr/>	
<b>Total</b>	<b>= 284 nm</b>
<b>Observed</b>	<b>= 283 nm</b>



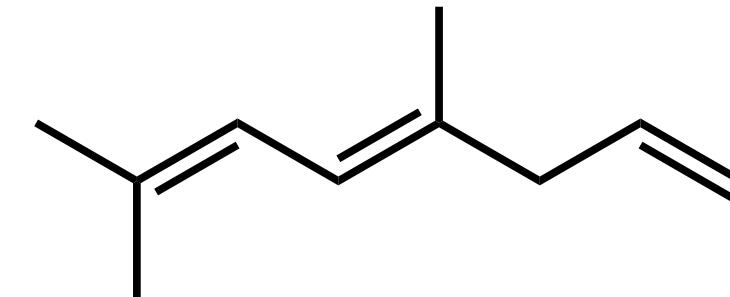
<b>Cisoid (base)</b>	<b>253</b>
<b>3 ring residues</b>	<b>+15</b>
<b>1 alkyl substituent</b>	<b>+5</b>
<b>1 exocyclic C=C</b>	<b>+5</b>
<hr/>	
<b>Total</b>	<b>= 278 nm</b>
<b>Observed</b>	<b>= 275 nm</b>



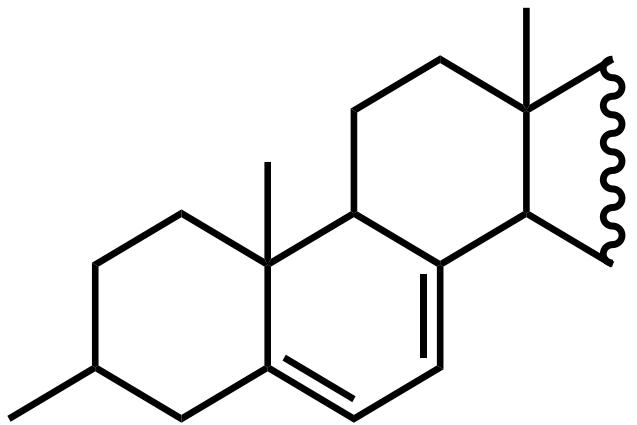
<b>Cisoid (base)</b>	<b>253</b>
<b>5 ring residues</b>	<b>+25</b>
<b>3 exocyclic C=C</b>	<b>+15</b>
<b>2 extra conjugation</b>	<b>+60</b>
<b>-OAc</b>	<b>+0</b>
<hr/>	
<b>Total</b>	<b>= 353 nm</b>
<b>Observed</b>	<b>= 355 nm</b>



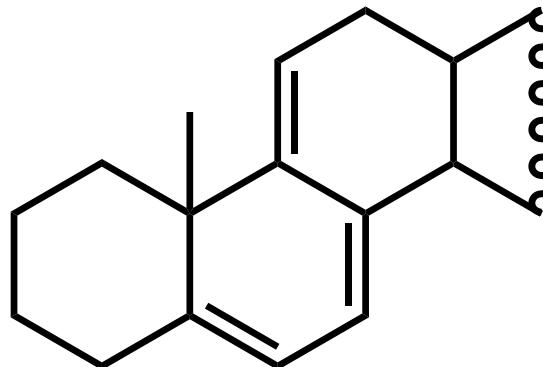
<b>Transoid (base)</b>	<b>214</b>
<b>3 alkyl group</b>	<b>+15</b>
<hr/>	
<b>Total</b>	<b>= 229 nm</b>
<b>Observed</b>	<b>= 232 nm</b>



<b>Transoid (base)</b>	<b>214</b>
<b>4 alkyl group</b>	<b>+20</b>
<hr/>	
<b>Total</b>	<b>= 234 nm</b>
<b>Observed</b>	<b>= 235 nm</b>



<b>Cisoid (base)</b>	<b>253</b>
<b>4 ring residues</b>	<b>+20</b>
<b>2 exocyclic C=C</b>	<b>+10</b>
<hr/>	
<b>Total</b>	<b>= 383 nm</b>
<b>Observed</b>	<b>= 382 nm</b>

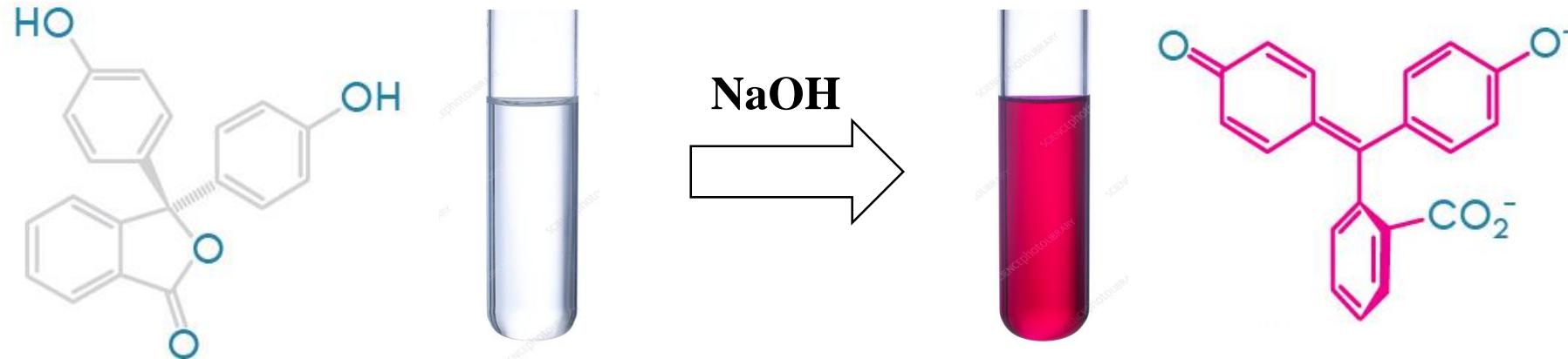


<b>Cisoid (base)</b>	<b>253</b>
<b>5 ring residues</b>	<b>+25</b>
<b>3 exocyclic C=C</b>	<b>+15</b>
<b>1 extra conjugation</b>	<b>+30</b>
<hr/>	
<b>Total</b>	<b>= 323 nm</b>
<b>Observed</b>	<b>= 325 nm</b>

# Application of UV-Visible Spectroscopy

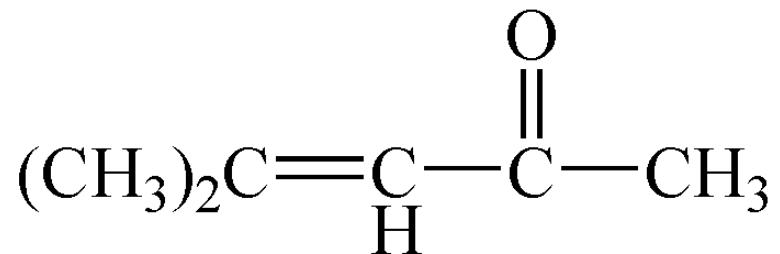
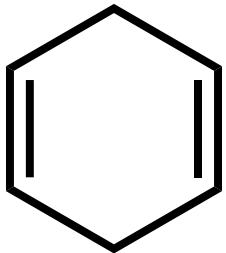
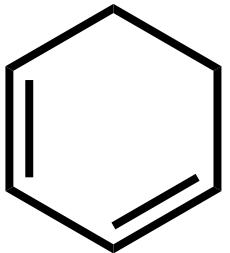
## 1. Detection of conjugation

Addition of unsaturation shifts the absorption to longer wavelength and pertains colour.

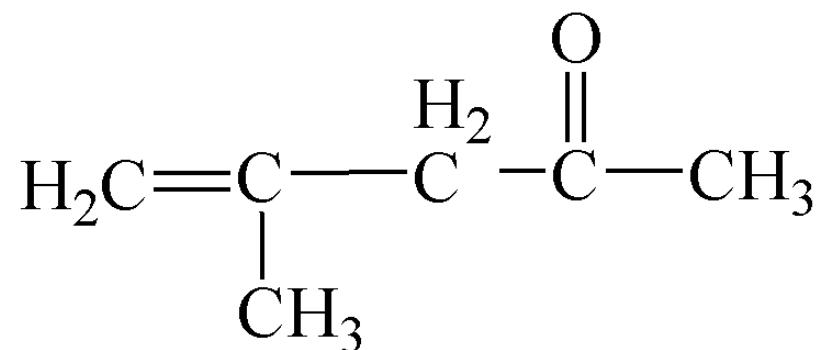


Phenolphthaleine in aqueous methanol

## 2. Distinction in conjugated & non conjugated isomers

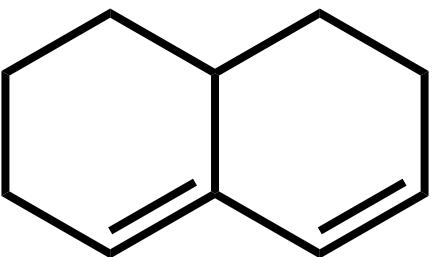
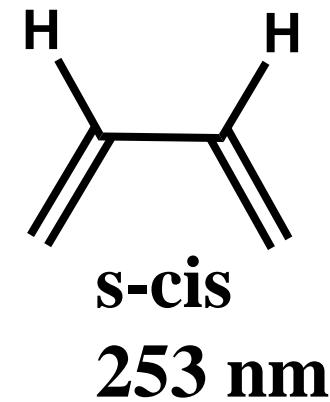
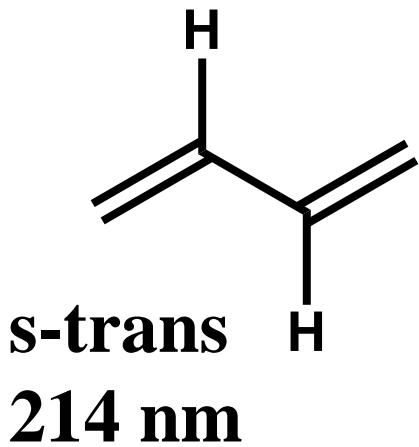


**Longer wave length**

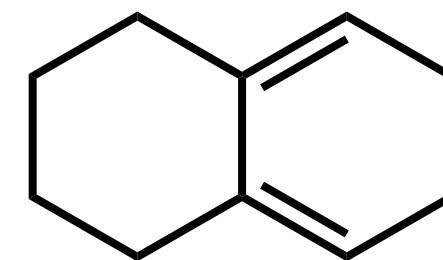


**Shorter wave length**

### 3. Detection of geometrical isomers

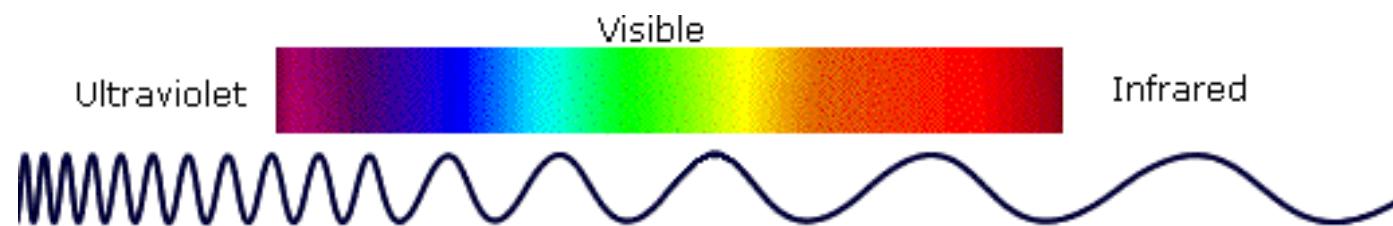


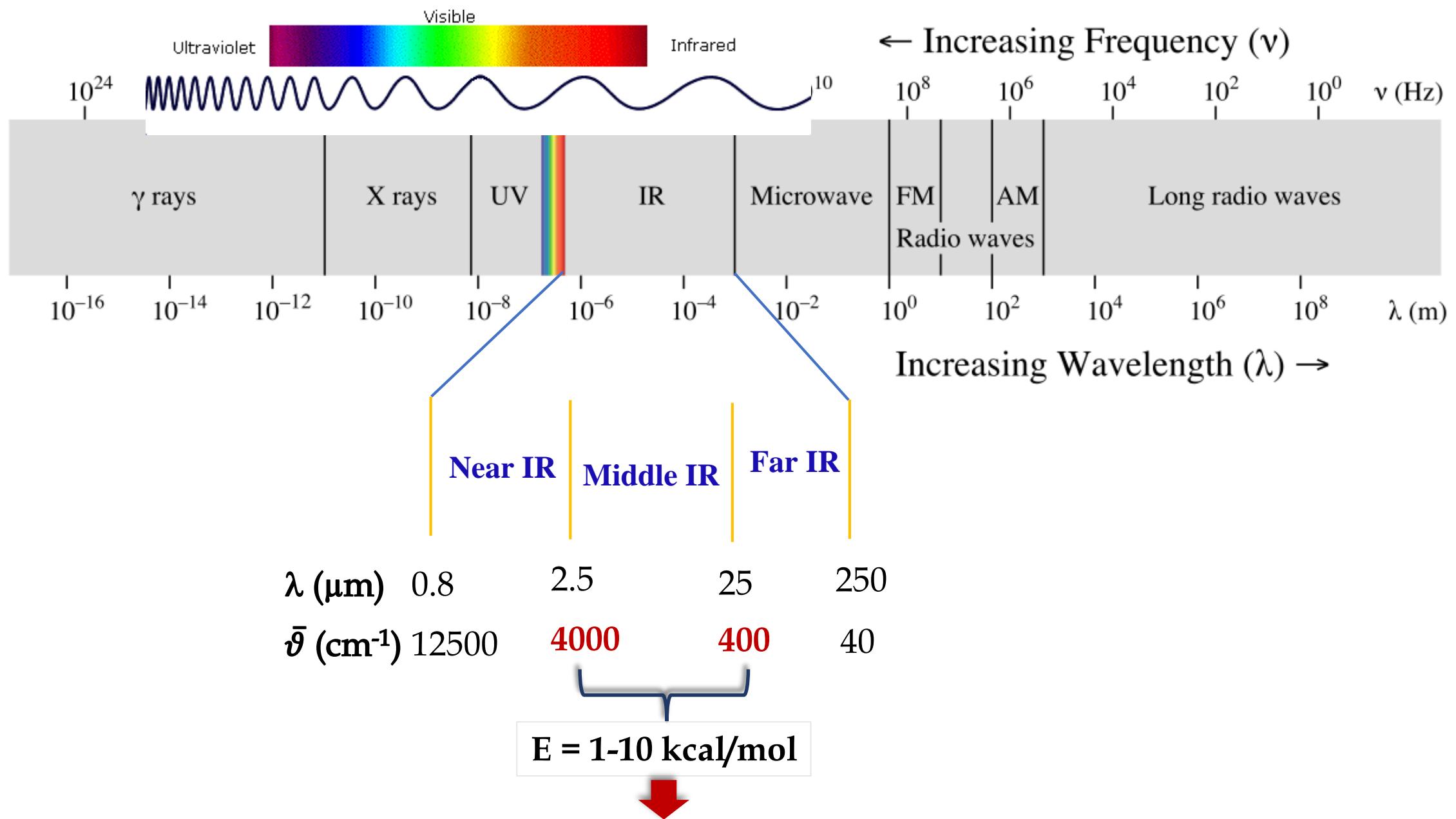
$\lambda_{\max} = 234 \text{ nm}$   
 $\varepsilon_{\max} = 12000-28000$

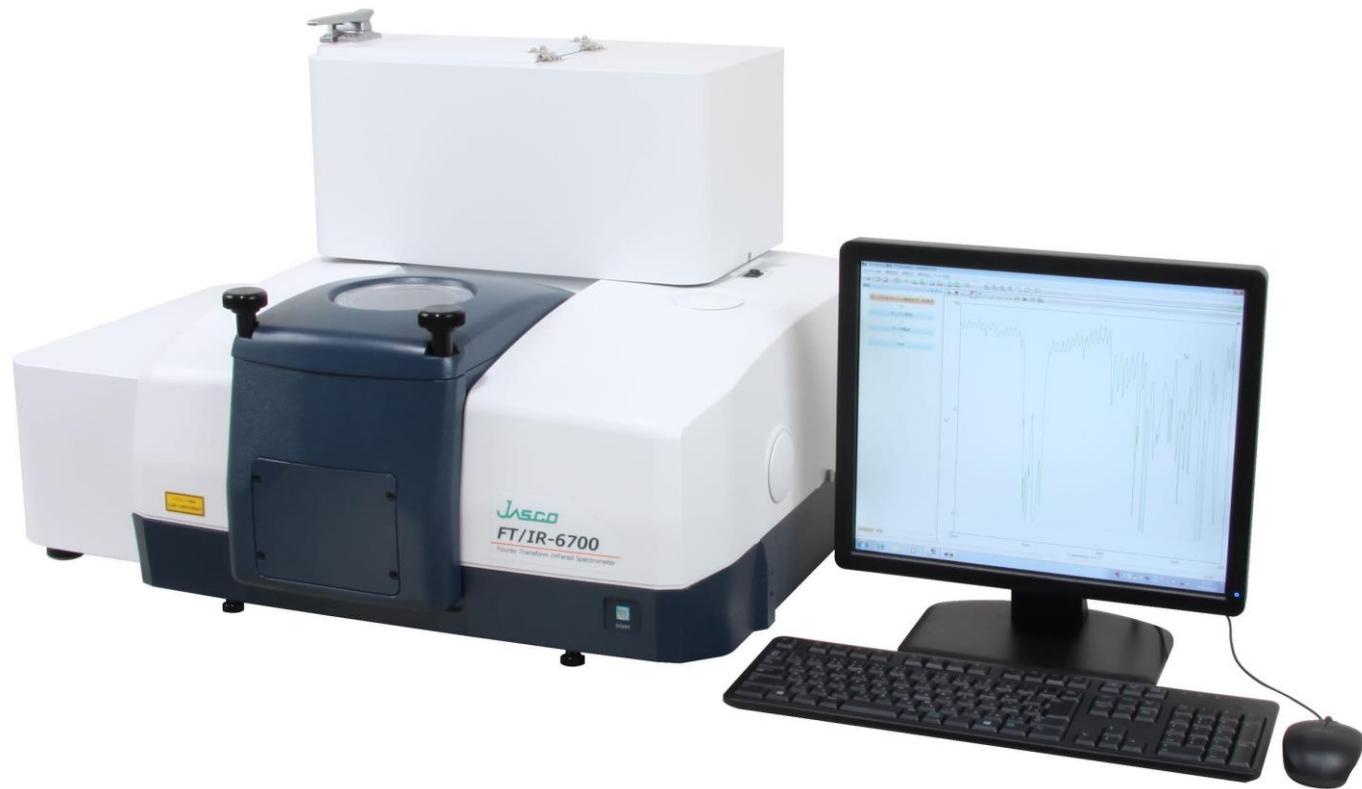


$\lambda_{\max} = 283 \text{ nm}$   
 $\varepsilon_{\max} = 5000-15000$

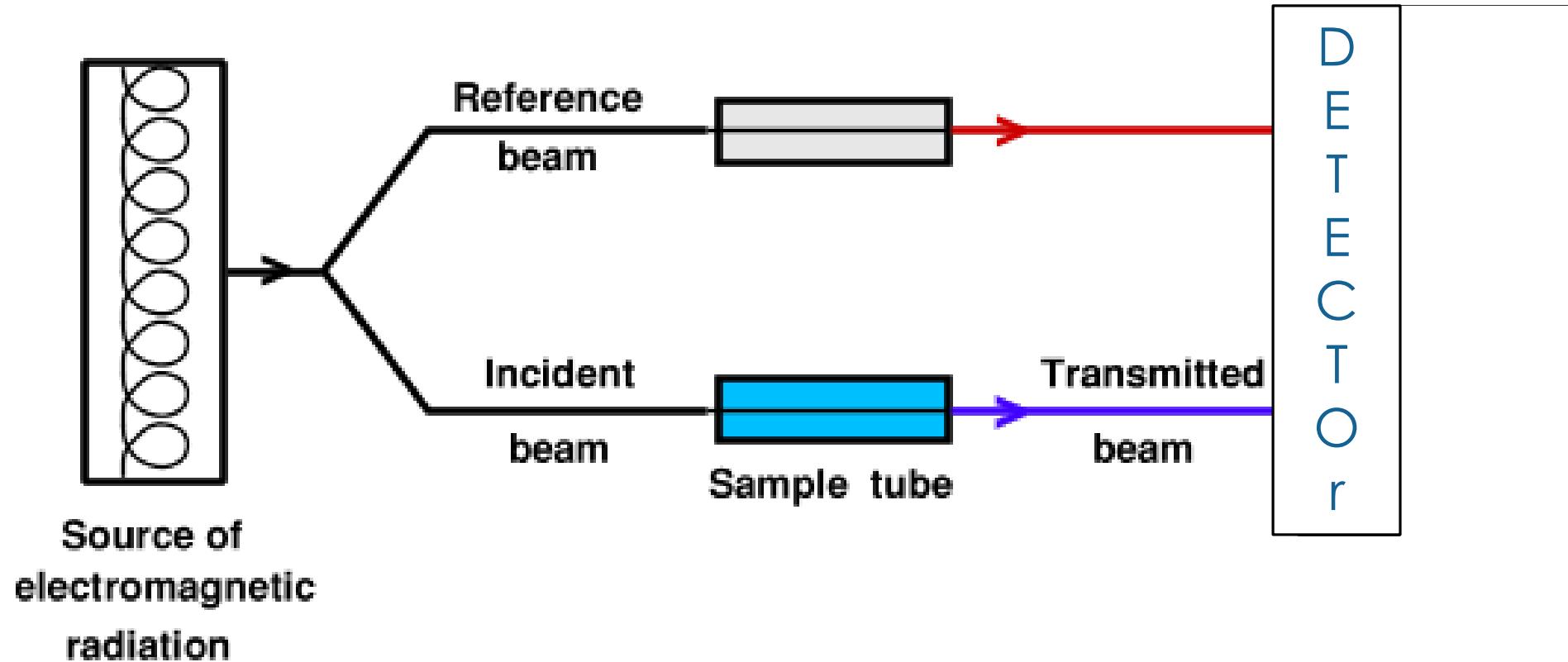
# Infra-Red spectroscopy and application

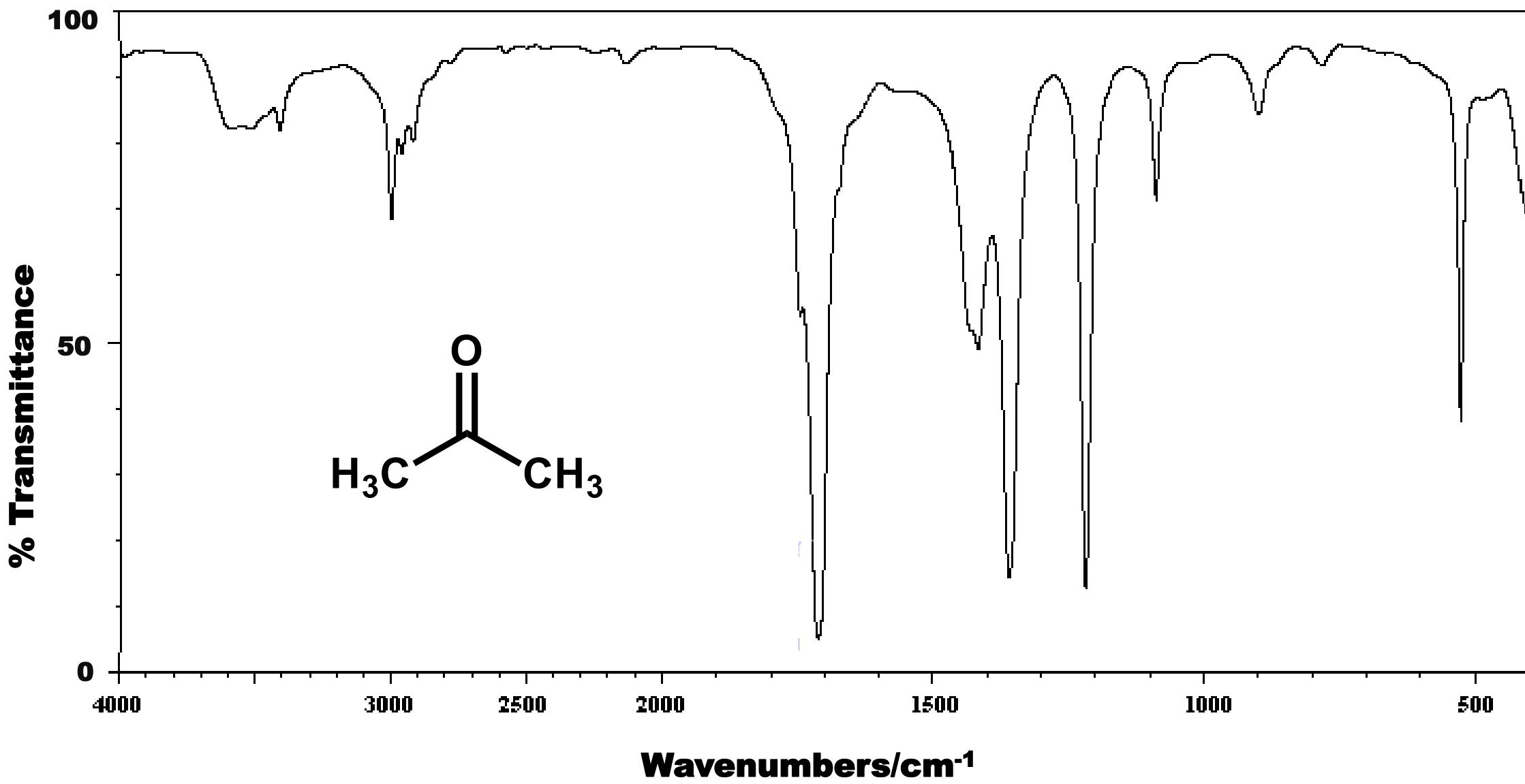




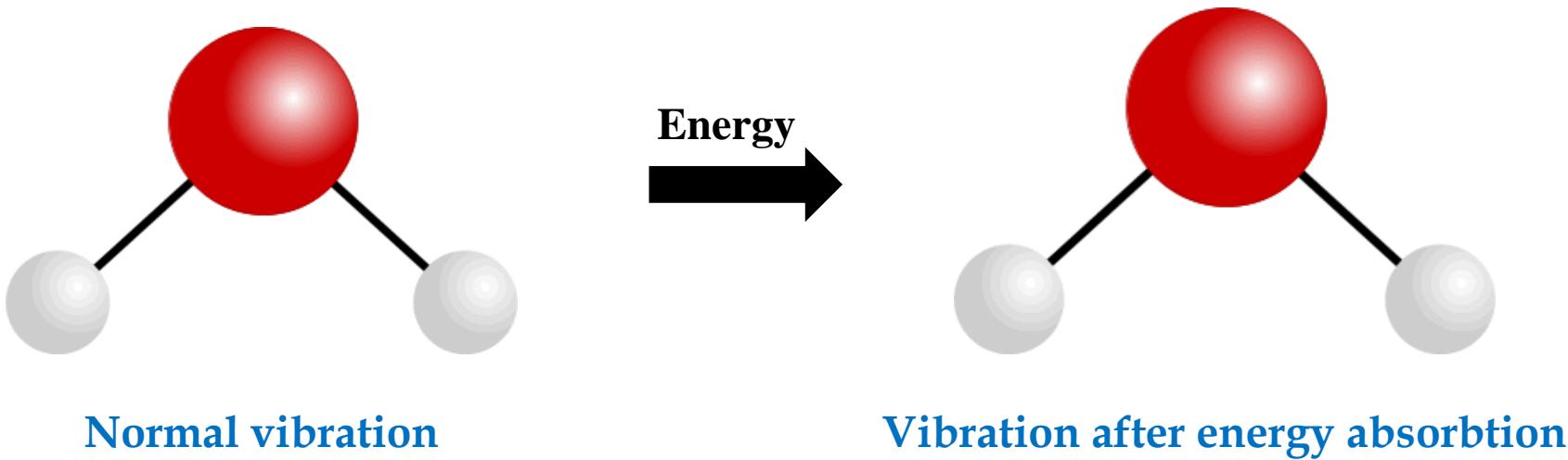


## IR Spectrometer



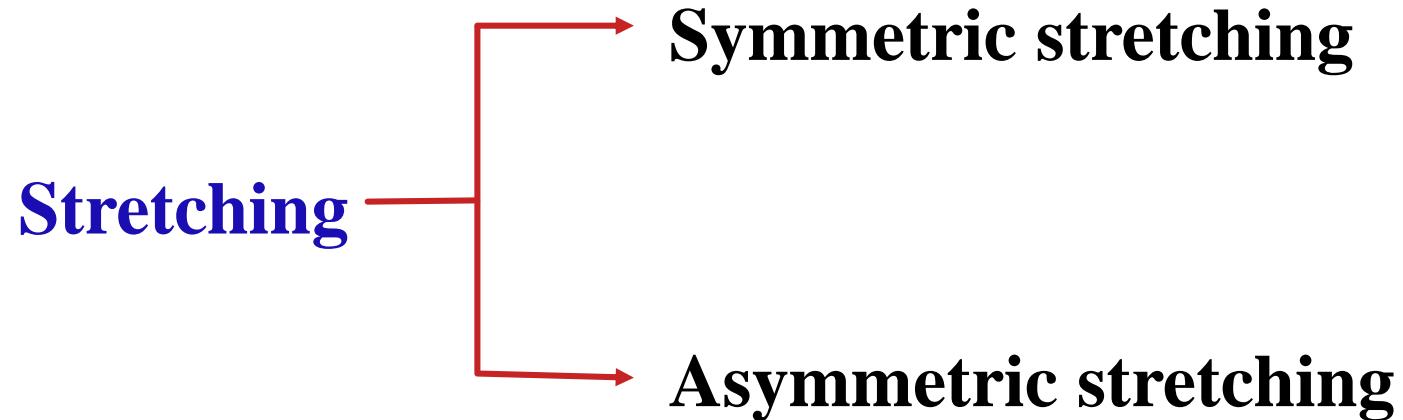


# IR Spectra: Vibrational motion in covalent bond

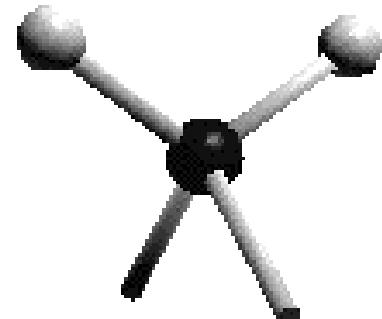
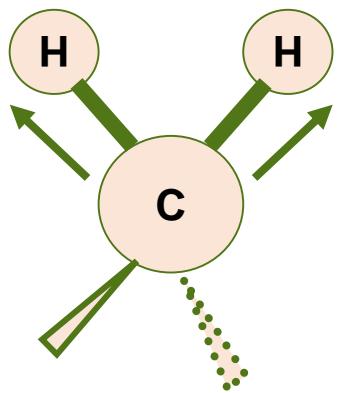


Absorb frequency of radiation is similar to bond vibration(s)

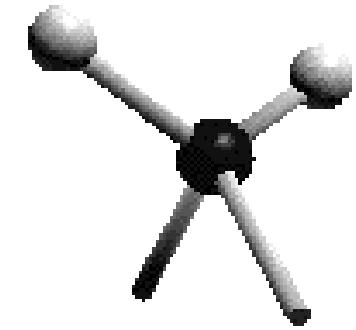
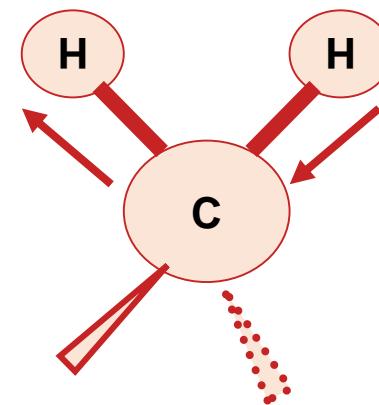
# Types of bond vibration



## Symmetric Stretching



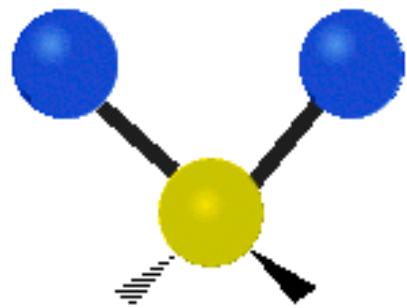
## Asymmetric Stretching



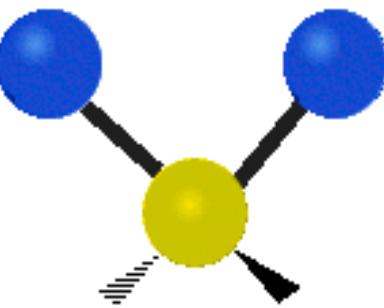
In plane

Bending

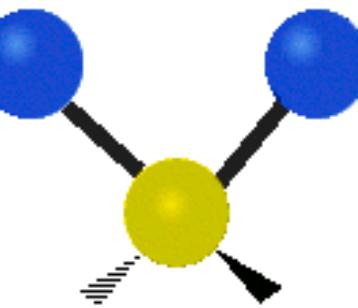
Out of plane



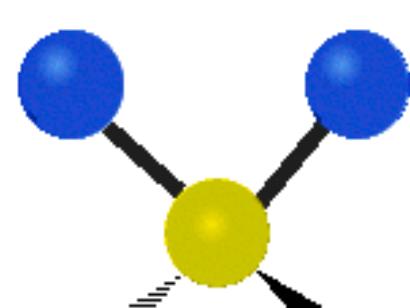
*Scissoring*



*Rocking*

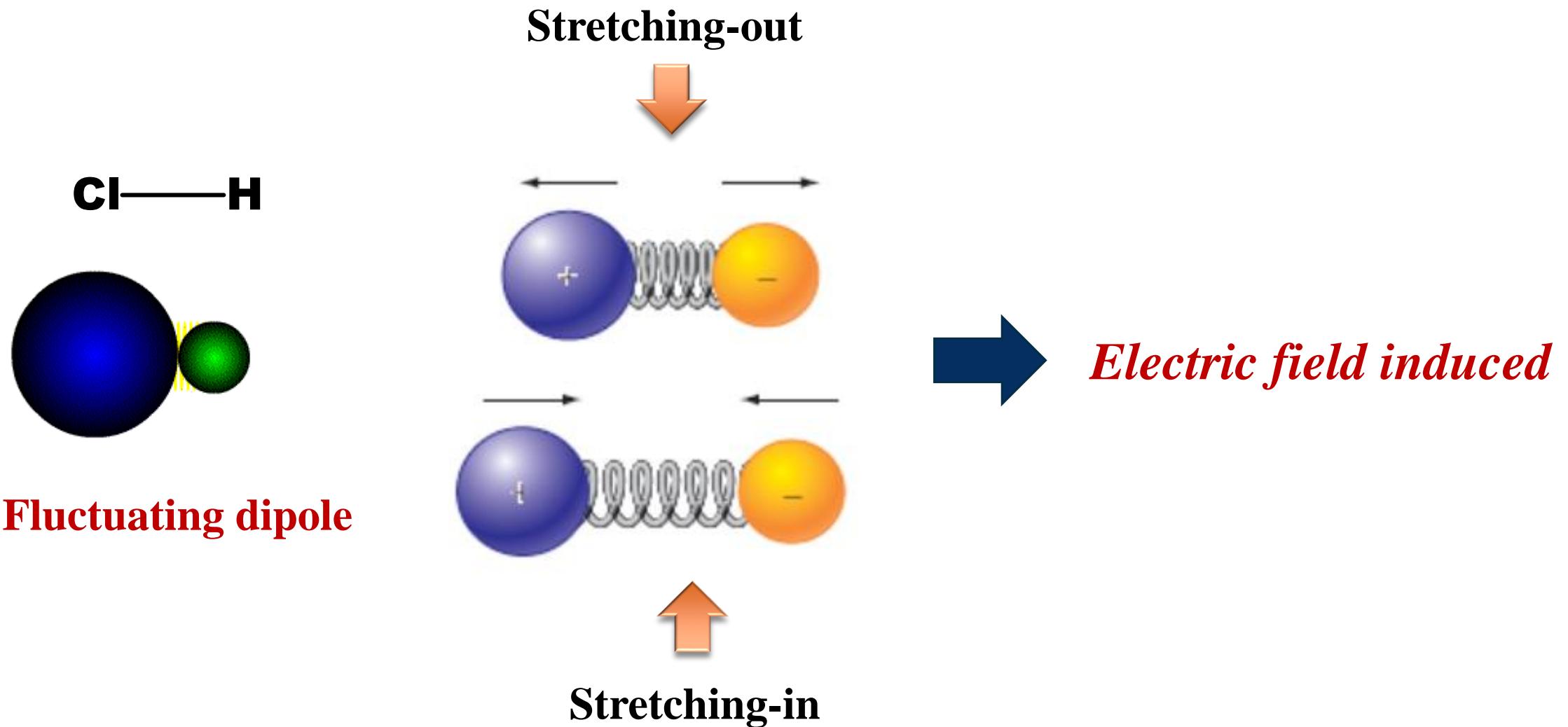


*Twisting*



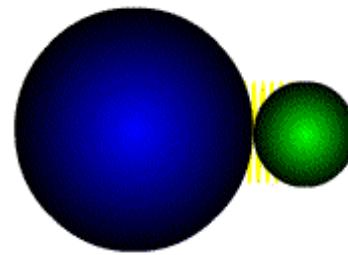
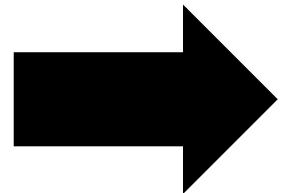
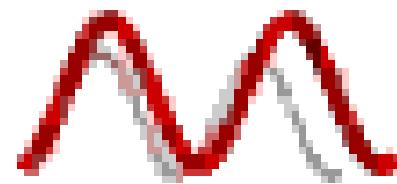
*Wagging*





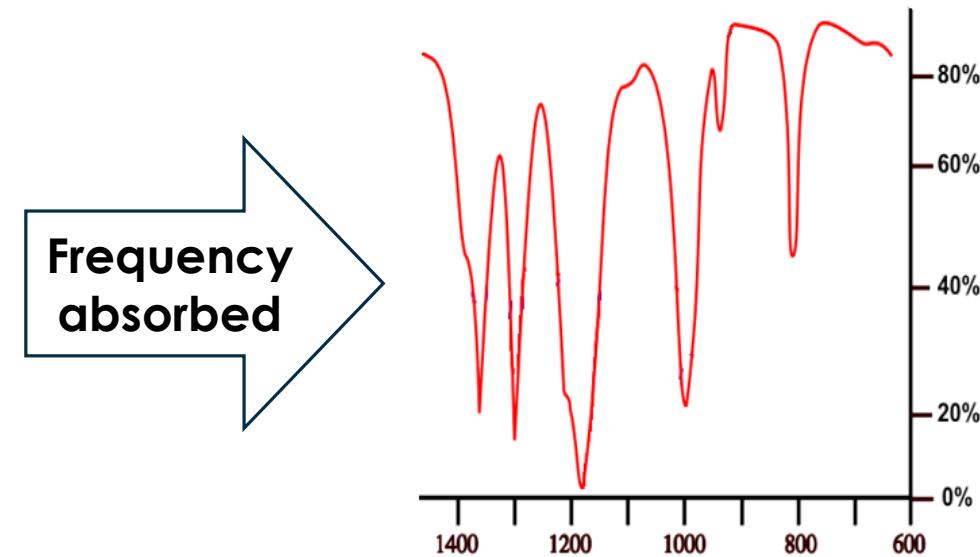
Induced electric field interacts with the EM radiation

# The vibrating bond absorb IR radiation when its frequency is same as the frequency of the oscillating dipole



EM radiation  
Frequency  $\nu$

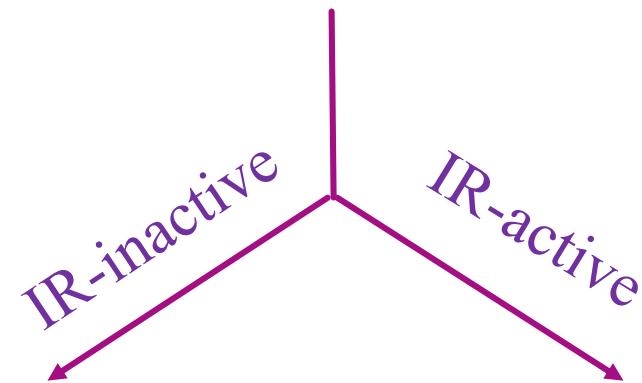
Fluctuating dipole  
Frequency  $\nu$



Each vibrational mode with change in dipole moment of the system leads to absorption of frequency in IR range

# Criteria for IR absorption

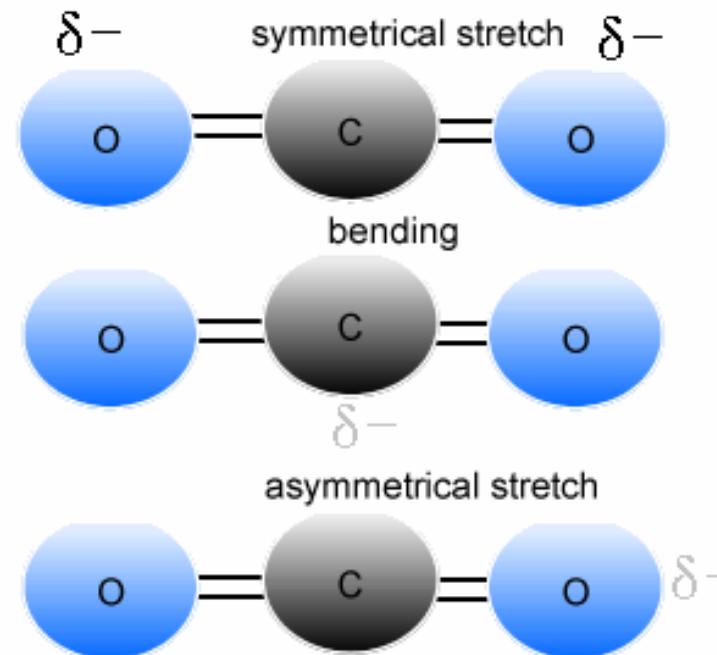
Dipole moment of the bond must change during vibrational motion



*e.g.* H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>

*e.g.* H<sub>2</sub>O, SO<sub>2</sub>, HCl

# Though CO<sub>2</sub> is non polar molecule, why it is IR active?



No Change in Dipole

Change in Dipole

Change in Dipole

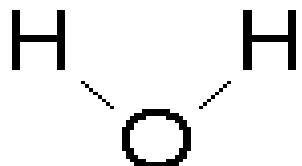
## Mode of Vibrations in Molecules

Linear Molecules have  **$3N-5$**  number of fundamental frequency

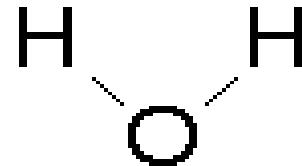
Non-linear Molecules have  **$3N-6$**  number of fundamental frequency

Where N is the number of atoms present in the molecule

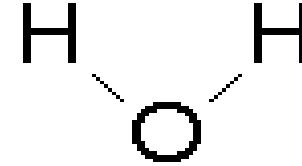
# Three Fundamental Modes of Vibration for Water



$\nu_1$ , Asymmetric Stretch  
 $\sim 3755 \text{ cm}^{-1}$



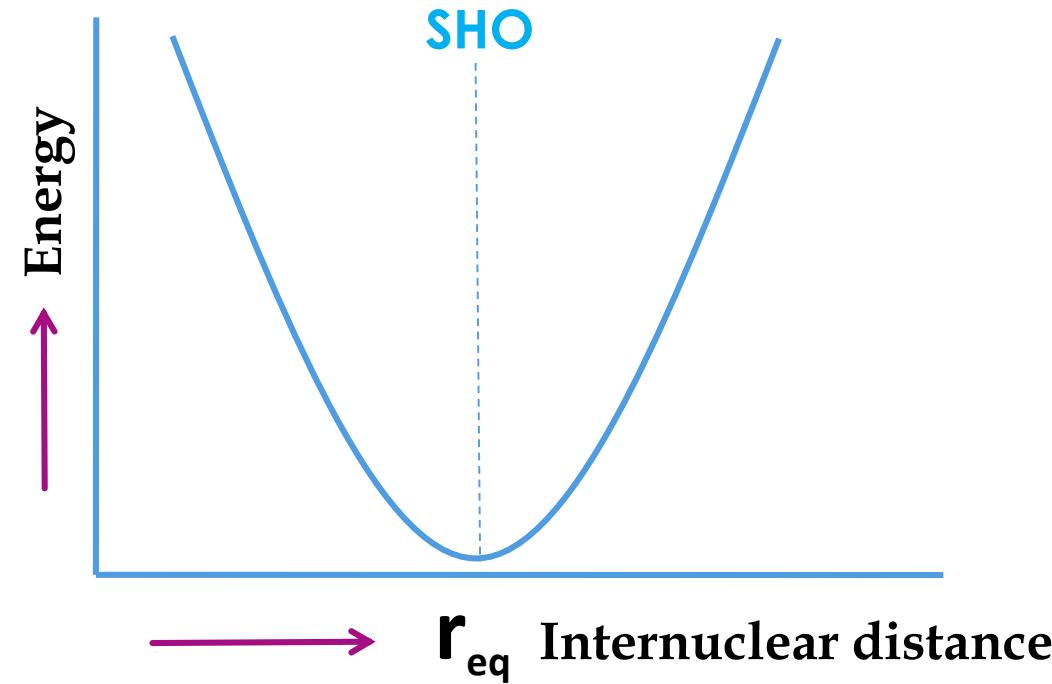
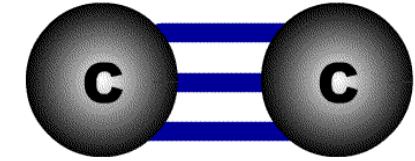
$\nu_2$ , Symmetric  
Stretch  
 $\sim 3651 \text{ cm}^{-1}$



$\nu_3$ , Bending  
 $\sim 1595 \text{ cm}^{-1}$

# Simple Harmonic Oscillator (SHO)

## Morse Energy Diagram



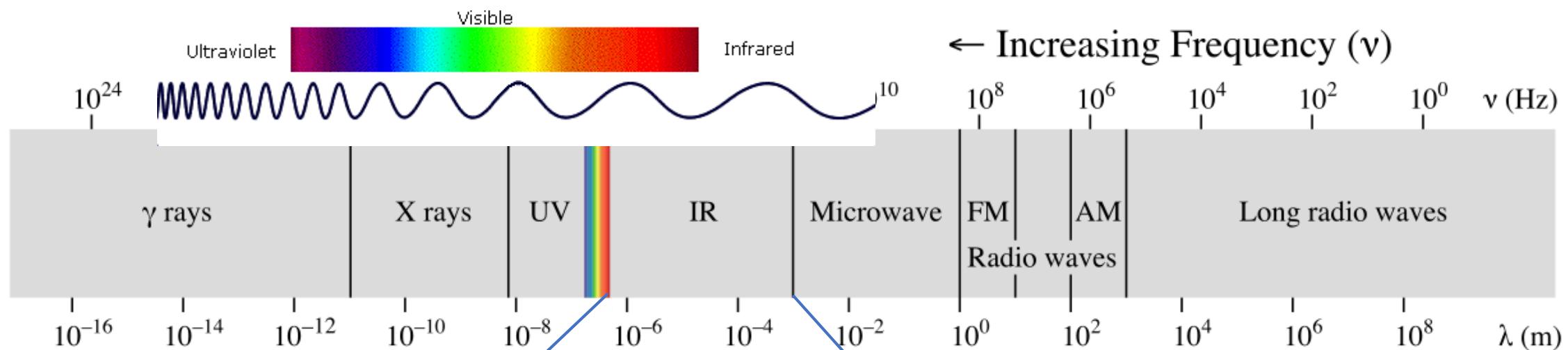
For diatomic molecule behaving as SHO  
Frequency of a vibrational stretching

$$\bar{\vartheta} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{cm}^{-1}$$

$$\mu = \text{Reduced Mass} = \frac{m_1 m_2}{m_1 + m_2}$$

$\bar{\vartheta} \propto \sqrt{k}$ , means stronger bonds absorbs frequency in high range.

$\bar{\vartheta} \propto \sqrt{\frac{1}{\mu}}$ , means heavier atoms absorb frequency in low wave number



Increasing Wavelength ( $\lambda$ ) →

Near IR      Middle IR      Far IR

$\lambda$  ( $\mu\text{m}$ )      0.8      2.5      25      250

$\bar{\nu}$  ( $\text{cm}^{-1}$ )      12500      4000      400      40

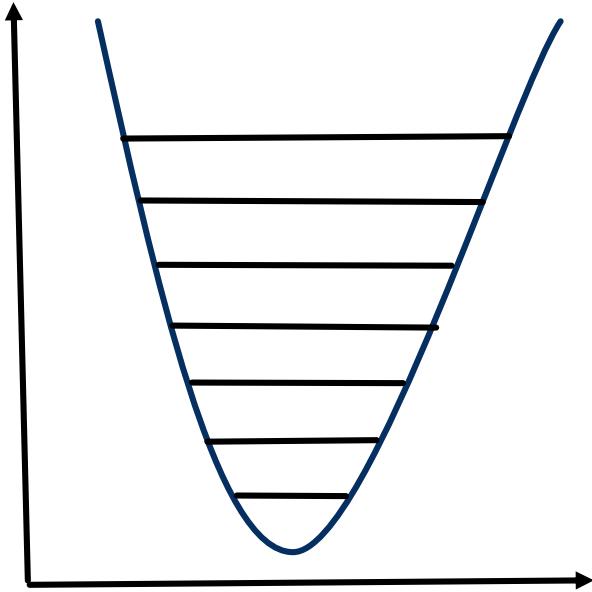
$E = 1-10 \text{ kcal/mol}$

Bond Vibrations (most useful I.R. region)

$$\bar{\vartheta} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

Identify the order of decreasing vibrational frequency for  
C - H and C - D bond

Identify the increasing order of stretching frequencies for  
C ≡ C, C = C and C - C bond

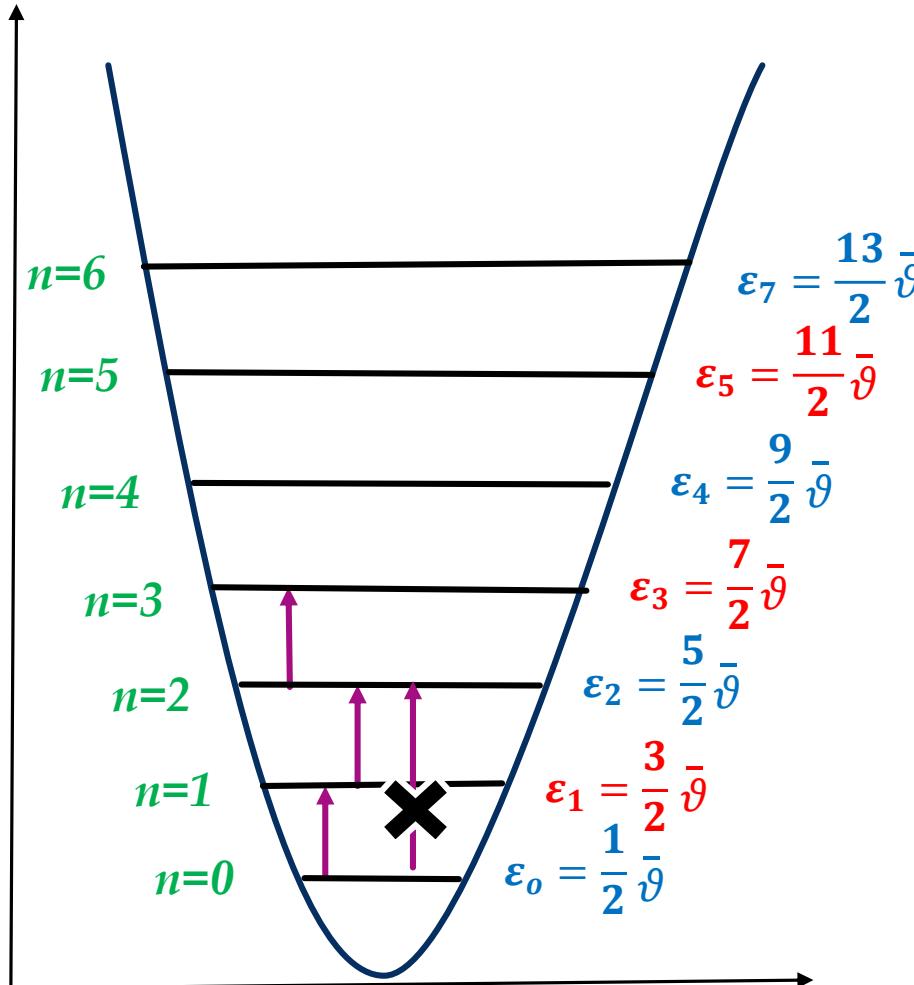


Energy of Vibrational Energy level is expressed as

$$E_n = \left( n + \frac{1}{2} \right) h\vartheta \quad Joules$$

$$\varepsilon_n = \frac{E}{hc} = \left( n + \frac{1}{2} \right) \bar{\vartheta} \quad cm^{-1}$$

Where,  $n$  = vibrational quantum number = 0,1,2,3, ... ....



**Energy levels of SHO are equally spaced**

Why A molecule can never have zero vibrational energy?

The energy of the molecule corresponding to  $n = 0$  level is known as **zero point energy**

$$\varepsilon_n = \left(n + \frac{1}{2}\right) \frac{1}{2} \theta \text{ cm}^{-1}$$

$$n = 0, \quad \varepsilon_0 = \frac{1}{2} \frac{1}{2} \theta \text{ cm}^{-1}$$

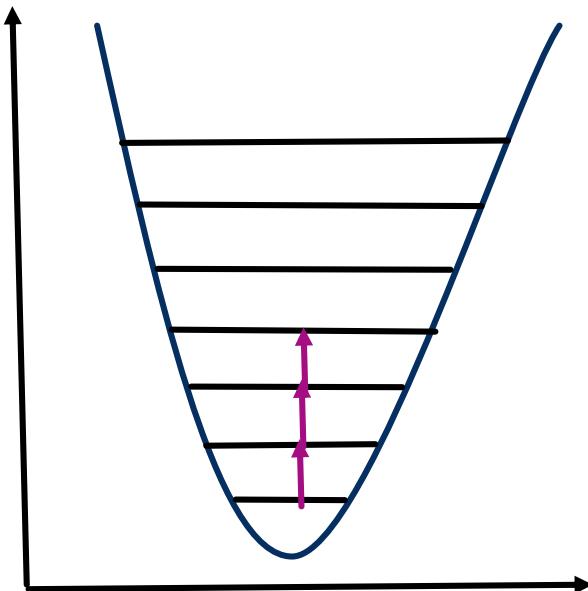
$$n = 1, \quad \varepsilon_1 = \frac{3}{2} \frac{1}{2} \theta \text{ cm}^{-1}$$

$$n = 2, \quad \varepsilon_2 = \frac{5}{2} \frac{1}{2} \theta \text{ cm}^{-1} \text{ and so on}$$

Selection rule for a SHO undergoing vibrational changes

$$\Delta n = \pm 1$$

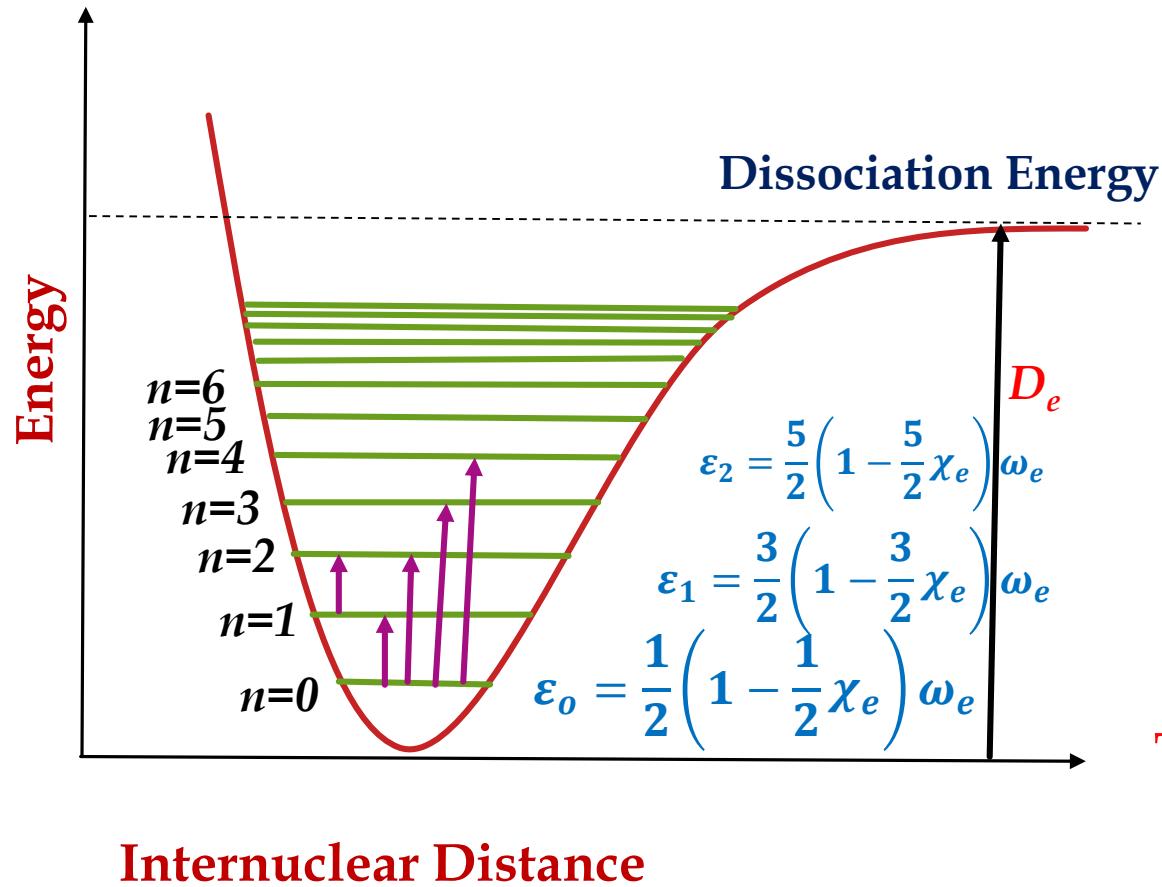
## Energy between two adjacent levels



$$\varepsilon_{n \rightarrow n+1} = \left( n + 1 + \frac{1}{2} \right) \bar{\vartheta} - \left( n + \frac{1}{2} \right) \bar{\vartheta} \text{ cm}^{-1} = \bar{\vartheta} \text{ cm}^{-1}$$

# Anharmonic Oscillator (AHO)

Real molecules do not obey laws of SHO for large amplitude of vibrations



$$\varepsilon_n = \left( n + \frac{1}{2} \right) \omega_e - \left( n + \frac{1}{2} \right)^2 \omega_e \chi_e \quad \text{cm}^{-1}$$

Where,  $n = 0, 1, 2, \dots$

$\chi_e$  = Anharmonicity Constant

$\omega_e$  = Equilibrium Oscillation Frequency in  $\text{cm}^{-1}$

The selection rules for anharmonic oscillator

$$\Delta n = \pm 1, \pm 2, \dots \text{etc}$$

## Probable transitions

$n = 0 \rightarrow n = 1, \Delta n = 1$ : ***Intense Absorption (Fundamental Absorption)***

$$\Delta\epsilon = \omega_e (1 - 2\chi_e) \text{ cm}^{-1}$$

$n = 0 \rightarrow n = 2, \Delta n = 2$ : ***With Small Intensity (First overtone)***

$$\Delta\epsilon = 2\omega_e (1 - 3\chi_e) \text{ cm}^{-1}$$

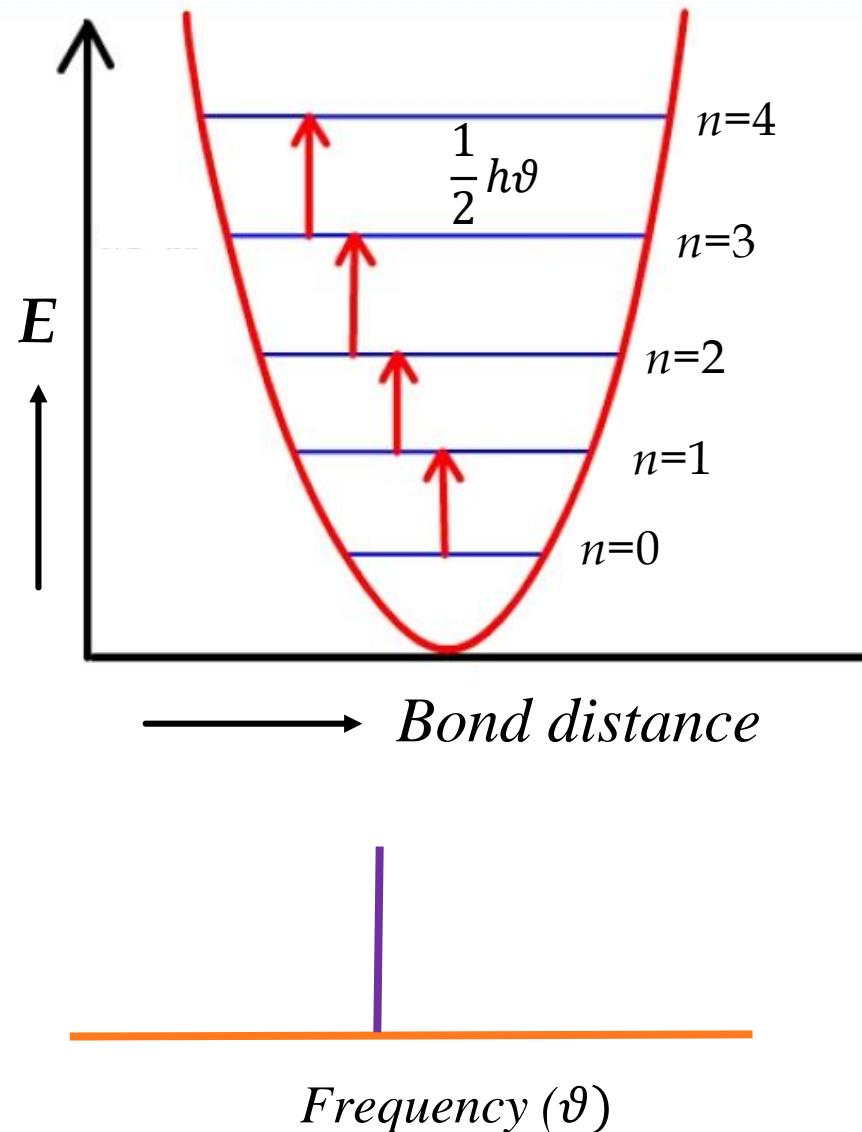
$n = 0 \rightarrow n = 3, \Delta n = 3$ : ***negligible intensity (Second overtone)***

$$\Delta\epsilon = 3\omega_e (1 - 4\chi_e) \text{ cm}^{-1}$$

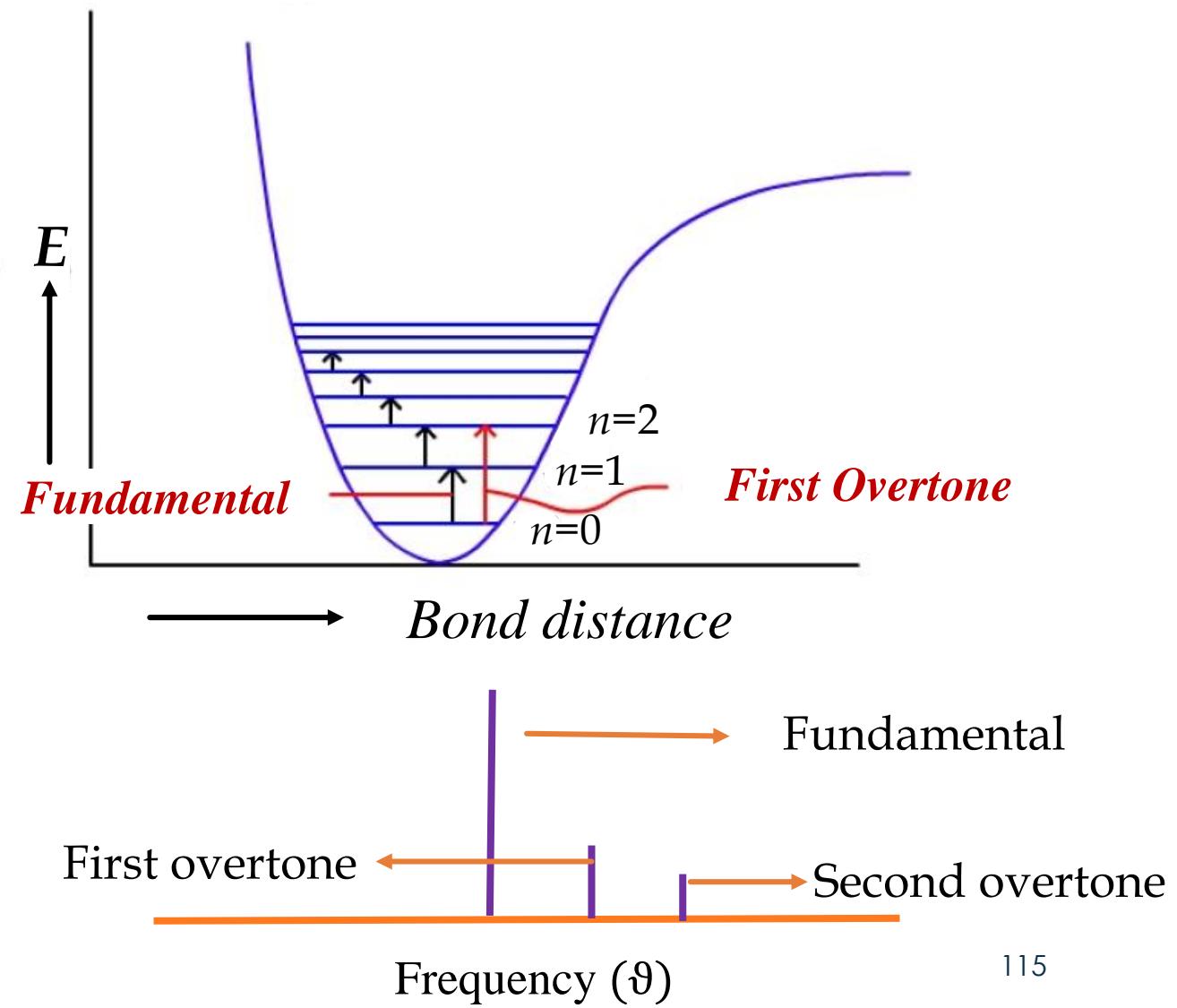
Q. The fundamental and first overtone transitions of NO are centred at  $1876\text{ cm}^{-1}$  and  $3724\text{ cm}^{-1}$  respectively. Evaluate the equilibrium vibrational frequency, the anharmonicity constant, the zero point energy.

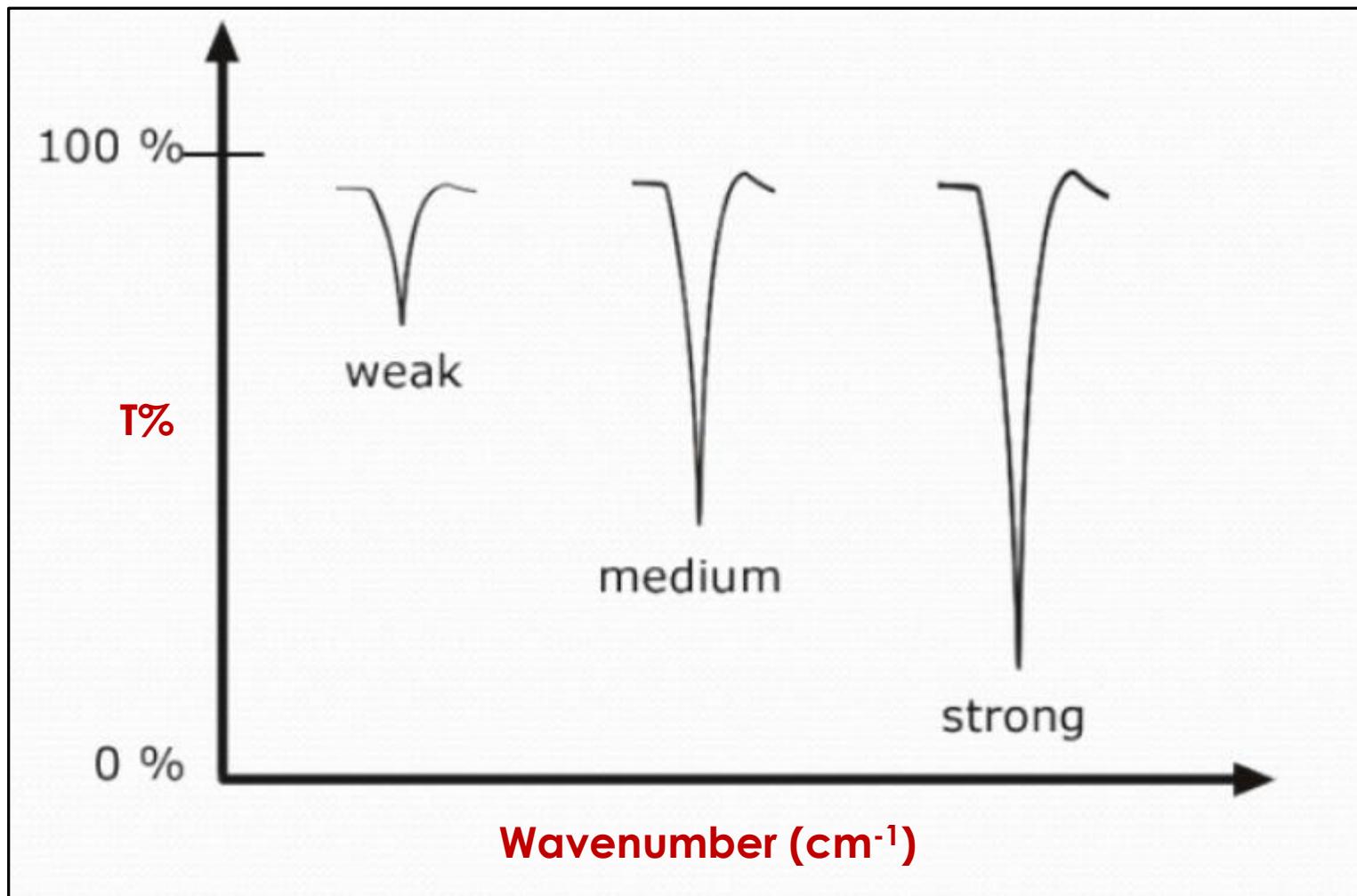
Ans:  $\sim \omega_e = 1903\text{ cm}^{-1}$ ,  $\chi_e = 7.3 \times 10^{-3}\text{ cm}^{-1}$ , zero point energy =  $949\text{ cm}^{-1}$

## Harmonic oscillator



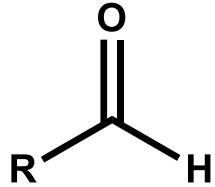
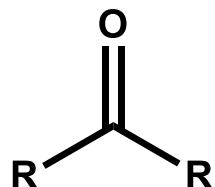
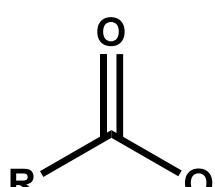
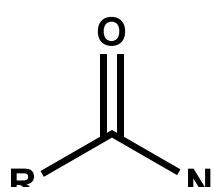
## Anharmonic oscillator





# Group Frequencies

<u>Bond</u>	<u>Class of compound</u>	<u>Range (cm<sup>-1</sup>)</u>
C-C	Alkane	1200 - 700
C=C	Alkene	1680 - 1620
C ≡ C	Alkyne	2130 - 2150
C-H	Alkane	<b>2965 - 2850</b>

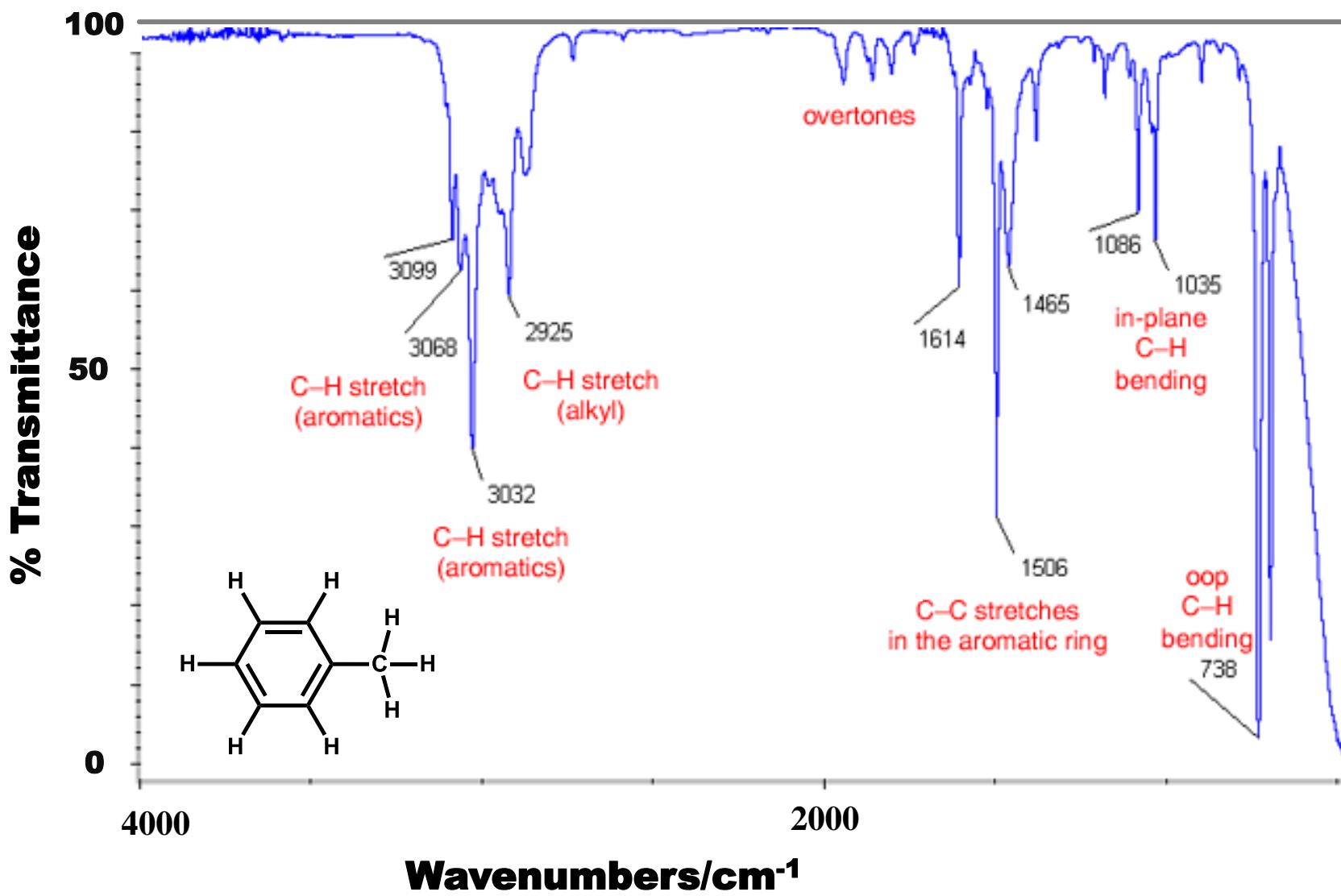
<u>Bond</u>	<u>Class of compound</u>	<u>Range (cm<sup>-1</sup>)</u>
	Aldehyde	1740 – 1720
	Ketone	1725 - 1705
	Carboxylic acid	1725 - 1700
	Amide	1700 - 1630

<b>Bond</b>	<b><u>Class of compound</u></b>	<b>Range (cm<sup>-1</sup>)</b>
O-H	Alcohol (monomer)	<b>3650 - 3590</b>
O-H...O	Alcohol (H-bonded)	<b>3420 - 3200</b>
	Carboxylic acid (H-bonded)	<b>3300 - 3250</b>
C-O	Alcohol, ester, acid, ether	<b>1300 - 1000</b>

<u>Bond</u>	<u>Class of compound</u>	<u>Range / cm<sup>-1</sup></u>
N-H	Amine, Amide	3500 (approx)
C≡N	Nitrile	2260 - 2240

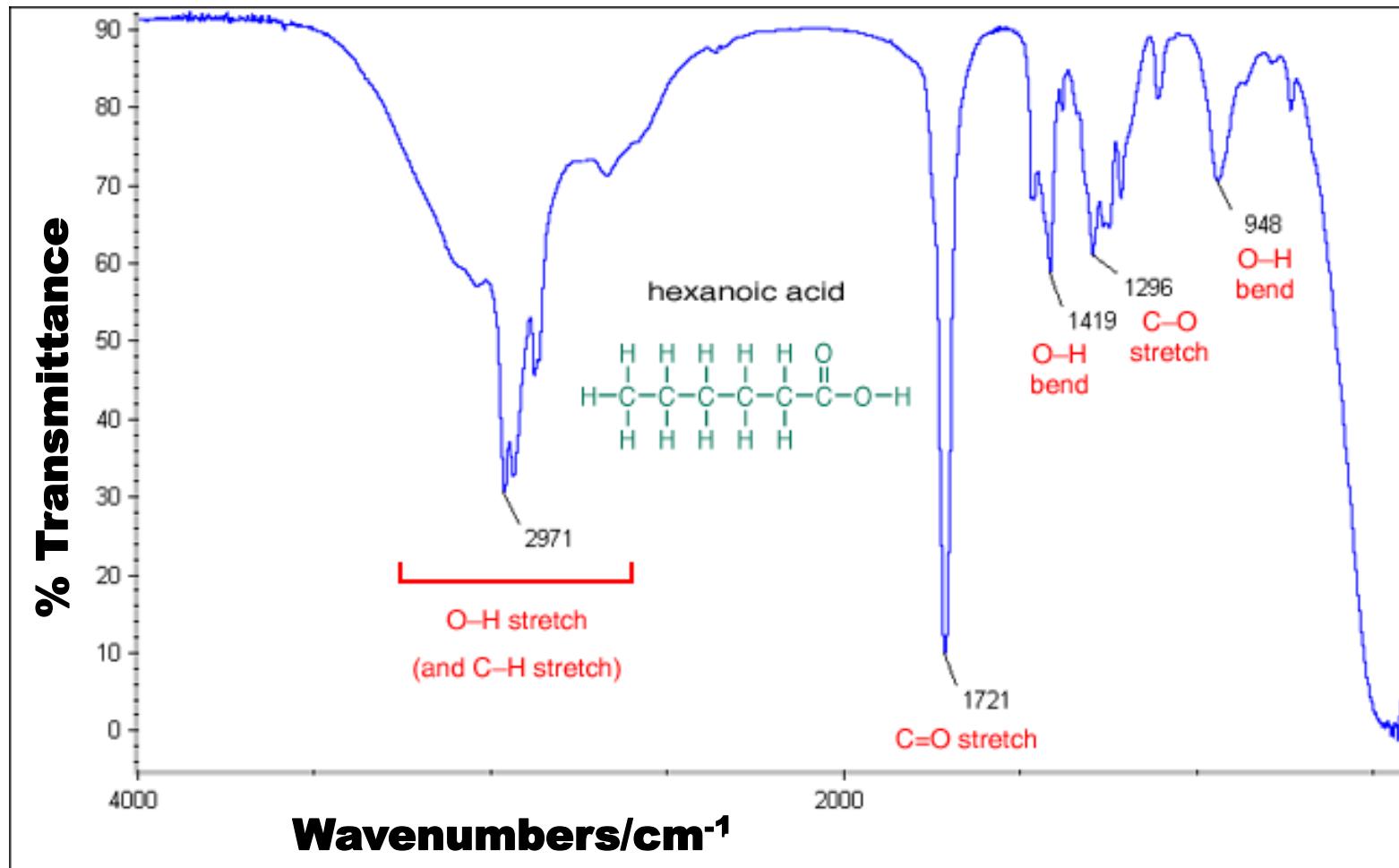
<u>Bond</u>	<u>Class of compound</u>	<u>Range / cm<sup>-1</sup></u>
C-X	Chloride	800 - 600
	Bromide	600 - 500
	Iodide	500 (approx)

# IR Spectra of Toluene



Stretching:	
C-H(Aromatic)	3099 $\text{cm}^{-1}$
C-H(Aromatic)	3032 $\text{cm}^{-1}$
C-H(Alkyl)	2925 $\text{cm}^{-1}$
C=C	1506 $\text{cm}^{-1}$

# Carboxylic Acid



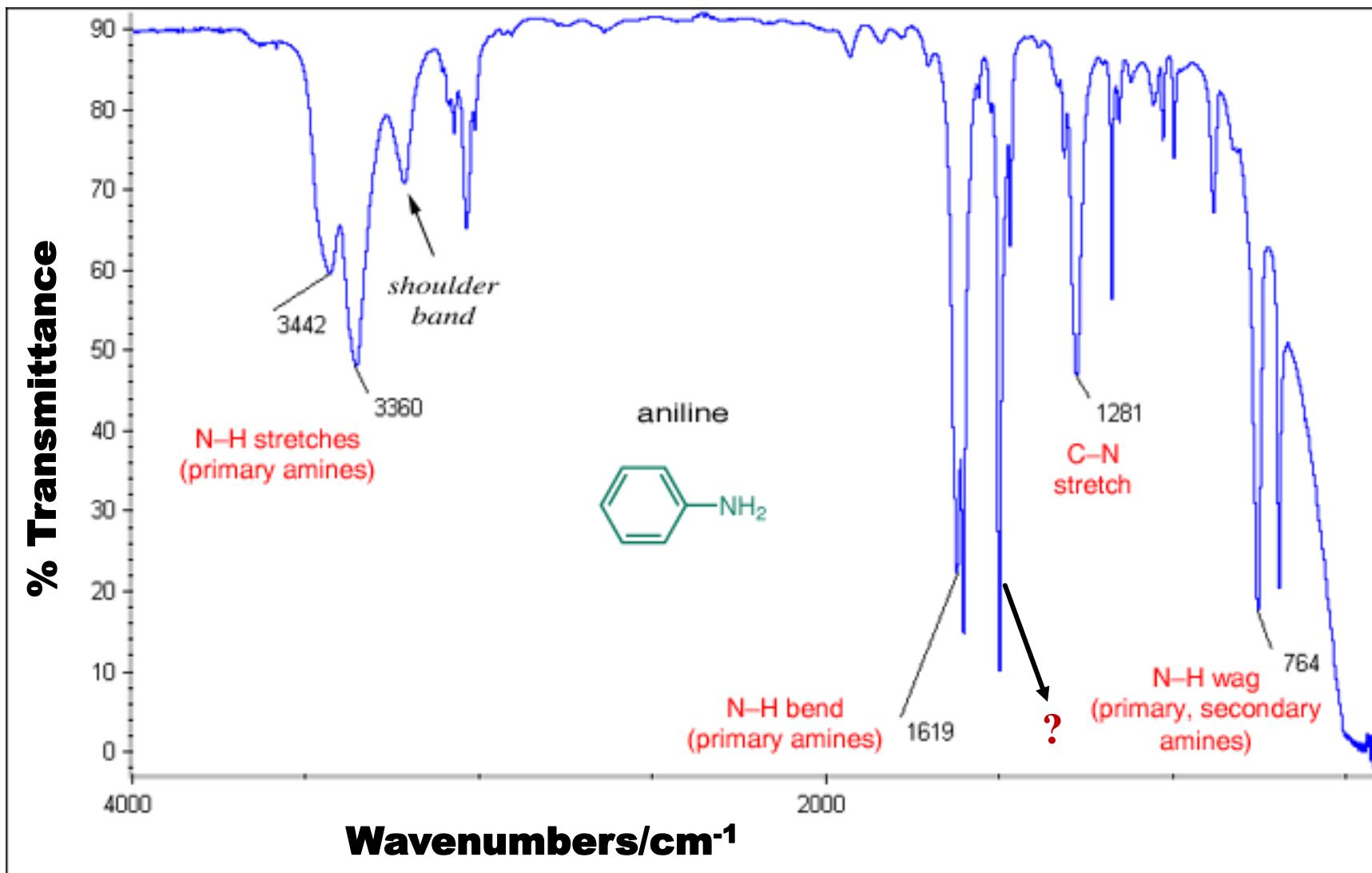
## Stretching:

O-H (Stretch)  $3300\text{-}2500\text{ }cm^{-1}$

C=O (Stretch)  $1760\text{-}1690\text{ }cm^{-1}$

C-O (Stretch)  $1320\text{-}1210\text{ }cm^{-1}$

# Aniline



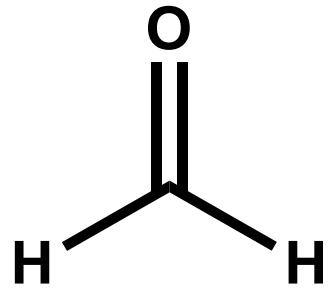
**Stretching:**  
N–H 3400–3250 cm<sup>-1</sup>

# IR frequency of C=O bond

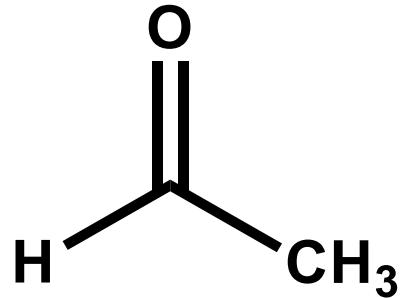
## Factors can influence

### Inductive Effect

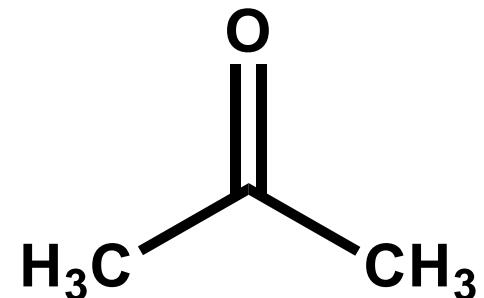
Addition of +I groups result in weakening of CO bond and the  $\vartheta_{co}$  value decreases



$1750 \text{ cm}^{-1}$



$1745 \text{ cm}^{-1}$

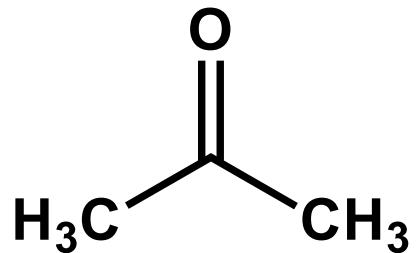


$1715 \text{ cm}^{-1}$

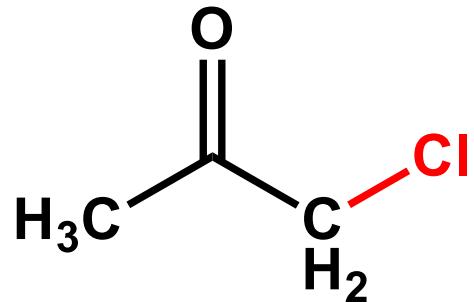
**Reason:** decrease in bond order and hence the bond strength

## Introduction of groups having –I effect

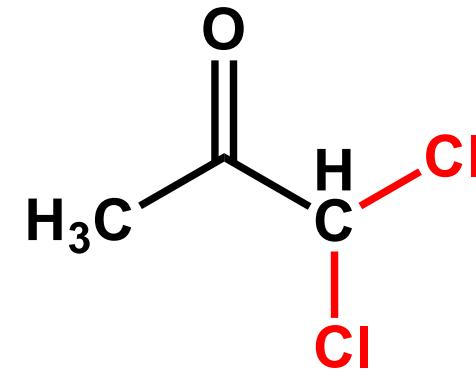
results in increase in bond order of CO and hence increase the absorption frequency ( $\vartheta$  values).



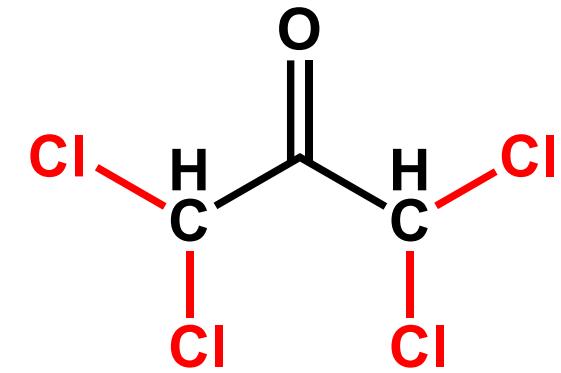
1715 cm<sup>-1</sup>



1725 cm<sup>-1</sup>



1740 cm<sup>-1</sup>

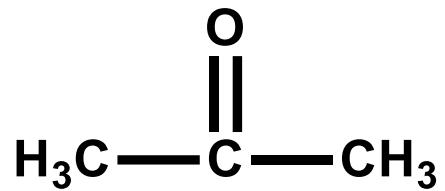


1750 cm<sup>-1</sup>

# Mesomeric Effect

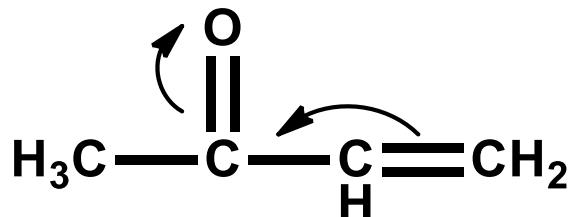
Conjugation lowers the  $\vartheta_{co}$  value by weakening the bond.

No Conjugation



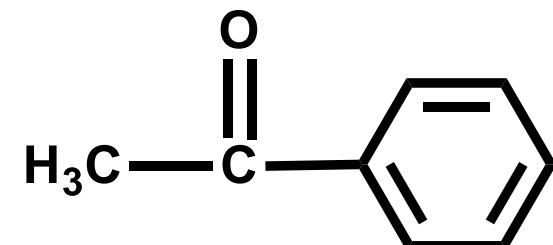
$1715 \text{ cm}^{-1}$

Conjugation



$1706 \text{ cm}^{-1}$

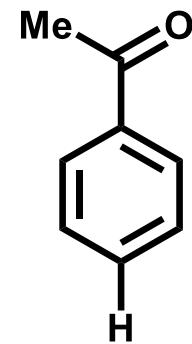
Extension of Conjugation



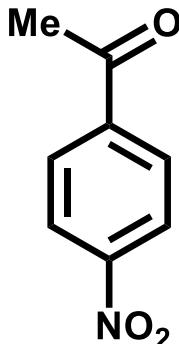
$1693 \text{ cm}^{-1}$

Q. In the IR spectra, Benzamide and Phenyl Acetate show  $\vartheta_{co}$  stretching frequency at  $1663\text{ cm}^{-1}$  and  $1730\text{ cm}^{-1}$  respectively. Justify?

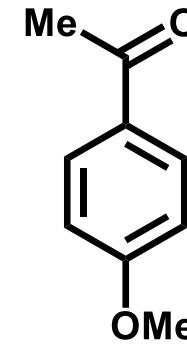
Q. Arrange the compounds ‘a’ ‘b’ and ‘c’ according to their  $\vartheta_{co}$  absorption frequency:  $1677\text{ cm}^{-1}$ ,  $1700\text{ cm}^{-1}$ ,  $1770\text{ cm}^{-1}$ .



(a)



(b)



(c)

# Hydrogen Bonding

H-bonding brings downward frequency shifts

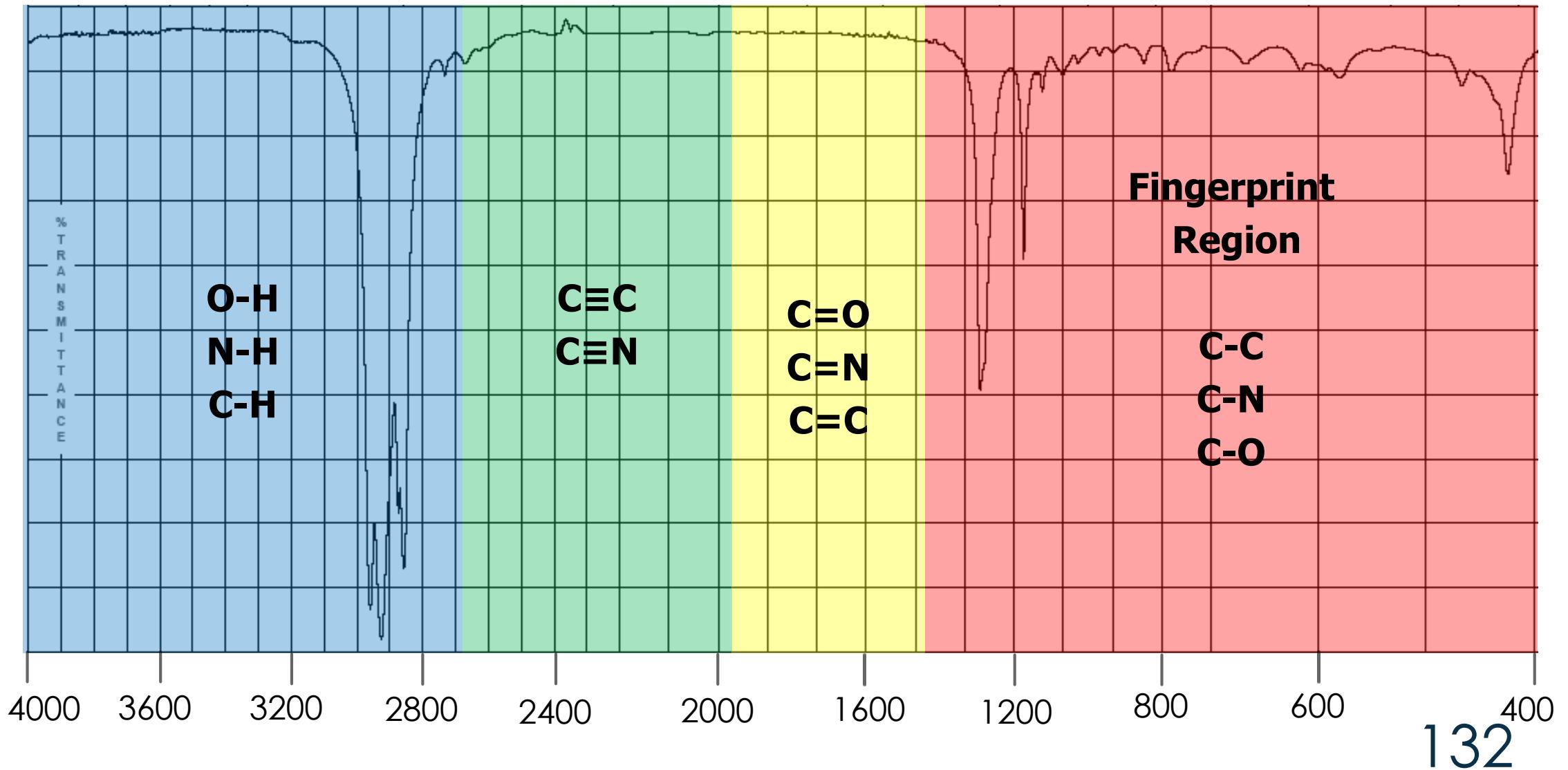
Stronger the H-bonding, greater is the absorption shift towards lower frequency

Inter-molecular H-bonding gives rise to broad peak

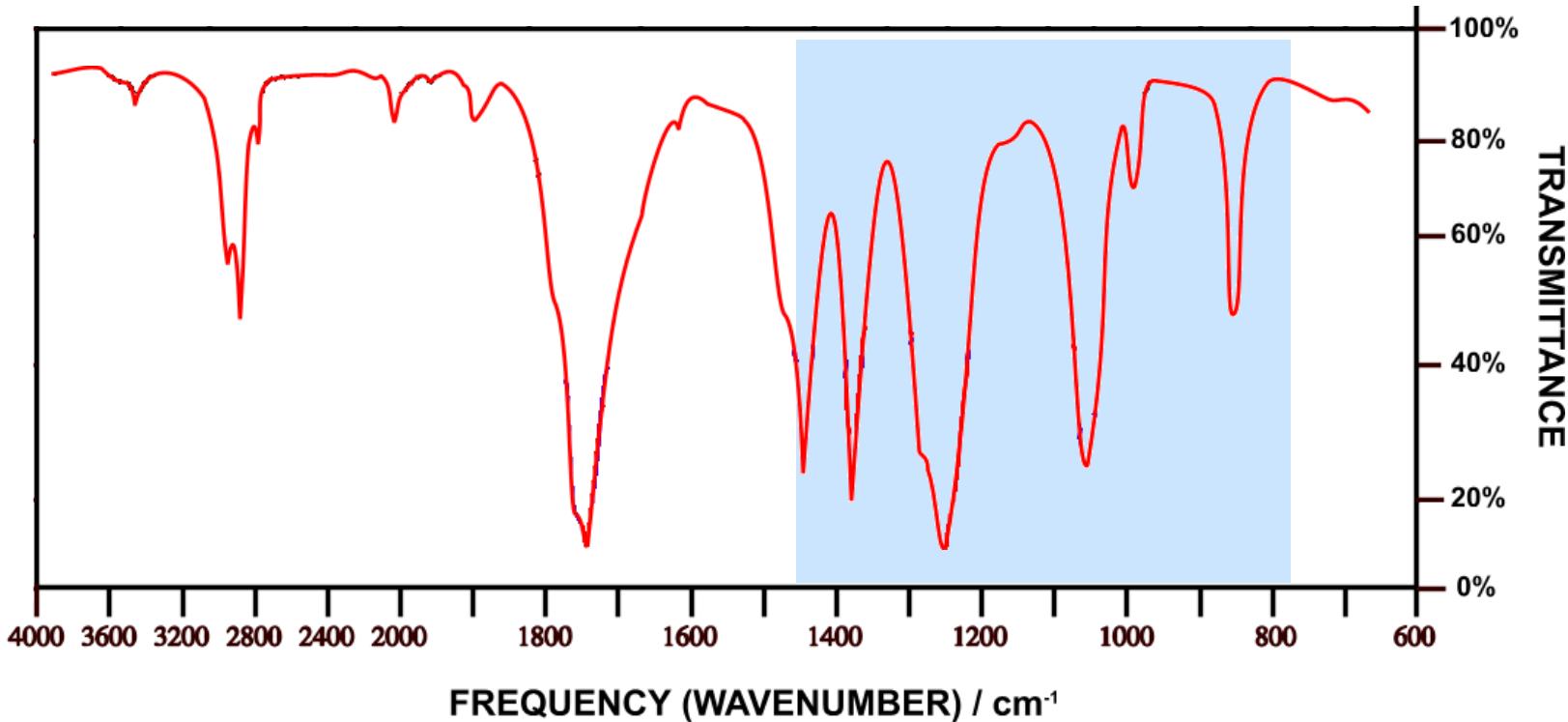
Intra-molecular H-bonding gives rise to sharp peak

Q. In dilute solution, Amines show stretching frequency at  $3650\text{ cm}^{-1}$ , while a broad band is appeared at  $3300\text{ cm}^{-1}$  in condense phase spectra. Explain why?

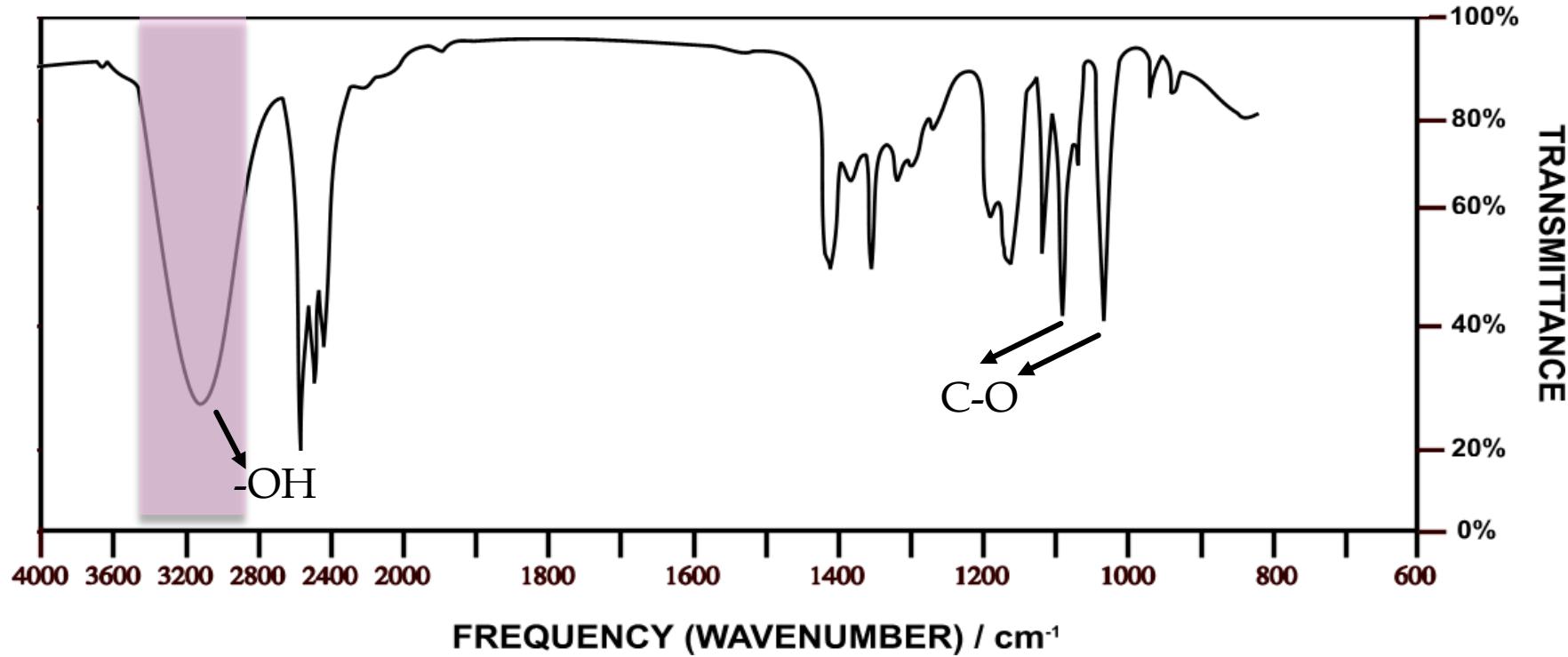
Q. Explain why, the spectrum of glycol in  $\text{CCl}_4$  shows two peak at  $3644$  and  $3612\text{ cm}^{-1}$ .



# Fingerprint region

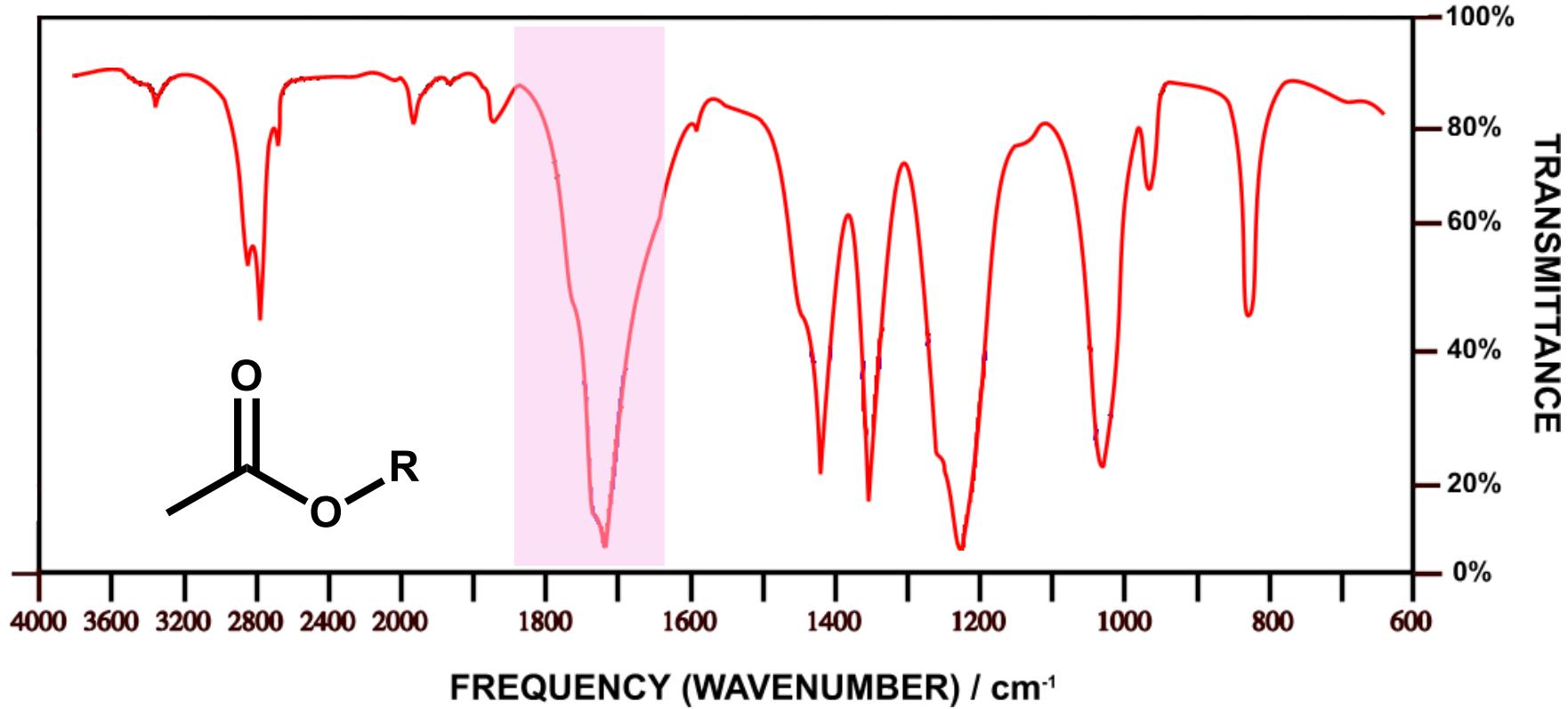


- Range ~ 1400  $\text{cm}^{-1}$  to 1000  $\text{cm}^{-1}$  range
- Rich in Bending Vibration of C-C, C-H, C-N, C-O etc.
- This is referred to as the “**fingerprint**” region

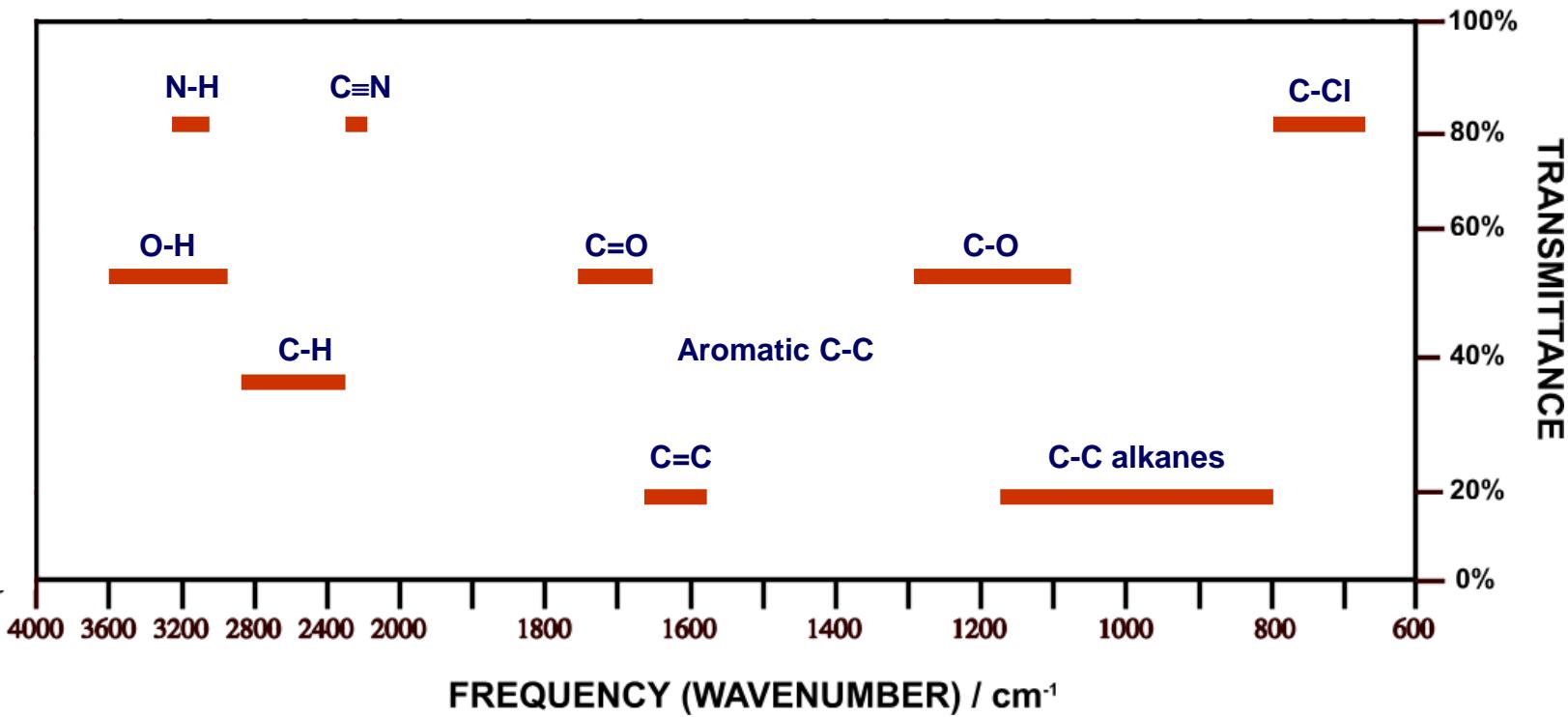


$\vartheta_{OH}$  for O-H stretching  $\sim 3230 \text{ cm}^{-1}$  and  $3550 \text{ cm}^{-1}$  (Broad)

Two peaks for C-O stretching at  $\sim 1000 \text{ cm}^{-1}$  and  $1300 \text{ cm}^{-1}$  in the fingerprint region.



Esters show a strong absorption between **1750 - 1730  $\text{cm}^{-1}$**  due to C=O bond stretching.





# Chromatography

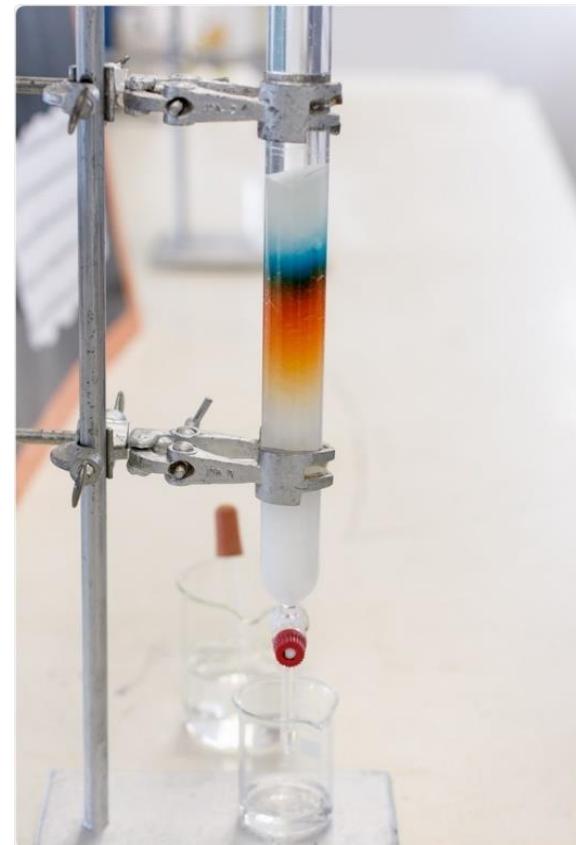
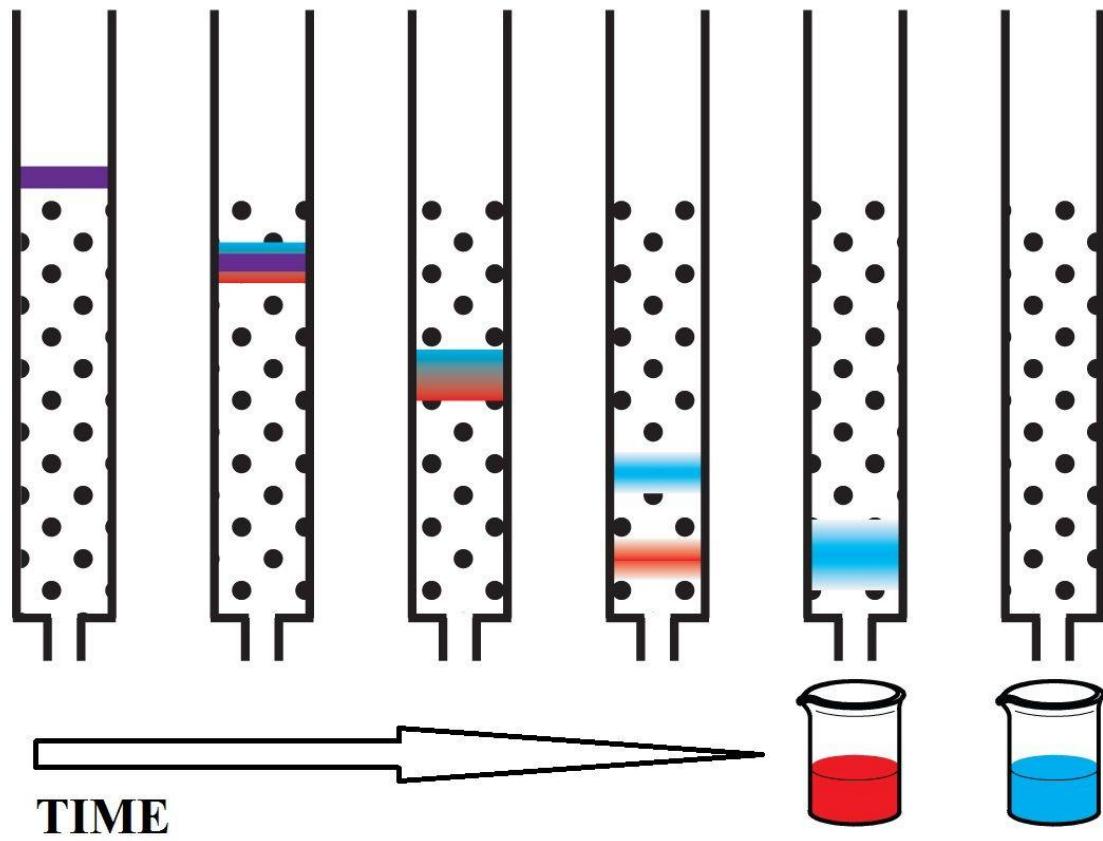
Retention and Separation factors, Theoretical plates, Instrumentation and uses  
of Gas Chromatography and High Performance Liquid Chromatography

**References:** Fundamentals of Analytical Chemistry, 9<sup>th</sup> Edition, Douglas A. Skoog, Donald M. West, F. James Holler, Stanley R. Crouch



Coffee filter art

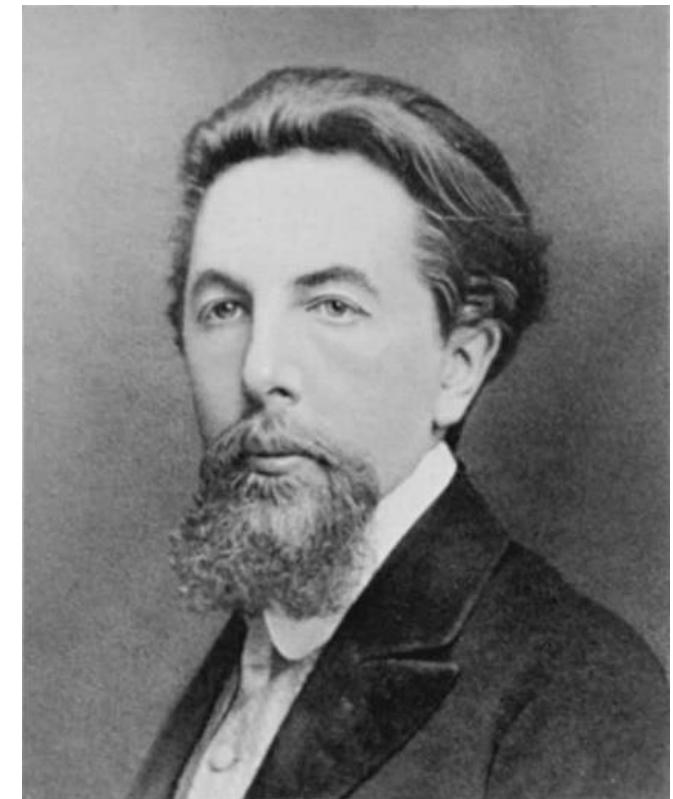


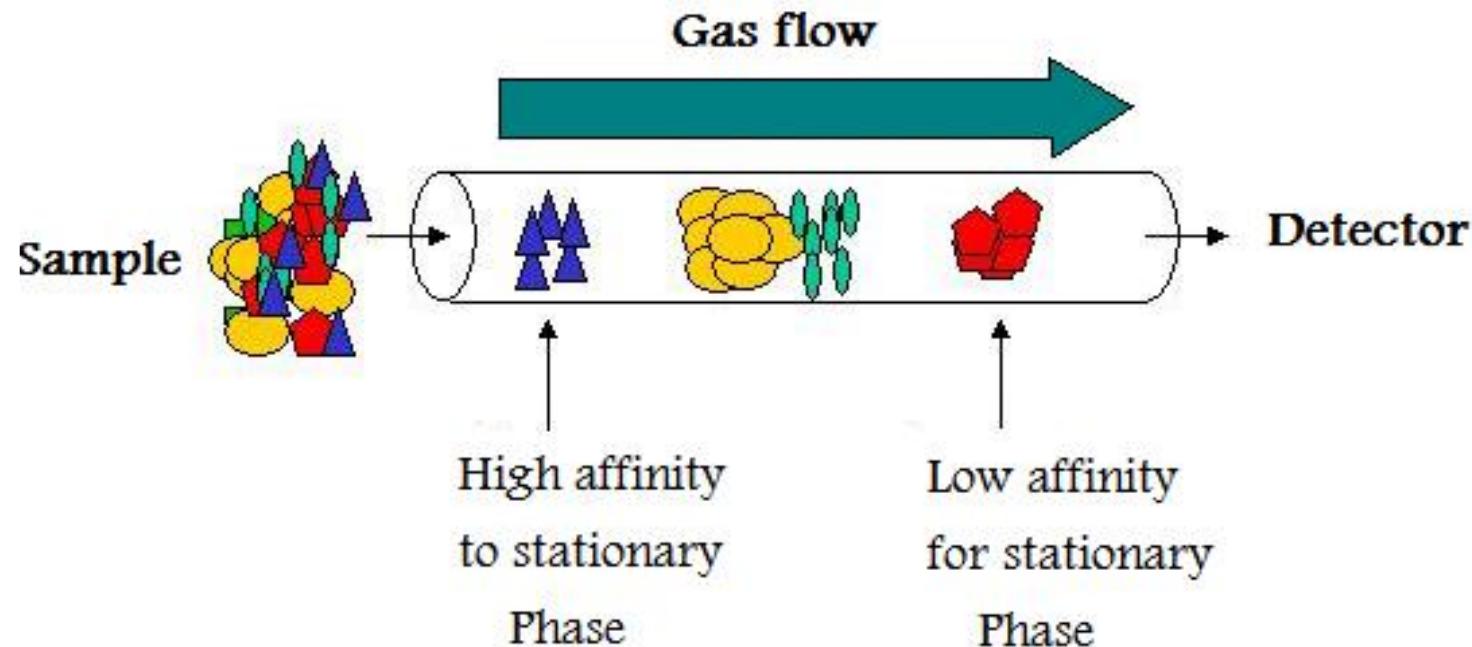


# History of Chromatography

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- Chromatography (color writing) was first employed by **Mikhail Tswett in 1903**
- He worked on the separation of plant pigments such as **chlorophyll, carotenes, and xanthophylls** which are have different colours.





It is a physical separation method in which the components of a mixture are separated by differences in their distribution between two phases

**Stationary phase**

**Mobile phase**

# Chromatography: Application

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**Purify** – Separate components in order to isolate one of interest for further study

**Identify** – Determine the identity of a mixture or components based on known components

**Quantify** – Determine the amount of the a mixture and/or the components present in the sample

**Analyze** – Examine a mixture, its components, and their relations to one another



- ❖ The substances must interact with the stationary phase to be retained and separated by it.
- ❖ Components that strongly retained by the stationary phase move slowly by mobile phase.
- ❖ Components that weakly held by the stationary phase move fast with the mobile phase.

# Terminologies

## Analyte:

The substance to be separated during chromatography



## Chromatograph:

Equipment for performing chromatography

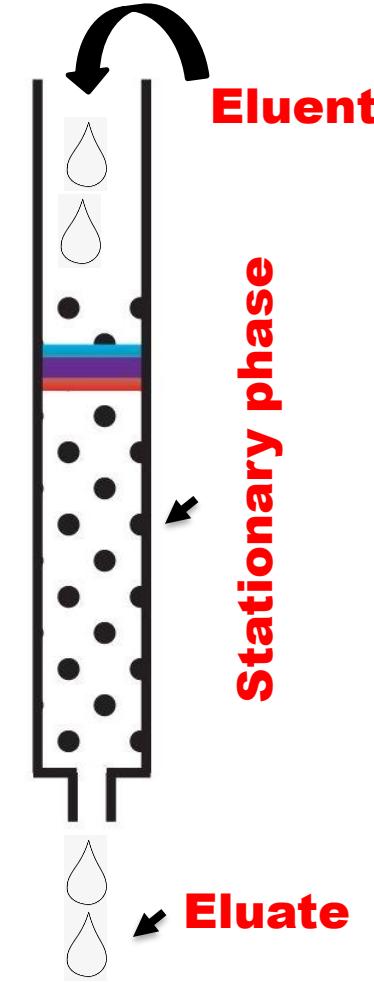


## Chromatogram:

The visual output of the chromatograph

## Retention time ( $R_T$ ):

Is a measure of the time taken for a solute to pass through a chromatography column  
It is calculated as the time from injection to detection



### **Flow rate ( $F_C$ ):**

Volume of mobile phase passed/minute (mL/min).

### **Eluent:**

Is the solvent that carries the analyte.

### **Eluate:**

Is the mobile phase leaving the column.

### **Elution/Development:**

The process of passing the mobile phase through the column.

# **Stationary Phase**

An immobilized phase in chromatography system through which the materials are to be separated

e.g. Silica, Alumina.

## **Characteristics:**

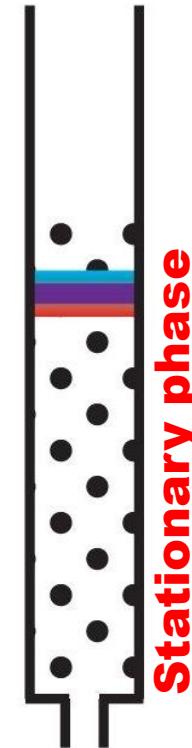
Spherical in shape & uniform in size

Chemically inert and high mechanical stability

Separating wide variety of compounds

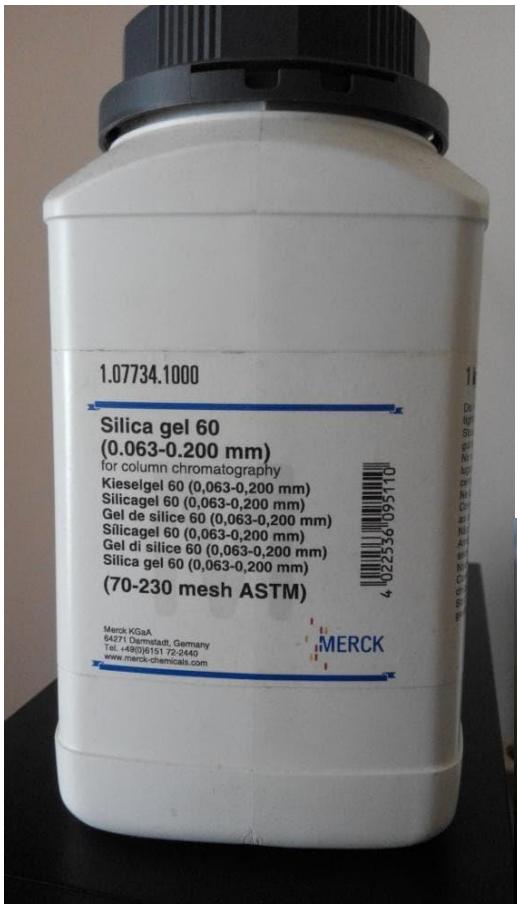
Easily available & inexpensive

Particle size is in the range 50-200  $\mu\text{m}$

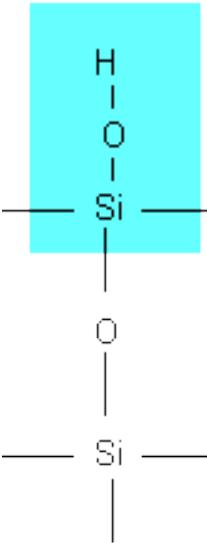


# Stationary Phase

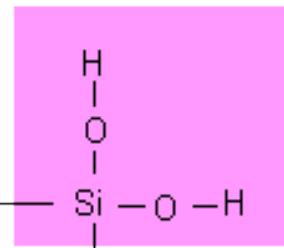
## Silica Gel



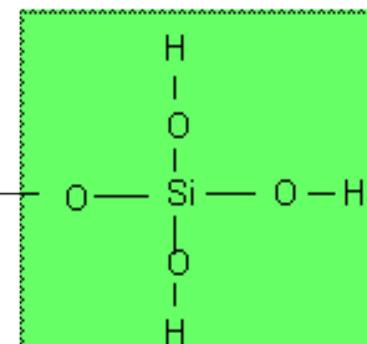
Single  
Silanol  
Group



Two Silanol  
Groups  
(Geminal  
Groups)



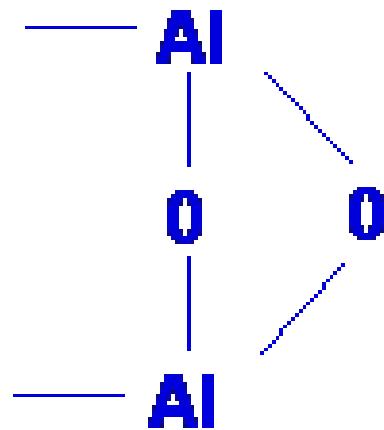
Three  
Silanol  
Groups



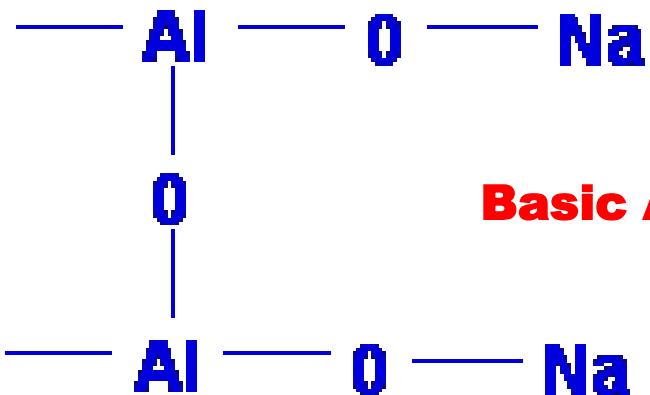
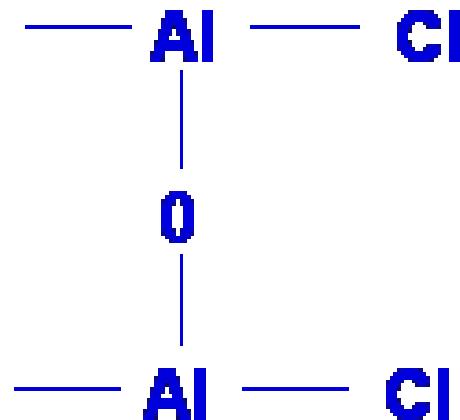
# Stationary Phase



**Nutral Alumina**



**Acidic Alumina**



**Basic Alumina**

**Neutral alumina** - Useful for separation of aldehydes, ketones, quinones, esters and lactones *etc.*

**Acidic alumina** - Useful for separation of acid pigments and strong acids.

**Basic alumina** - Useful for basic and neutral compounds that are stable to alkali, as well as for amines, steroids, alkaloids and natural pigments.

# Mobile Phase

Gas or liquid that carries the mixture of components through the stationary phase

The function of a mobile phase:

1. To introduce the mixture into the column – **as solvent**.
2. To remove or elute pure components out of the column – **as eluent**.
3. As color **developing agent**.

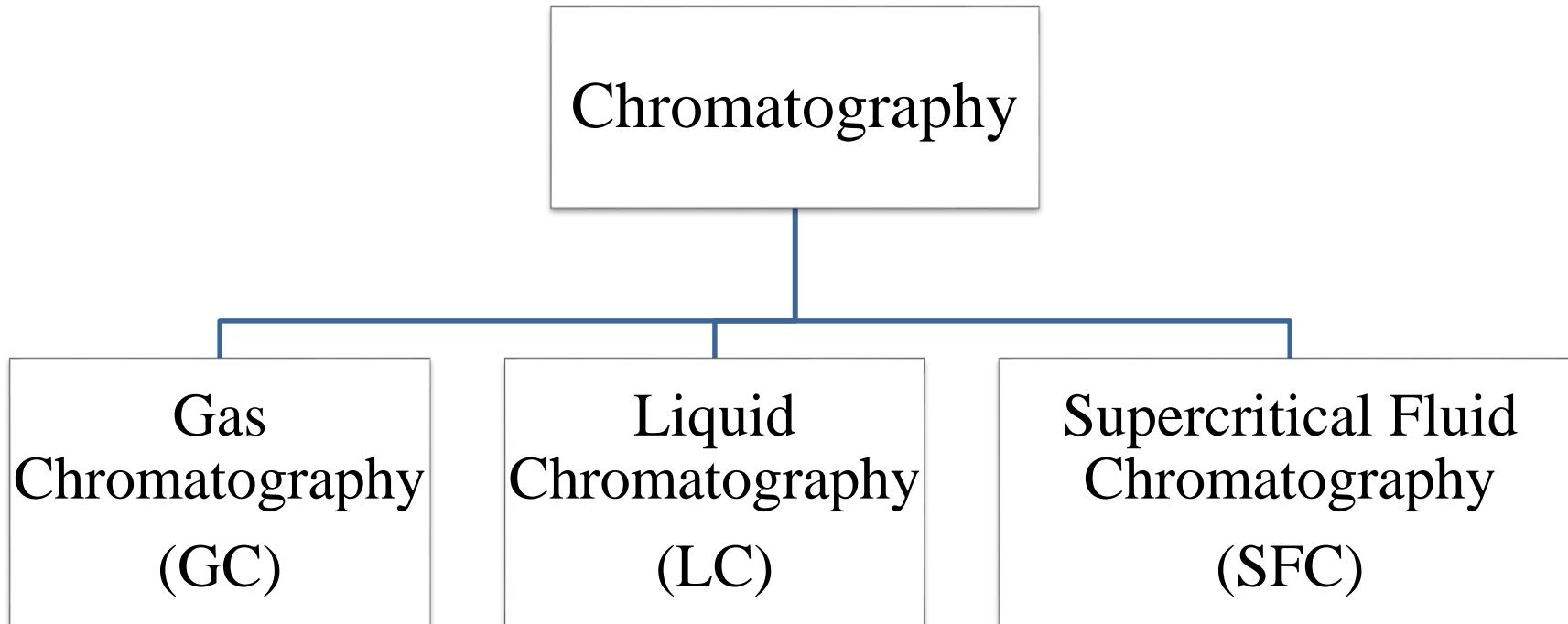
## **Selection of solvent as mobile phase**

- ❖ The solvents should have sufficiently low boiling points to permit ready recovery of eluted material
- ❖ However, polarity as seen the most important factor in adsorption chromatography
- ❖ It can be used in either pure form or as mixture of solvents

### **Polarity order of various solvents:**

Pure water > Methanol > Ethanol > Propanol > Acetone > Ether > Chloroform > Dichloromethane > Toluene > Hexane > Pentane.

# Classification: based on mobile and stationary phases



## **Gas Chromatography (GC)**

### **1. Gas-liquid Chromatography :**

**Stationary Phase:** Liquid bonded or adsorbed on solid surface

**Type of equilibrium:** Partition between gas and liquid

### **2. Gas-solid Chromatography :**

**Stationary Phase:** Solid surface

**Type of equilibrium:** Adsorption

## **Liquid Chromatography (LC)**

### **1. Liquid-liquid or Partition Chromatography :**

**Stationary Phase:** Liquid bonded or adsorbed on solid surface

**Type of equilibrium:** Partition between immiscible liquid

### **2. Liquid-solid or Adsorption Chromatography :**

**Stationary Phase:** Solid surface

**Type of equilibrium:** Adsorption

### **3. Ion Exchange Chromatography :**

**Stationary Phase:** Ion exchange resin

**Type of equilibrium:** Ion exchange

**4. Size Exclusion Chromatography :**

**Stationary Phase:** Liquid in interstices of a polymeric solid.

**Type of equilibrium:** Partition or sieving

**5. Affinity Chromatography:**

**Stationary Phase:**

Solid surface tagged with some specific group

**Type of equilibrium:**

Partition between surface liquid and mobile liquid

## **Supercritical Fluid Chromatography:**

**Mobile Phase:** Supercritical Fluid

**Stationary Phase:** Solid surface

**Type of equilibrium:**

Partition between supercritical fluid and solid surface

# **Adsorption chromatography**

**Stationary phase:** The most common are Silica-gel and Alumina

**Stationary phase interacted with solute molecules  
due to OH groups present on their surface**

**More polar molecules are adsorbed more strongly  
Hence, elute more slowly**

**Order of adsorption of polar groups on polar support :**

$-\text{C}=\text{C}- < -\text{OCH}_3 < -\text{COOR} < -\text{C}=\text{O} < -\text{CHO} < -\text{NH}_2 < -\text{OH} < -\text{COOH}$   
Olefins < Ethers < Esters < Aldehydes < Amines < Phenols < Acids

# Partition Chromatography

- ❖ **Stationary phase:** In this type, the packing consists of a theoretically inert support material coated with a film of the liquid stationary phase
- ❖ **The division** into adsorption and partition is only of theoretical significance as in partition chromatography the adsorption effects of the support can also be felt
- ❖ **Partition coefficient / Distribution Constant (K):** The ratio of the concentrations of a solute in two immiscible or slightly miscible liquids

$$K = C_S/C_M$$

Where,  $C_S$  = Concentration of solute in stationary phase  
 $C_M$  = Concentrations of solute in mobile phase

## Distribution constant : partition chromatography

$$K = C_S/C_M$$

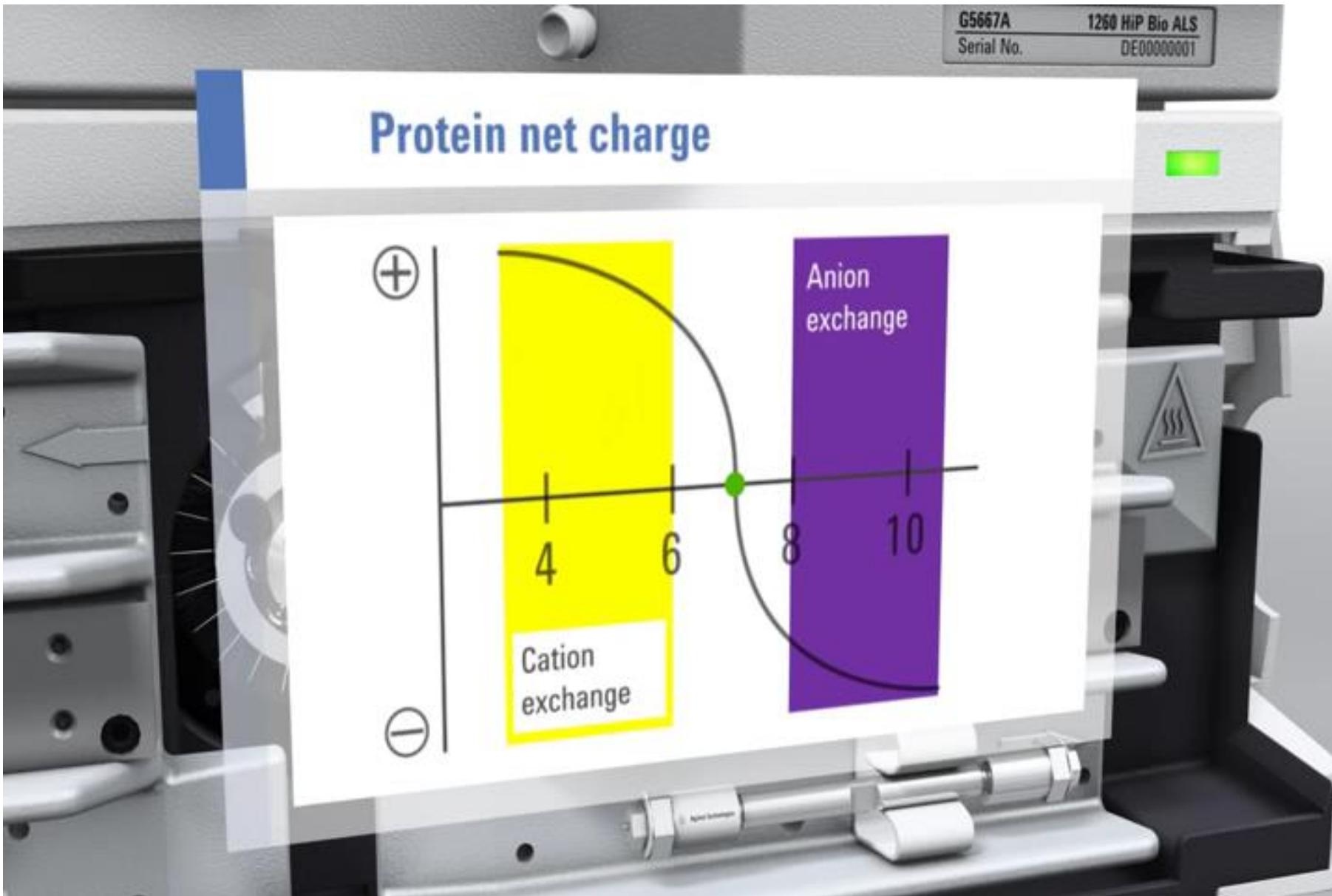
$$C_S = n_S/V_S$$

$$C_M = n_M/V_M$$

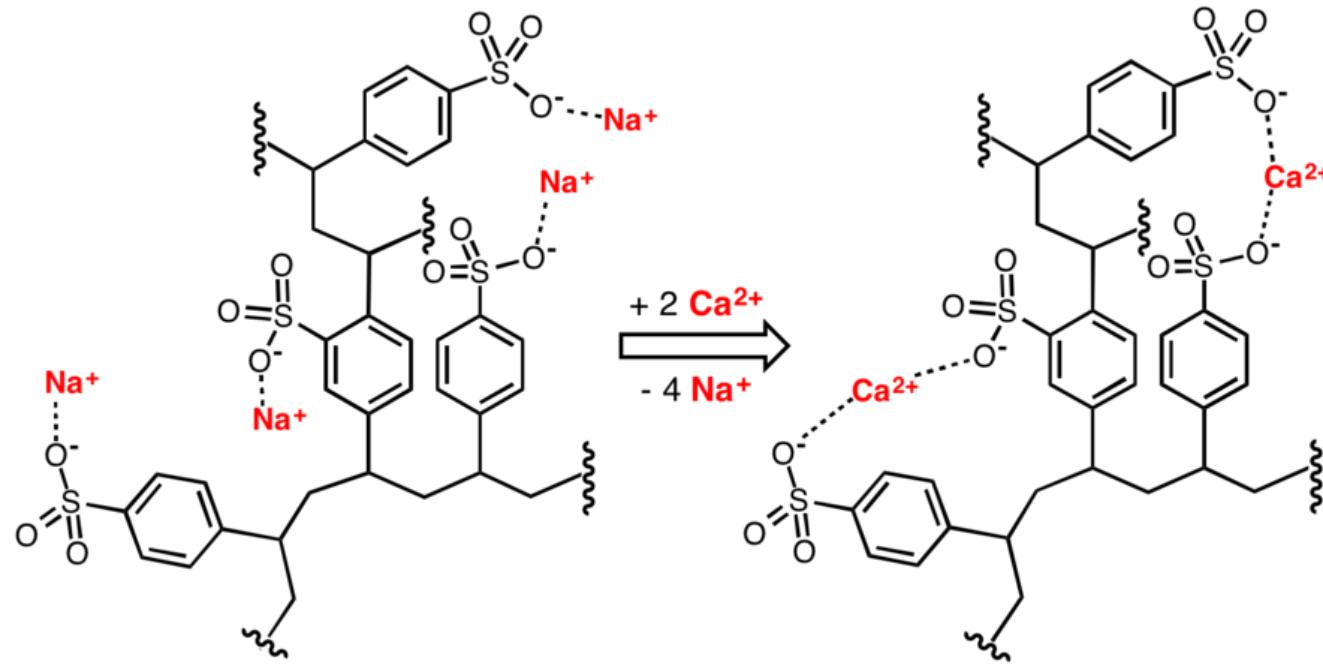
Therefore,  $K = (n_S/V_S)/(n_M/V_M)$

$$= (n_S/n_M) \times (V_M/V_S)$$

# Ion-exchange Chromatography



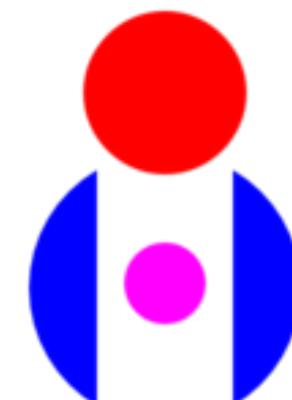
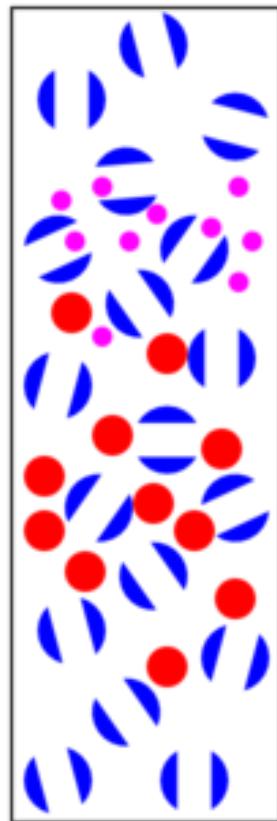
# Ion-exchange Chromatography



The water softening process involving replacement of calcium ions in water with sodium ions by a cation-exchange resin.

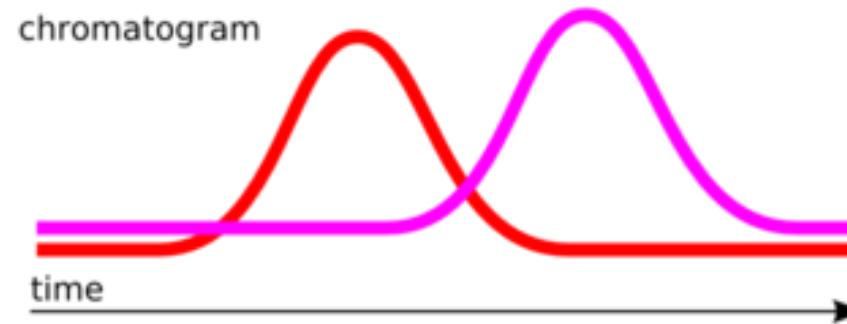
# Size exclusion Chromatography

Useful for macromolecules, proteins and polymers separation



Large particles cannot enter into the gel and excluded  
They have less volume to traverse and elute sooner

Small particles can enter into the gel and have less  
volume to traverse and elute latter

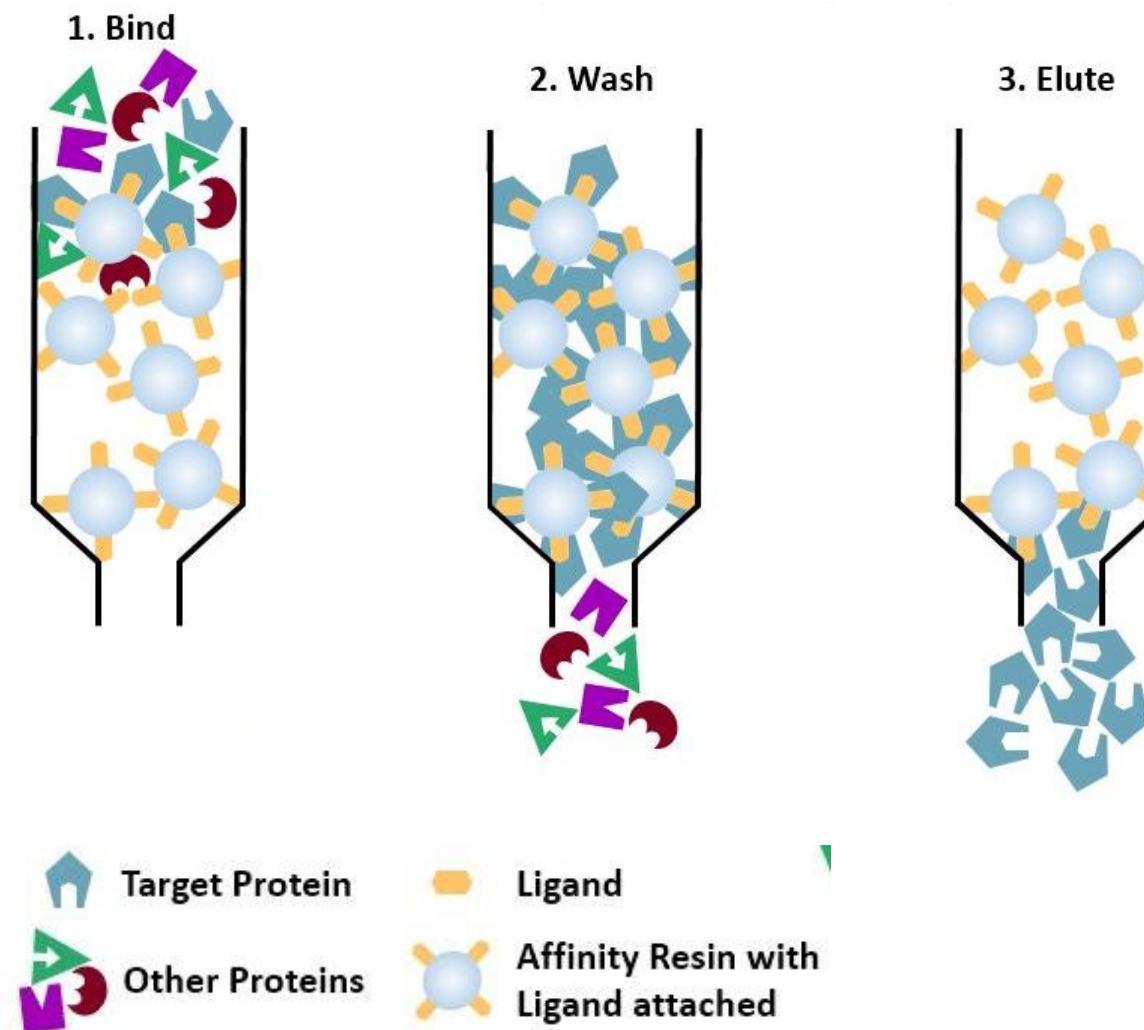


## **Size exclusion Chromatography**

**Gel Permeation Chromatography (GPC):** Organic solvent can be used as mobile phase. Semi-rigid/rigid gels like polystyrenes, alkylated dextrans are used as stationary phase.

**Gel Filtration Chromatography (GFC):** Aqueous or buffer solution can be used as mobile phase. Dextran polymers (Sephadex), agarose (Sephadex), or polyacrylamide (Sephacryl or BioGel P) can be used as mobile phase.

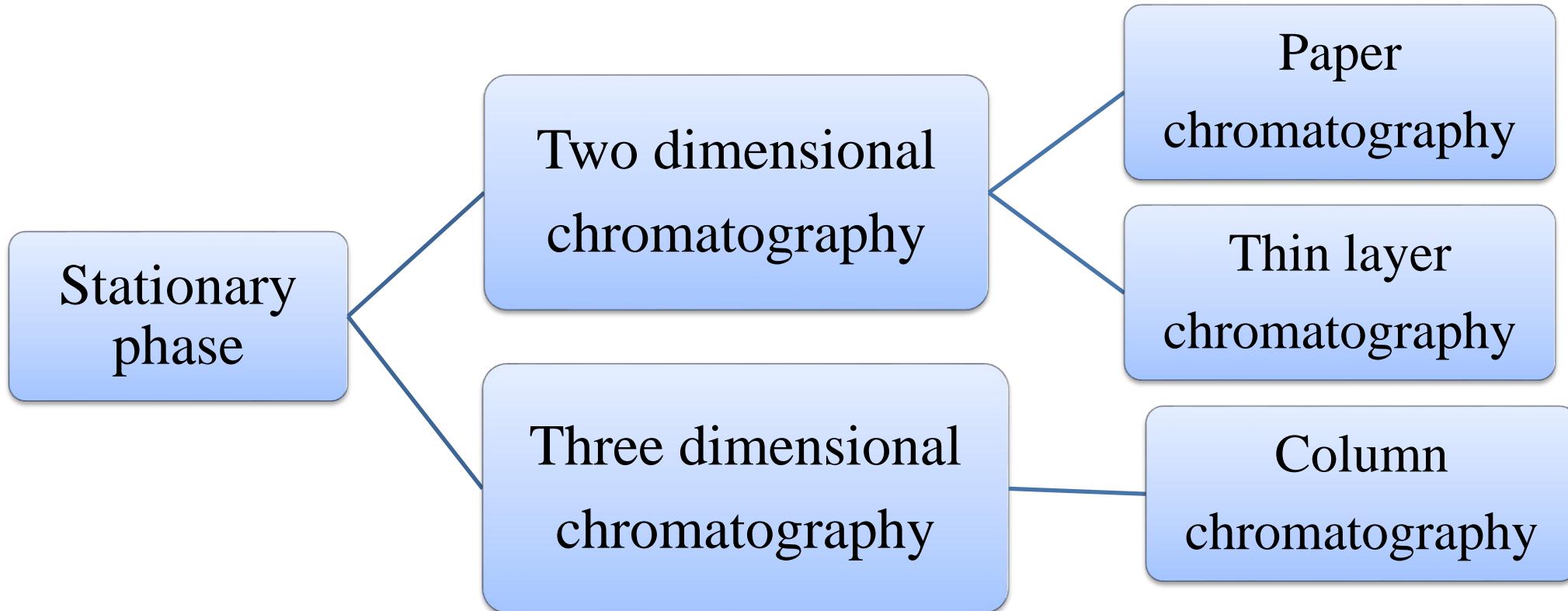
# Affinity Chromatography



# Affinity Chromatography

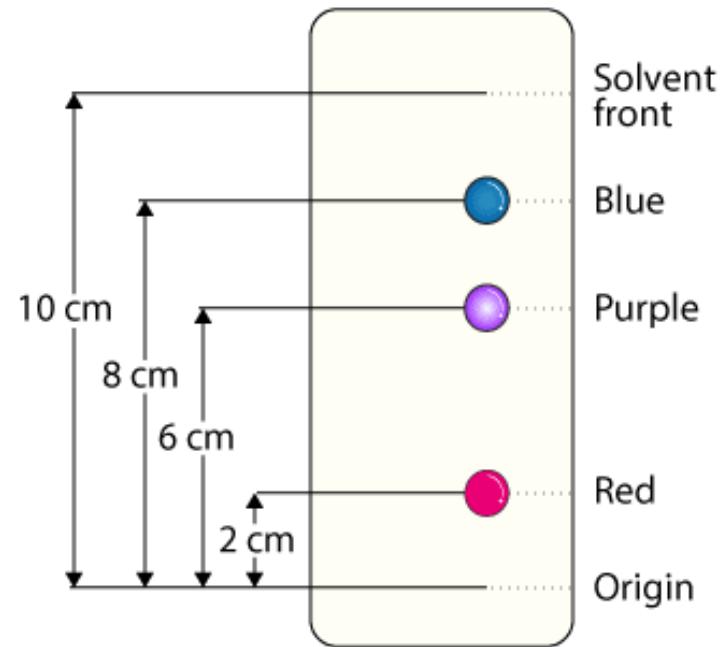
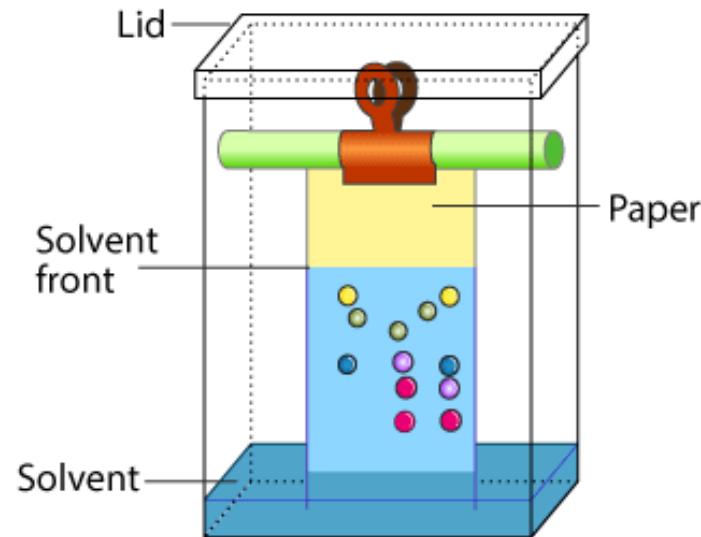
- Useful for separation of biochemical mixtures based on highly specific interaction between **antigen and antibody**, **enzyme and substrate**, **receptor and ligand** or **protein and nucleic acid**.
- Mostly used for the **purification of proteins**. It separates proteins on the basis of reversible interaction between protein (or group of proteins) and a specific ligand coupled to a chromatography matrix.

# Classification based on the physical means (Methods holding the stationary phase)



# Planar Chromatography

**Planar Chromatography:** Stationary phase is supported on a flat plate on which the mobile phase moves on it by **capillary action**



## **Classification based on the Technique**

- **Thin Layer Chromatography (TLC):** The stationary phase is a thin layer supported on glass, plastic or aluminium plates.
- **Paper Chromatography (PC):** The stationary phase is a thin film of liquid supported on an inert support or paper.

# Planar Chromatography: Thin layer Chromatography (TLC)

Separations on TLC involve distributing a mixture of two or more substances between a **stationary phase** and a **mobile phase**

- ❖ **The stationary phase:** Thin layer of adsorbent (usually silica gel or alumina) coated on a plate (Glass or Aluminium plate)
- ❖ **The mobile phase:** It is a developing liquid which travels up the stationary phase, carrying the samples with it

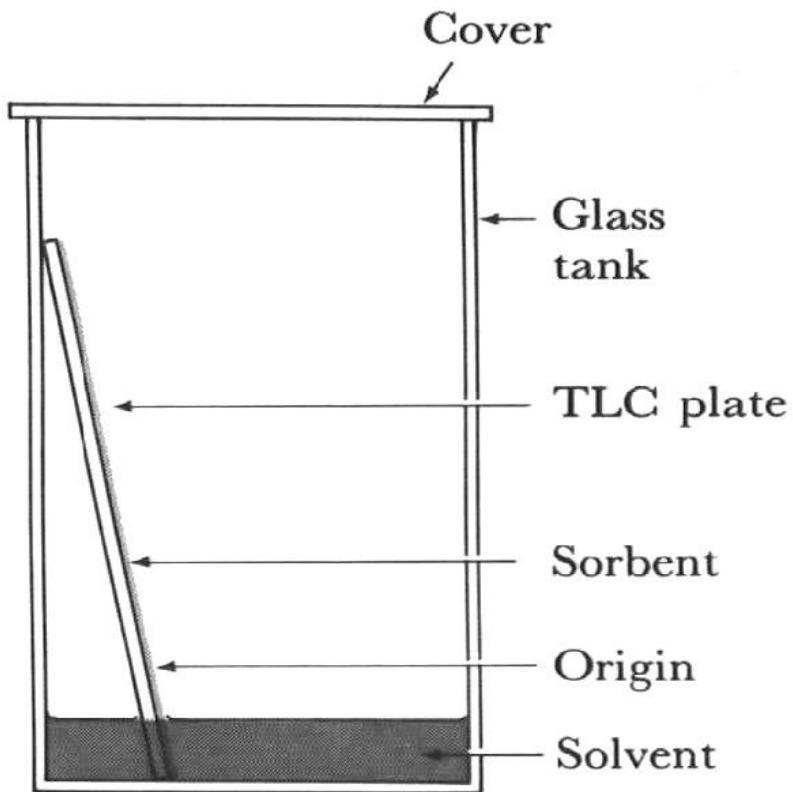
# Planar Chromatography: Thin layer Chromatography (TLC)

Components of the samples will separate on the stationary phase according to how much they adsorb on the stationary phase versus how much they dissolve in the mobile phase.



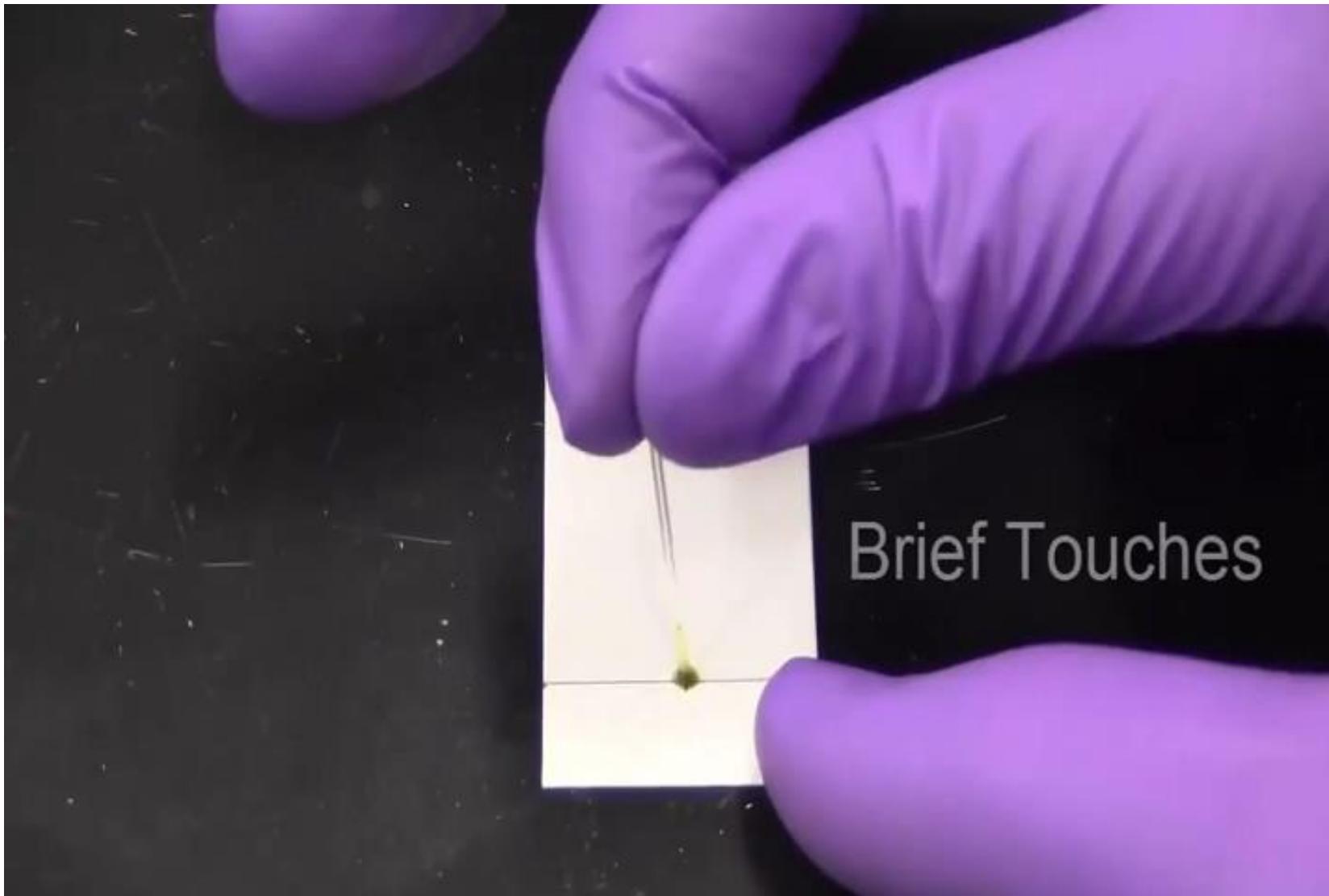


# Thin layer chromatography (TLC): How to perform



When the plates are removed from the chamber, quickly trace the solvent front (the highest solvent level on the plate) with a pencil.

# Thin layer Chromatography (TLC): How to Perform



# **Thin layer Chromatography (TLC): Identifying the Spots**

The most common visualization technique is to hold the plate under a UV lamp

## **Visualizing Agents:**

- Alkaloids: Dragendorff's reagent
- Cardiac glycosides: Antimony trichloride
- Sugar: Aniline phthalate
- Amino acids: Ninhydrin

## **Calculation for retention factor ( $R_f$ )**

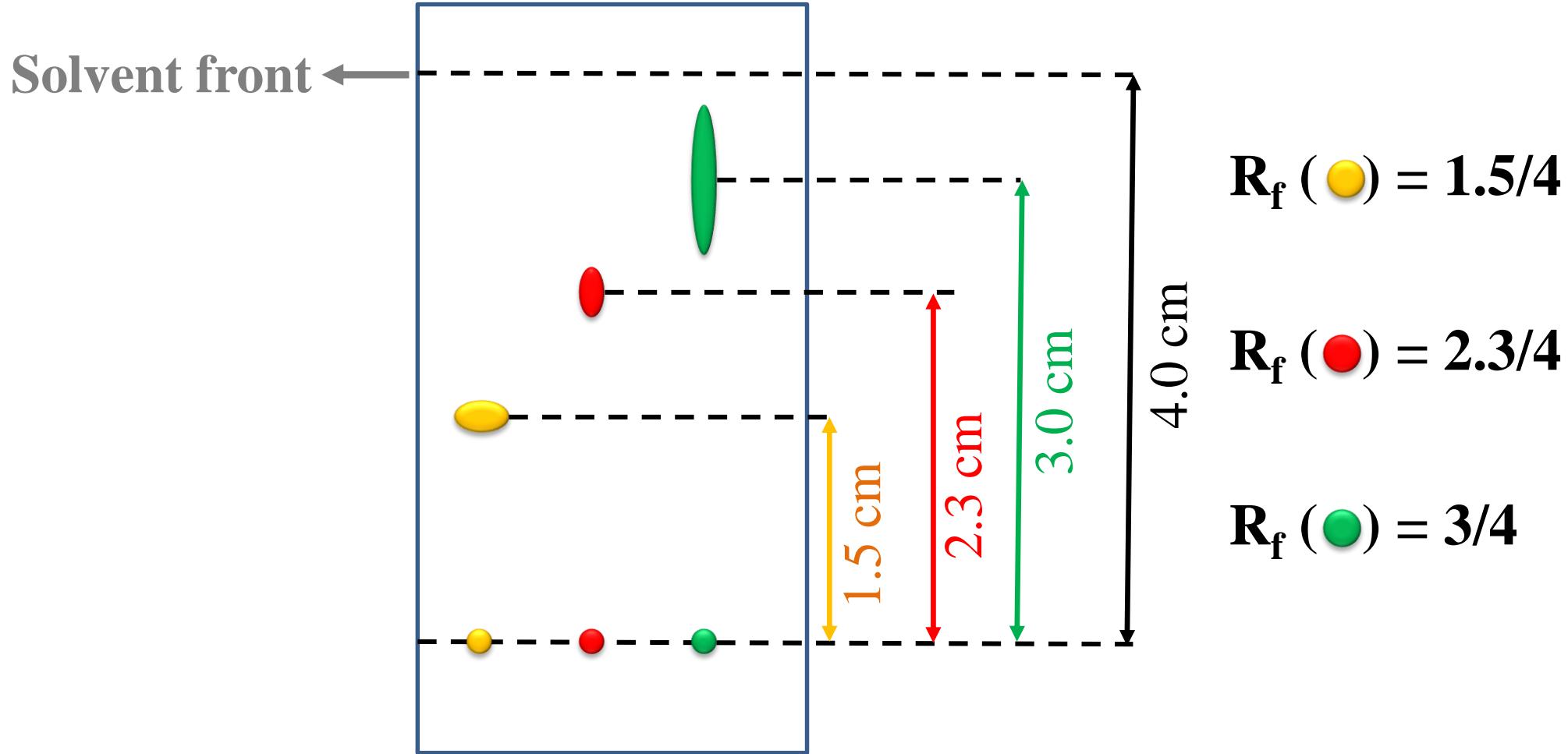
$$R_f = \frac{\text{distance travelled by the center of the spot}}{\text{distance simultaneously travelled by the mobile phase}}$$

**OR**

$$R_f = \frac{\text{distance travelled by the compound}}{\text{distance travelled by the solvent front}}$$

The  $R_f$  (retention factor) value for each spot should be calculated

# Thin layer Chromatography (TLC): Interpreting the Data



## **Thin layer Chromatography (TLC): Retention Factor ( $R_f$ )**

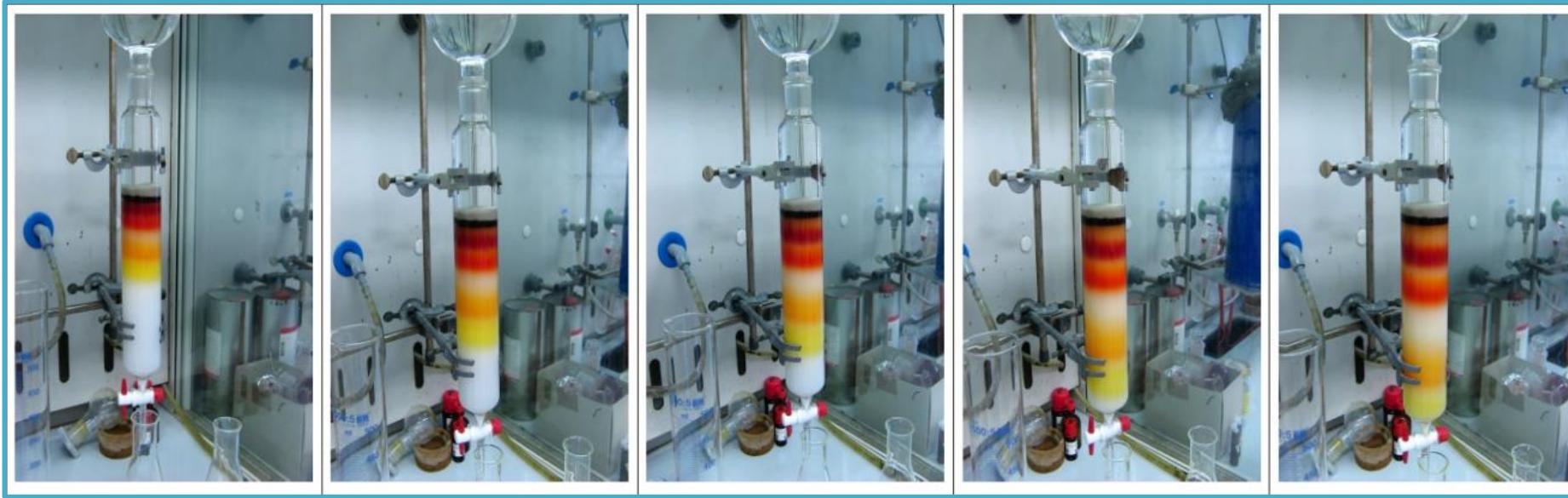
- ❖ It is characteristic for any given compound on the same stationary phase using the same mobile phase
- ❖ Hence, known  $R_f$  values can be compared to those of unknown substances to aid in their identifications

## **Classification Based on the Technique:**

**Column Chromatography (CC):** Stationary phase is packed in a glass column



# Column Chromatography (CC): Column Characteristics



- ❖ The main function of the column is **to support the stationary phase**
- ❖ Column is mostly **good quality neutral glass** and not affected by solvents
- ❖ Column dimensions - length and diameter ratio (10:1, 30:1 or 100:1)

# **Column Chromatography (CC): Column Packing**

The stationary phase is packed into a column

**Packing of column:** Packing depends mainly on the density of the solid

Techniques used are the wet, dry and slurry methods

In all cases avoid inclusion of air bubbles

**Sample addition:** Apply evenly and in a concentrated solution to the top of the column which is protected from disturbance

## Column Chromatography (CC): Types of Elution

**Isocratic elution:** Addition of solvent mixture of fixed composition during the whole process.

*e.g.* Single solvent or solvent mixture with fixed composition

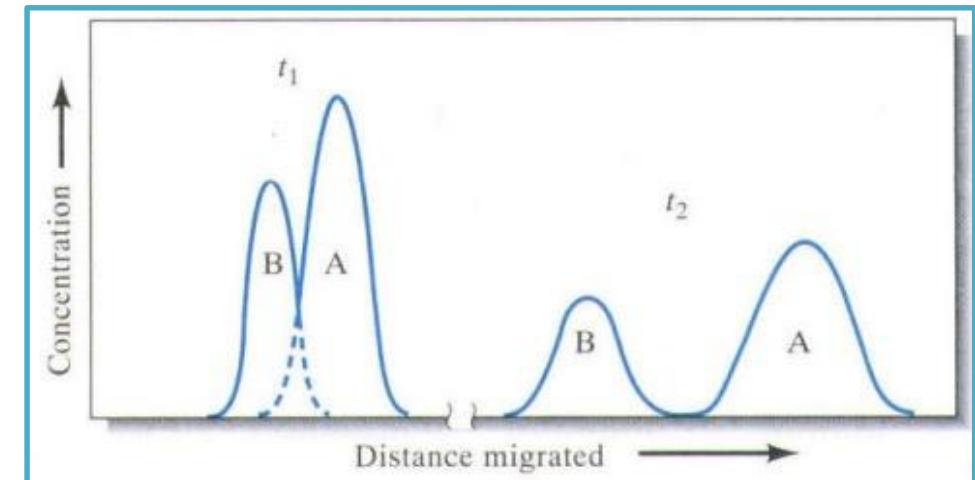
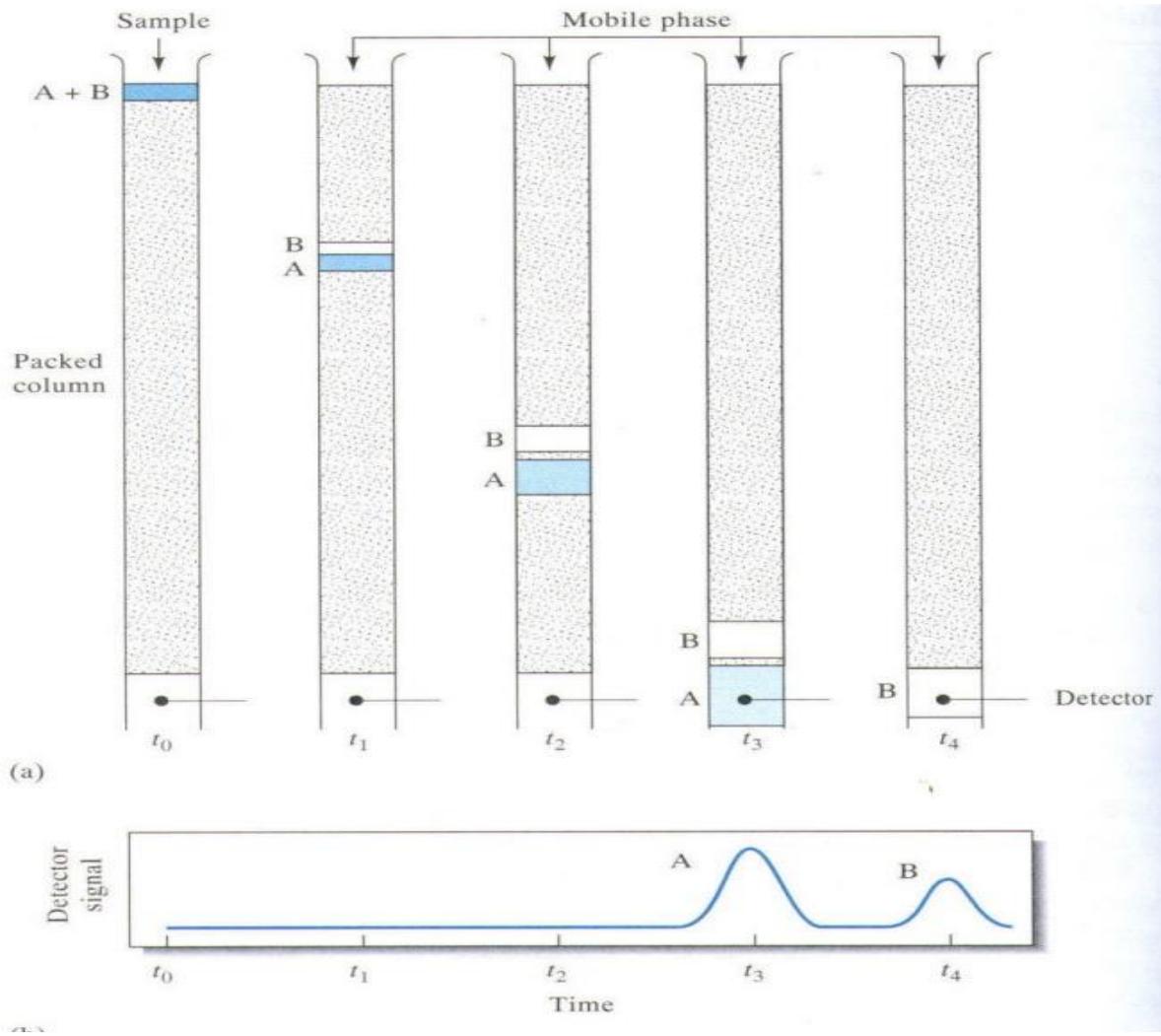
**Gradient elution:** Continuous change in the composition of the mobile phase over a period of time (*e.g.* polarity, pH or ionic strength).

Usually mixture of solvents *e.g.* Ethyl acetate-hexane, Methanol-dichloromethane

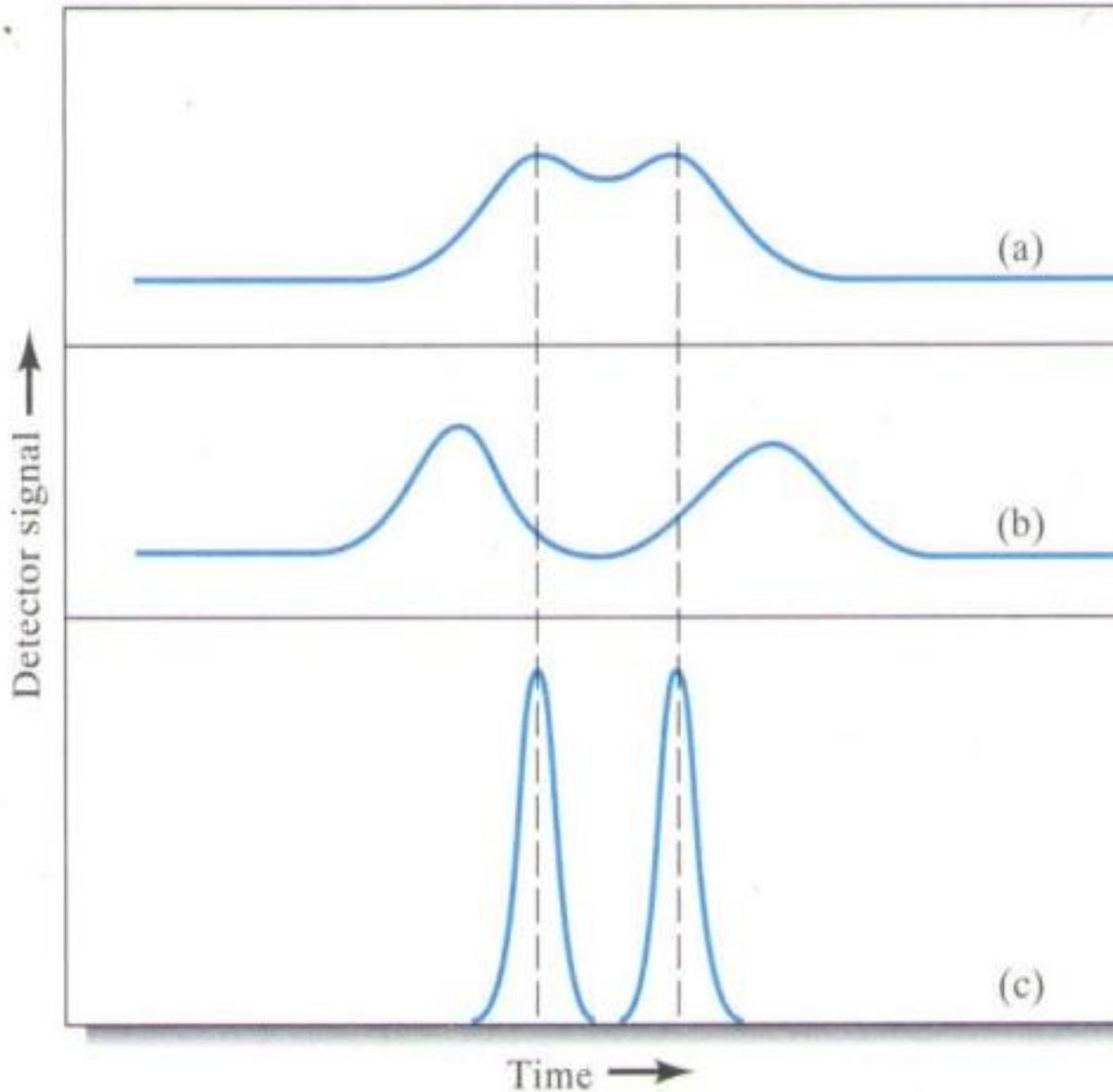
## Column Chromatography (CC): Detection

- ❖ On-column detection: For colored or fluorescent compounds directly after developing the chromatogram.
- ❖ Monitoring the eluted fractions with TLC or PC.
- ❖ Using special detectors: Connected to the column such as refractive index, UV detectors, etc.

# Column Chromatography (CC): Detection



# Column Chromatography (CC): Peak Resolution



Poor resolution

Good resolution

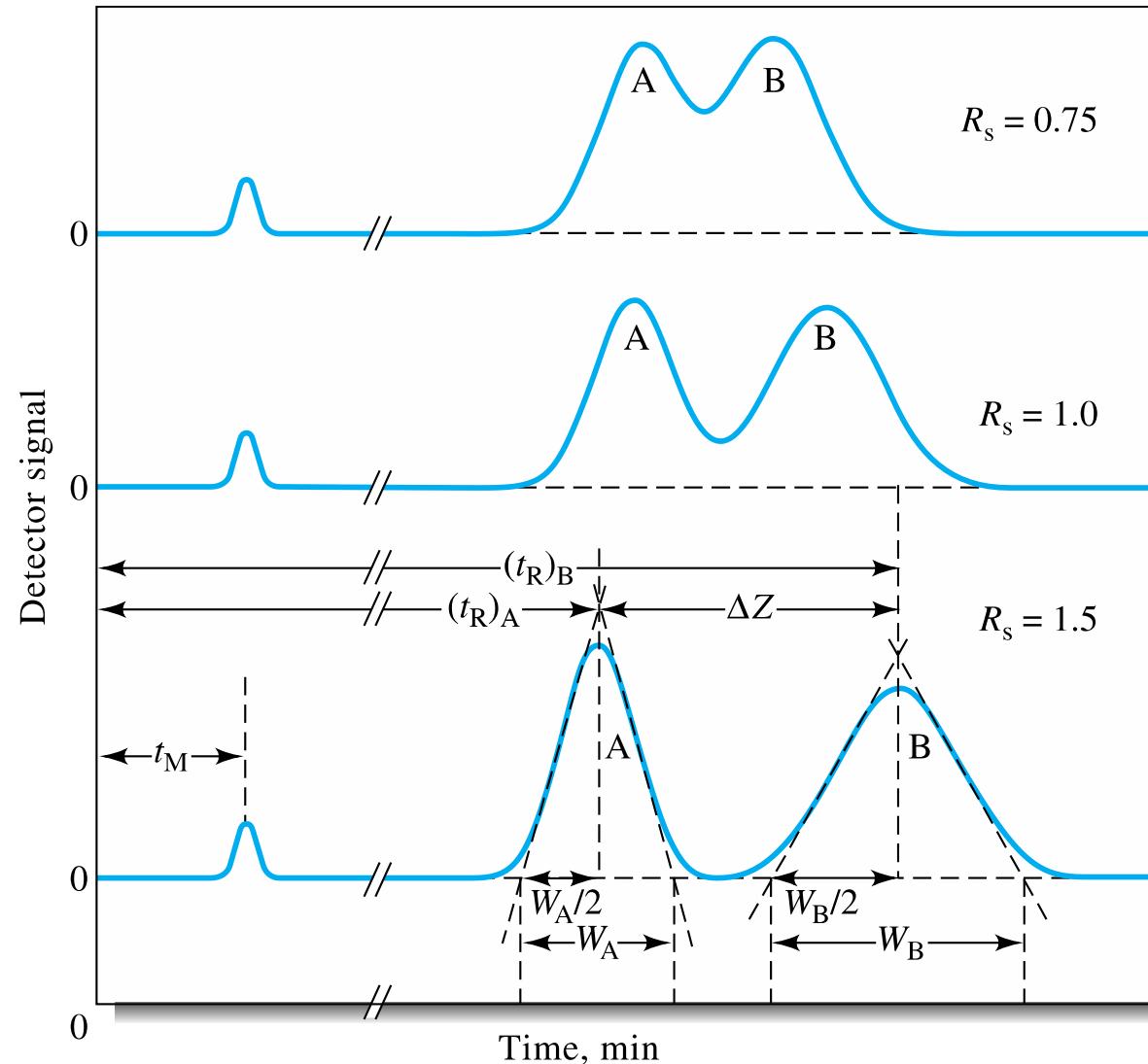
# Column Resolution

The **resolution ( $R_s$ )** of the column tells us how far apart two bands are relative to their widths.

$$R_s = \frac{\Delta Z}{W_A/2 + W_B/2}$$

$$R_s = \frac{2\Delta Z}{W_A + W_B}$$

$$R_s = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$$



## CC: Factors Affecting Column Efficiency

**Particle size of solid stationary phase :** Decrease of size improves separation

**Column dimensions:** Efficiency increases as ratio length / width increases

**Uniformity of packing:** Non uniform packing results in irregular movement of solutes through column and less uniform zone formation (i.e. band broadening or tailing)

**Column temperature:** Increase in column temperature results in speed of elution but does not improve separation (tailing)

## **CC: Factors Affecting Column Efficiency**

**Eluting solvent:** Solvents should be of low viscosity (to give efficient resolution) and high volatility (to get rapid recovery of the substances)

**Solvent flow rate:** Uniform and low flow rate gives better resolution

**Continuity of flow:** Discontinuous flow disturbs resolution

**Condition of adsorbent:** Deactivation of adsorbent decreases separation

**Concentration of solutes:** Substances of high concentration move slowly

# Column Chromatography (CC): An Automated Machine



# Column Chromatography (CC): Migration Rates of Solutes

All chromatographic separations are based on differences in the extent to which solutes are distributed between mobile and stationary phase

$$A_{\text{stationary}} \rightleftharpoons A_{\text{mobile}}$$

The equilibrium constant for this reaction is called as distribution constant.

$$K_C = C_S / C_M$$

$K_C$  is equilibrium constant (distribution constant)

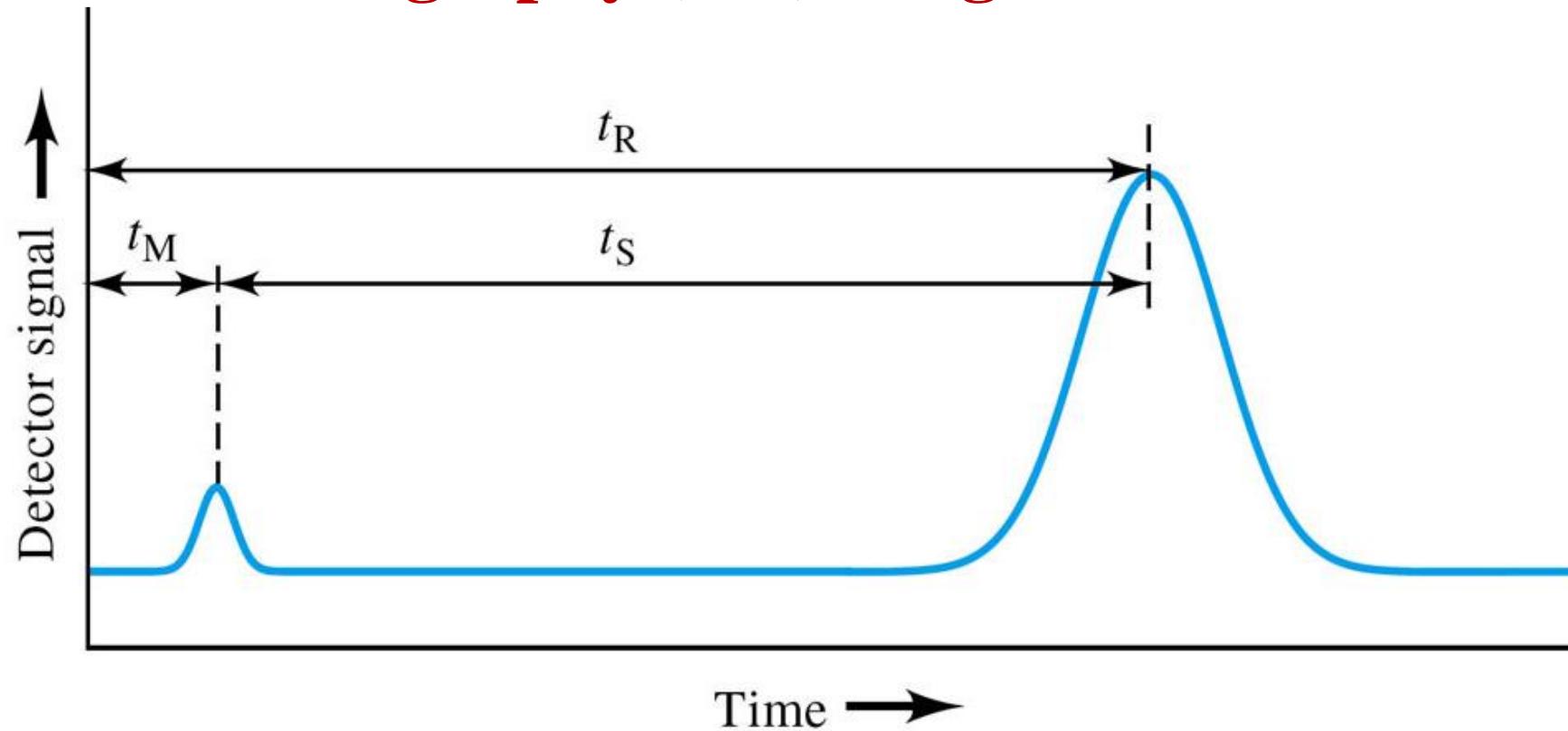
$C_S$  = Concentration of solute in stationary phase

$C_M$  = Concentrations of solute in mobile phase.

**$C_S$  is directly proportional to  $C_M$**

$$C_S = n_S / V_S, \quad C_M = n_M / V_M$$

# Column Chromatography (CC): Migration Rates of Solutes



$$t_R = t_M + t_S;$$

$t_S$  = time duration of the analyte retained in the stationary phase

$$\text{Volumetric flow rate } F_C = V_R / t_R$$

# **Column Chromatography (CC): Migration Rates of Solutes**

- **Retention Volume ( $V_R$ )** - Volume of eluent needed to convey a solute band from the point of injection , through the column, to the detector
- **Retention time ( $t_R$ )** - Time needed for each component of the mixture after injection to reaches the detector
- **Dead or void time ( $t_M$ )** - Transit time of the un-retained solute to reach the detector, known as void time

# Column Chromatography (CC): Velocities

Velocity = Distance/Time → Length of column/ Retention times

$$\text{Velocity of Solute: } \bar{v} = \frac{L}{t_R} \quad \text{Velocity of Mobile Phase: } \mu = \frac{L}{t_M}$$

$$\text{Velocity of solute: } \bar{v} = \frac{L}{t_R} \times t_M/t_M$$

$$\bar{v} = \mu \times t_M/t_R$$

$\bar{v} = \mu \times$  fraction of time solute spends in mobile phase

$$\bar{v} = \mu \times \frac{\text{no. of moles of solute in mobile phase}}{\text{total no. of moles of solute}}$$

## CC: Velocity, Distribution Constant and Retention Factor

$$\bar{v} = \mu \times \frac{c_M V_M}{c_M V_M + c_S V_S}$$

$$\bar{v} = \mu \times \frac{1}{1 + c_S V_S / c_M V_M}, K = \frac{c_S}{c_M} \quad \text{Distribution Constant}$$

$$\bar{v} = \mu \times \frac{1}{1 + K V_S / V_M}$$

where  $\frac{K_A V_S}{V_M} = k_A \quad \text{Retention factor for solute A}$

$$\bar{v} = \mu \times \frac{1}{1 + k_A}$$

$$\bar{v} = \frac{L}{t_R}$$

$$\frac{L}{t_R} = \frac{L}{t_M} \times \frac{1}{1 + k_A}$$

$$\mu = \frac{L}{t_M}$$

$$k_A = \frac{t_R - t_M}{t_M} = \frac{t_S}{t_M}$$

Ideally the retention factor for analytes  
in a sample between 1 and 5

## CC: Selectivity factor/Separation factor ( $\alpha$ )

In two component system; Can “A” be separated from “B”?

For example; B retained in the column more than A  $\rightarrow \alpha > 1$

$$\alpha = \frac{k_B}{k_A} \quad k_B \text{ and } k_A \text{ are Retention factors}$$

$$k_A = \frac{(t_R)_A - t_M}{t_M} \text{ and } k_B = \frac{(t_R)_B - t_M}{t_M}$$

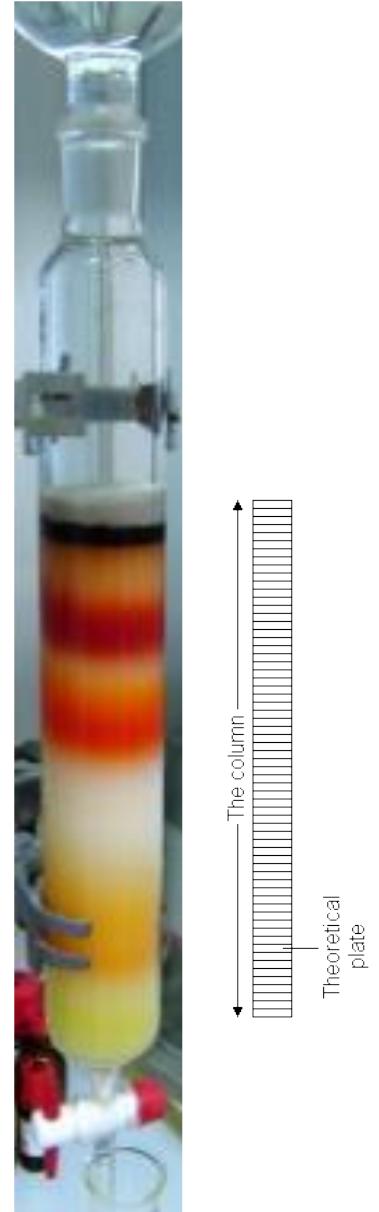
$$\alpha = \frac{(t_R)_B - t_M}{(t_R)_A - t_M} \quad t_M, t_R \text{ Retention times.}$$

# Column Efficiency - Plate Theory

## Assumption

The column is divided into a number of zones (theoretical plates)

Within each theoretical plates complete equilibration of analyte occurs between stationary and mobile phase



# Greater separation occurs with:

Greater number of theoretical plates (N)

**H**eight **E**quivalent to a **T**heoretical **P**late (**HETP**)

$$L = N \times H$$

$$H = L/N$$

Where, **L** - Length of the column

**N** - Number of plates

**H** - **H**eight **E**quivalent of **T**heoretical **P**lates

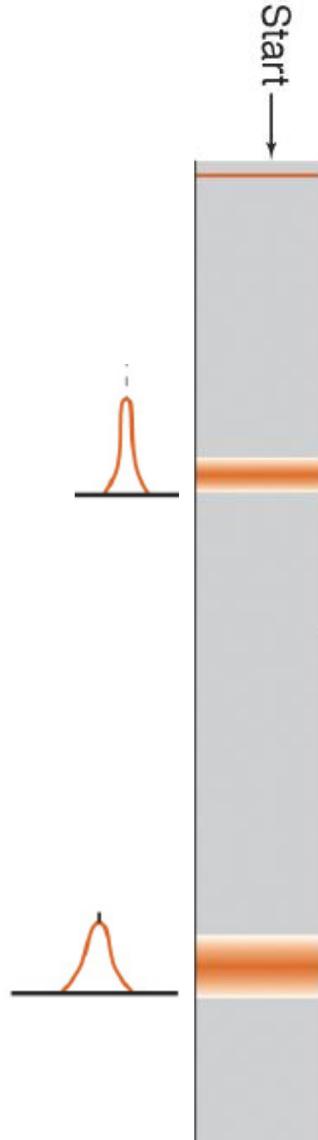


# Plate Theory

Solute moving through a column spreads into a **Gaussian shape** with standard deviation  $\sigma$ , and the variance is  $\sigma^2$ .

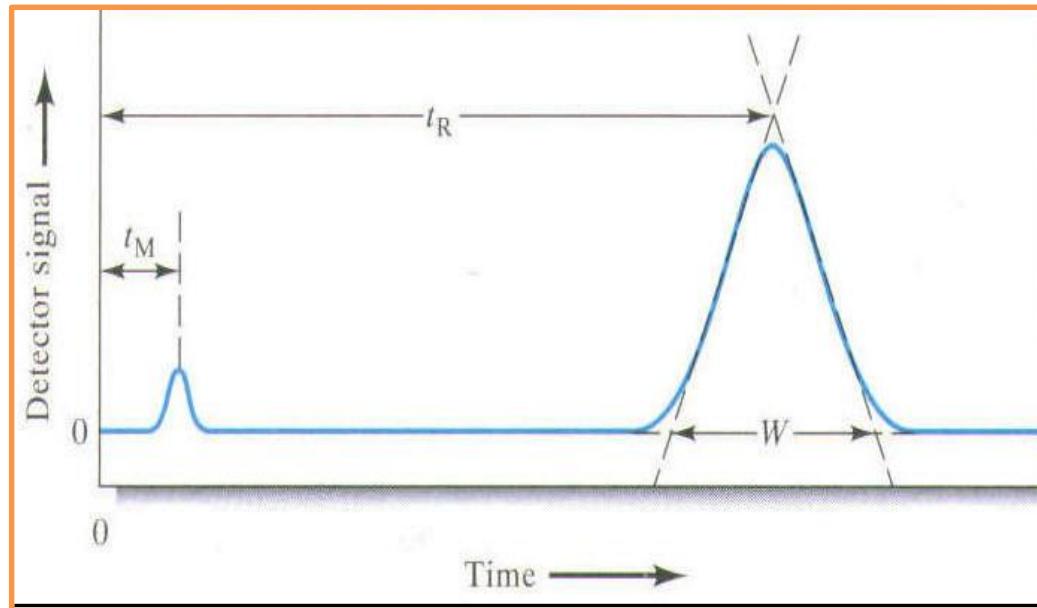
The variance per unit length of column is the measurement of column efficiency.

$$H = \frac{\sigma^2}{L}$$



# Band spreading

The width of bands increases as their retention time (volume) increases



$$N = L/H \text{ number of plates}$$

$$N = 16 \left( \frac{t_R}{W} \right)^2$$

Common measures of breadth are:

The width **W** at the baseline between tangents drawn to the steepest parts of the peak (inflection points).

Q. Substances A and B have retention times of 13.01 and 14.31 min, respectively, on a 25 cm column. The peak widths at base for A and B are 1.45 and 1.61 min, respectively.

Calculate (a) The column resolution, (b) The average number of plates in the column, (c) The average plate height

**Ans:** Given,  $(t_R)_A = 13.01 \text{ min}$ ;  $(t_R)_B = 14.31 \text{ min}$

$$L = 25 \text{ cm}$$

$$W_A = 1.45 \text{ min}; W_B = 1.61 \text{ min}$$

(a) Resolution;  $R_S = 2 [(t_R)_B - (t_R)_A] / (W_A + W_B) = 0.85$

(b) Number of Plates  $N_A = 16 [(t_R)_A / W]^2 = 1288$

$$N_B = 16 [(t_R)_B / W]^2 = 1264$$

Average number of plates;  $N_{\text{Average}} = [N_A + N_B] / 2 = 1276$

(c)  $L = H \times N$

$$H = L / N_{\text{average}} = 25 / 1276 = 2.35 \times 10^{-2} \text{ cm}$$

Q. Substances **A** and **B** have retention times of **16.40** and **17.63 min**, respectively, on a **30 cm** column. An unretained species passes through the column in **1.30 min**. The peak widths at base for A and B are **1.11** and **1.21 min**, respectively.

Calculate (a) The column resolution, (b) The average number of theoretical plates in the column, (c) The average plate height

**Ans:** Given,  $(t_R)_A = 16.40 \text{ min}$ ;  $(t_R)_B = 17.63 \text{ min}$ ;  $t_M = 1.30 \text{ min}$   
 $L = 30 \text{ cm}$

$$W_A = 1.11 \text{ min}; W_B = 1.21 \text{ min}$$

(a) Resolution;  $R_S = 2 [(t_R)_B - (t_R)_A] / (W_A + W_B) = 1.06$

(b) Number of Plates  $N_A = 16 [(t_R)_A / W]^2 = 3493$   
 $N_B = 16 [(t_R)_B / W]^2 = 3397$

Average number of plates;  $N_{\text{Average}} = [N_A + N_B] / 2 = 3445$

(c)  $L = H \times N$

$$H = L / N_{\text{average}} = 30 / 3445 = 8.7 \times 10^{-3} \text{ cm}$$

Q. Two components **A** and **B** are separated by elution with hexane from a column packed with silica-gel (water adsorbed on silica surface). Distribution coefficients ( $K = C_{\text{aq}}/C_{\text{org}}$ ) of compounds A and B in water/hexane system are **5.99** and **6.16** respectively. The ratio  $V_S/V_M$  for the packing is **0.425**.

Calculate, (a) Retention factor for A and B, (b) Selectivity factor, (c) Length of the column if the number of theoretical plates and plate height of packing are  $9.03 \times 10^4$  and  $1.53 \times 10^{-3} \text{ cm}$  respectively.

**Ans:** Given,  $K_A = 5.99$ ;  $K_B = 6.16$ ;  $V_S/V_M = 0.425$

(a) Retention factor;  $k_A = K_A \times (V_S/V_M) = 2.546$

$$k_B = K_B \times (V_S/V_M) = 2.618$$

(b) Selectivity factor;  $\alpha = k_B / k_A = 1.03$

(c)  $L = HN = 9.03 \times 10^4 \times 1.53 \times 10^{-3} = 138.159 \text{ cm}$

Q. The following data are for a liquid chromatographic column:

Length of packing: 24.7 cm, Flow rate: 0.313 mL/min,  $V_M$ : 1.37 mL,  $V_S$ : 0.164 mL

A chromatogram of a mixture of species A, B, C and D provided the following data:

	Retention Time, min	Width of Peak Base (W), min
Nonretained	3.1	—
A	5.4	0.41
B	13.3	1.07
C	14.1	1.16
D	21.6	1.72

### Calculate

- The number of plates from each peak
- Average plate height
- Standard deviation

### Ans:

- $N_A = 16 [(t_R)_A / W]^2$
- $H = L / N$
- $H = \sigma^2 / L$

Q. The following data are for a liquid chromatographic column:

Length of packing: 24.7 cm, Flow rate: 0.313 mL/min,  $V_M$ : 1.37 mL,  $V_S$ : 0.164 mL

A chromatogram of a mixture of species A, B, C and D provided the following data:

	Retention Time, min	Width of Peak Base (W), min
Nonretained	3.1	—
A	5.4	0.41
B	13.3	1.07
C	14.1	1.16
D	21.6	1.72

From the above data Calculate

(a) Retention factor

(b) The distribution constant.

Ans. (a) Retention factor;  $k_A = [(t_R)_A - t_M]/t_M = t_S/t_M$

Similarly,  $k_B$ ,  $k_C$ ,  $k_D$  can be calculated

(b) Distribution constant;  $K_A = k_A (V_M/V_S)$

Similarly,  $K_B$ ,  $K_C$ ,  $K_D$  can be calculated

Q. The following data were obtained by gas-liquid chromatography on a 40-cm packed column:

Compound	$t_R$ , min	$W$ , min
Air	1.9	—
Methylcyclohexane	10.0	0.76
Methylcyclohexene	10.9	0.82
Toluene	13.4	1.06

Calculate

- an average number of plates from the data.
- the standard deviation for the average in (a).
- an average plate height for the column.

Ans.

- $N_A = 16 [(t_R)_A / W]^2$
- $L = H \times N$
- $H = \sigma^2 / L$

Q. The following data were obtained by gas-liquid chromatography on a 40-cm packed column:

Compound	$t_R$ , min	$W$ , min
Air	1.9	—
Methylcyclohexane	10.0	0.76
Methylcyclohexene	10.9	0.82
Toluene	13.4	1.06

Calculate

- (a) an average number of plates from the data.
- (b) the standard deviation for the average in (a).
- (c) an average plate height for the column.

From the above data; Calculate the resolution for

- (a) Methylcyclohexene and methylcyclohexane
- (b) Methylcyclohexene and toluene
- (c) Methylcyclohexane and toluene

Ans. Resolution;

$$R_S = \frac{\Delta Z}{W_A/2 + W_B/2}$$

$$R_S = \frac{2\Delta Z}{W_A + W_B}$$

$$R_S = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$$

9. If  $V_S$  and  $V_M$  for the column in the problem 7 are 19.6 and 62.6 mL, respectively, and a non retained air peak appears after 1.9 min, Calculate

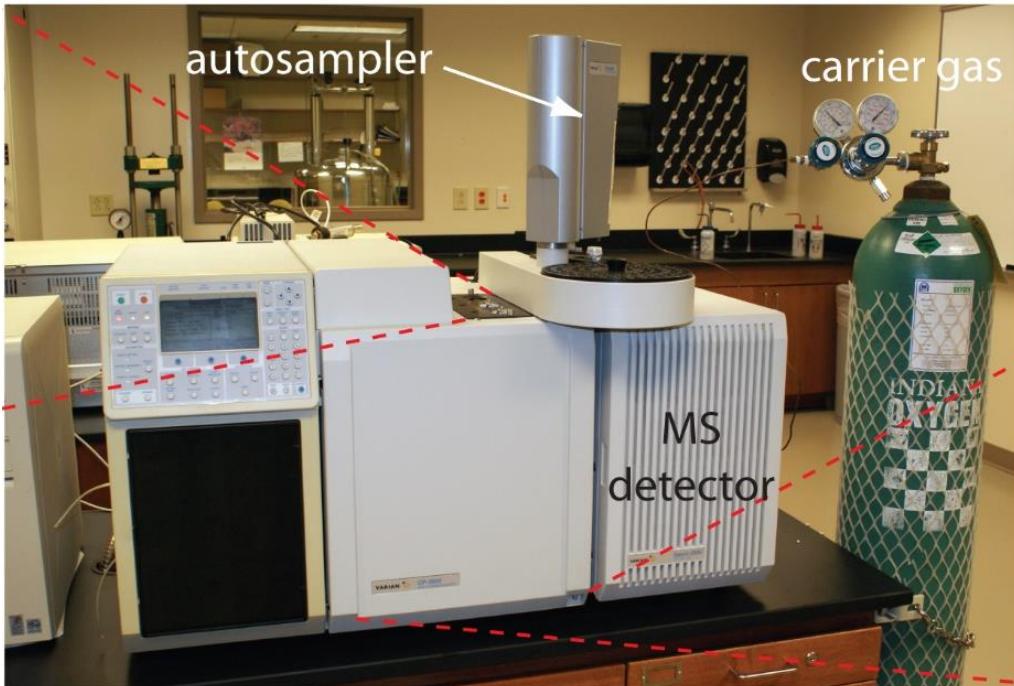
- (a) The retention factor for each compound
- (b) The distribution constant for each compound
- (c) The selectivity factor for methylcyclohexane and methylcyclohexene

Ans. (a) Retention factor,  $k_A = \frac{t_R - t_M}{t_M} = \frac{t_S}{t_M}$

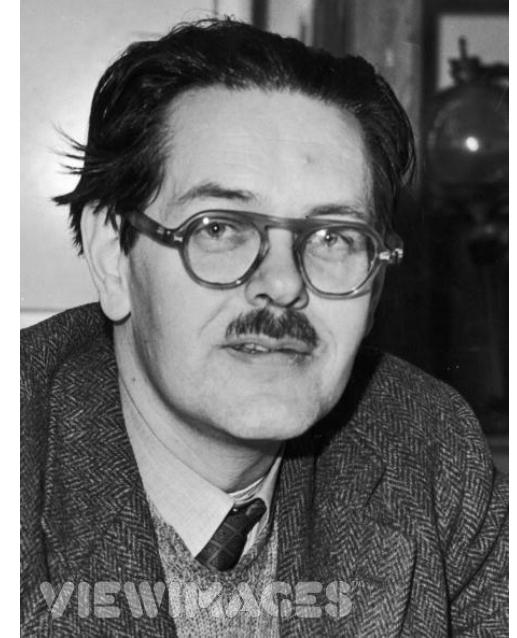
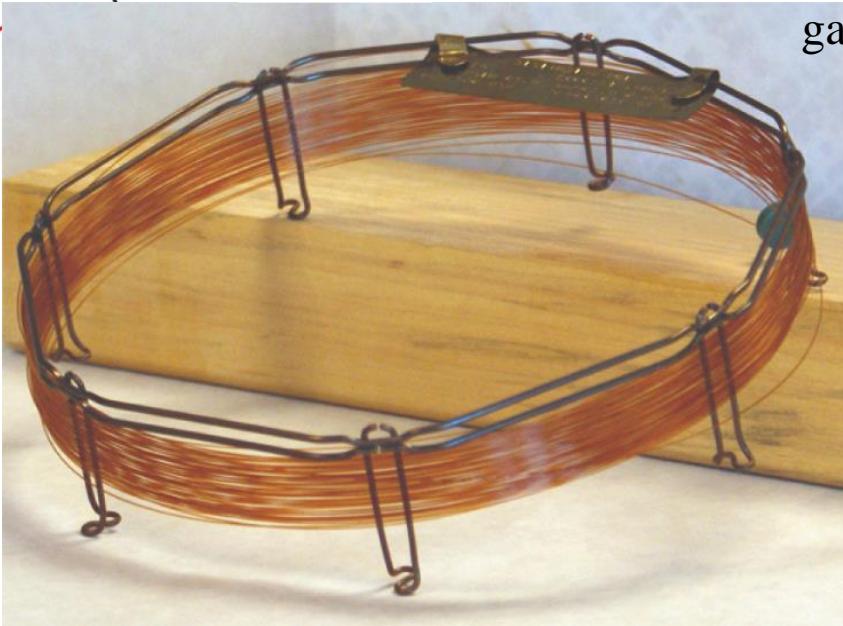
(b) Distribution constant,  $k_A = K_A \times (V_S/V_M)$

(c) Selectivity factor,  $a = \frac{(t_R)_B - t_M}{(t_R)_A - t_M}$

# Gas Chromatography



capillary column



John Porter Martin developed first gas-liquid chromatograph in 1950

# Gas Chromatography

Separation of gaseous and volatile substances

The mobile phase only transport the analyte

The mobile phase do not interact with the analyte

Inert gas (e.g. He, N<sub>2</sub>, Argon etc) are used as mobile phase

## Type of GC

**GSC** (Gas-solid chromatography)

**GLC** (Gas-liquid chromatography)

## **GSC** (Gas-solid chromatography)

- ❖ **GSC** principle is **ADSORPTION**
- ✓ not used because of limited no. of Stationary phase
- ✓ useful for separation of low molecular mass gaseous like air,  $\text{H}_2\text{S}$ , CO,  $\text{CO}_2$ ,  $\text{CS}_2$  and rare gases

## **GLC** (Gas-liquid chromatography)

- ❖ **GLC** principle is **PARTITION**

## Criteria for compounds to be analyzed by G.C

- ✓ Volatility
- ✓ Thermostability

## Advantages of Gas Chromatography

Strong separation power

Complex mixture can be resolved into constituents

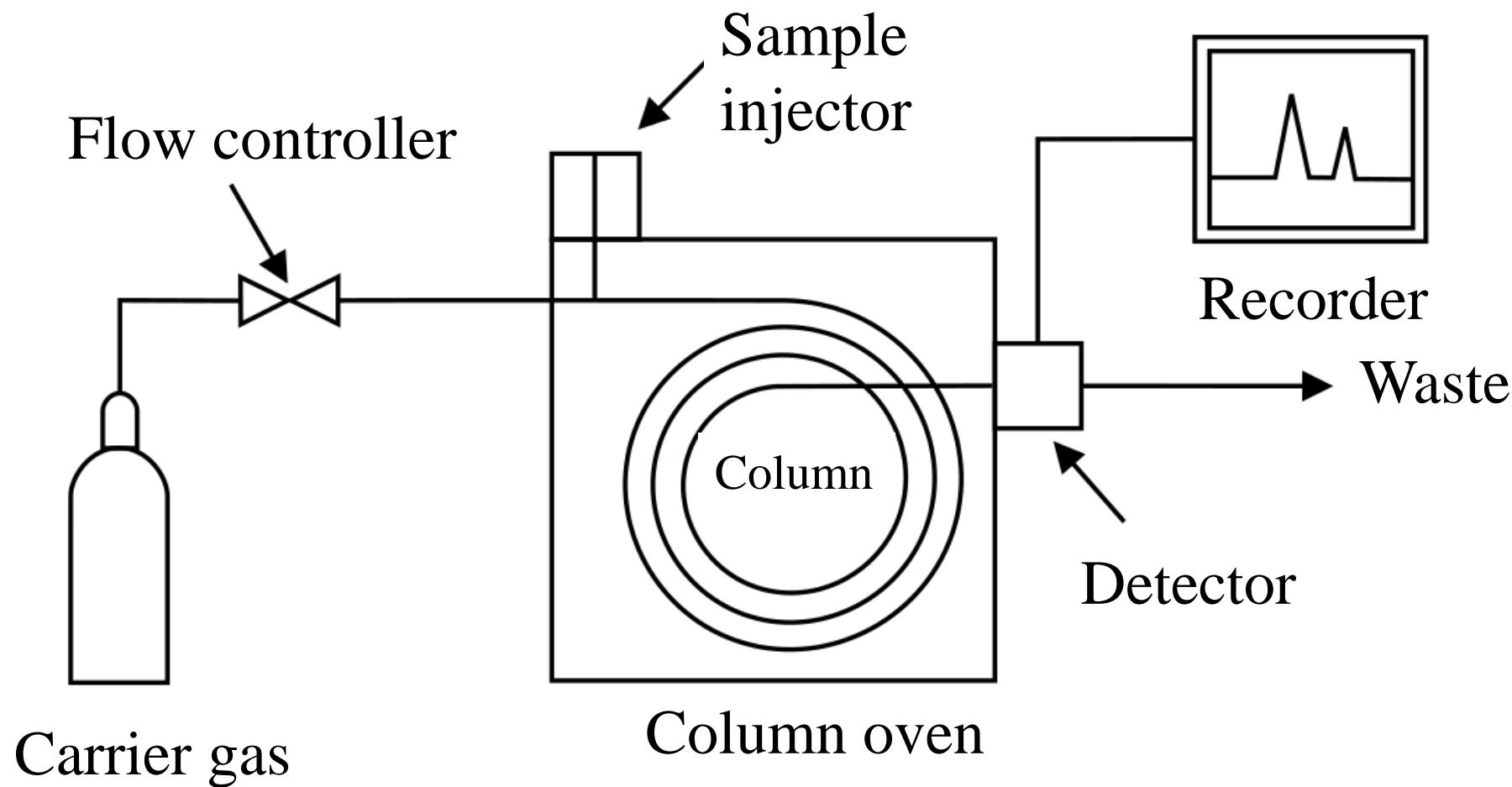
Good precision and accuracy

Separation completed in a short time

Low cost of instrument with generally long lifetime

Suitable for routine analysis

# Schematic diagram of a gas chromatograph



## How a GC machine works

- ✓ Sample is injected onto the machine.
- ✓ Sample converted into vapor and mixed with gaseous mobile phase
- ✓ The sample moves through the column along with the flow of inert gas and separation occurs
- ✓ Components are separated according to their Partition coefficient
- ✓ Components reaches the detector and recorded as a sequence of peaks as they leave the column

# **Components of Gas chromatography**

## **Carrier gas**

- ✓ He (common), N<sub>2</sub>, H<sub>2</sub> and Argon

## **Sample injection port**

- ✓ micro syringe

## **Columns**

- ✓ 2-50 m coiled stainless steel/glass/Teflon

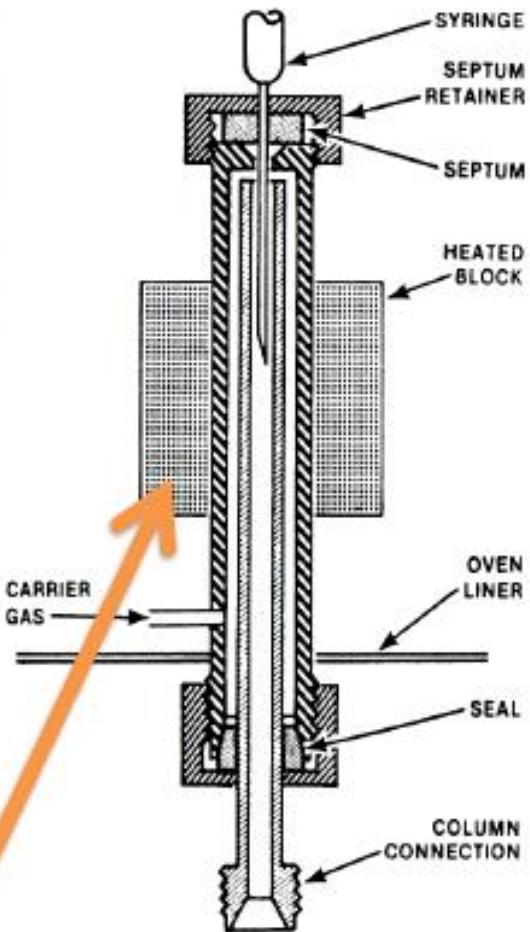
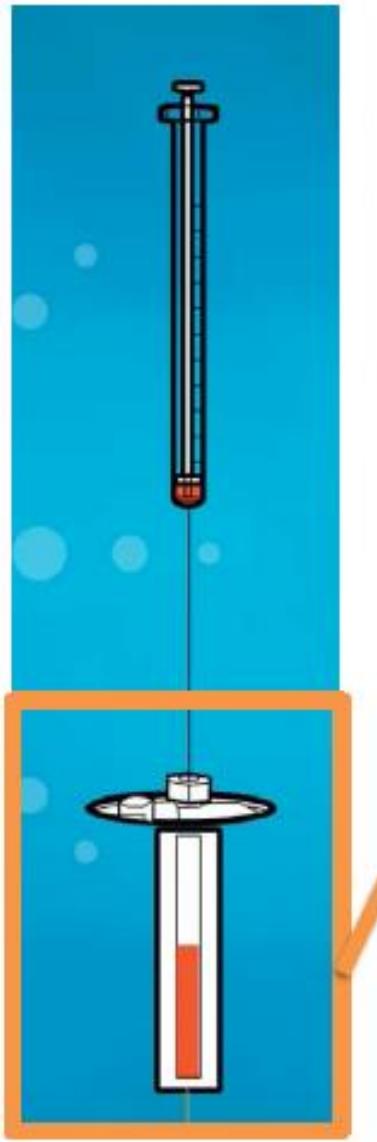
## **Detectors**

- ✓ Flame ionization (FID)
- ✓ Thermal conductivity (TCD)
- ✓ Electron capture (ECD)
- ✓ Flame photometric (FPD)
- ✓ Photo-ionization (PID)

## Carrier gas

- ✓ Must be chemically inert
- ✓ Commonly used gases include nitrogen, helium, argon, and carbon dioxide
- ✓ The choice of carrier gas is often dependant upon the type of detector which is used
- ✓ The carrier gas system also contains a molecular sieve to remove water and other impurities
- ✓ Pressure,  $P = \text{inlet } 10\text{-}50 \text{ psi (pound per inches}^2)$ 
  - Flow,  $F = 25\text{-}150 \text{ mL/min (packed column)}$
  - $F = 1\text{-}25 \text{ mL/min (open tubular column)}$

# Sample injection- Direct Injection



Packed Column Injector

CEE 772 #16

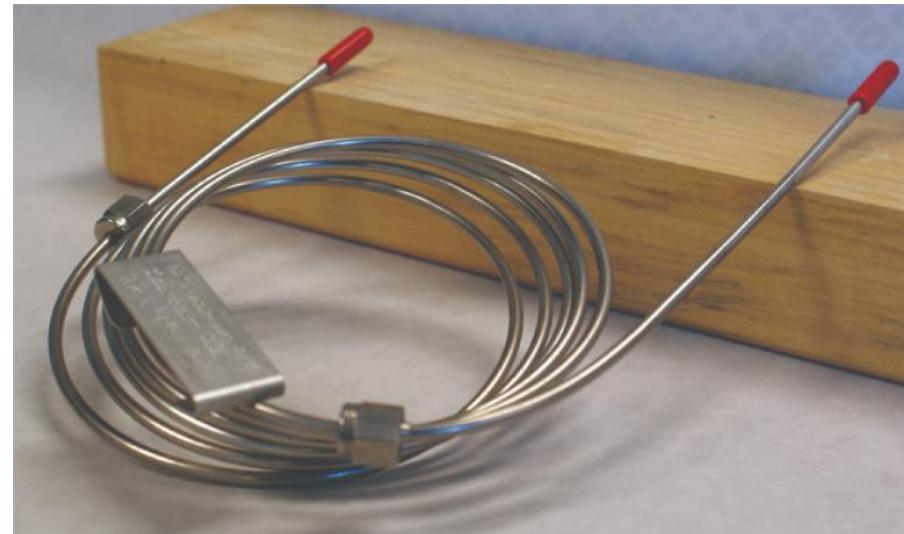
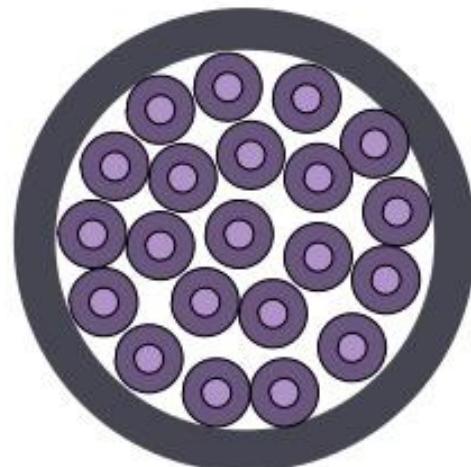
- Direct injection into heated port ( $>T$  oven) using micro syringe
- Slow injection or oversized samples cause band spreading and poor resolution
- The sample port is usually at about 50 °C

# Column types

## Packed column:

contain a finely divided, inert, solid support material coated with liquid stationary phase.

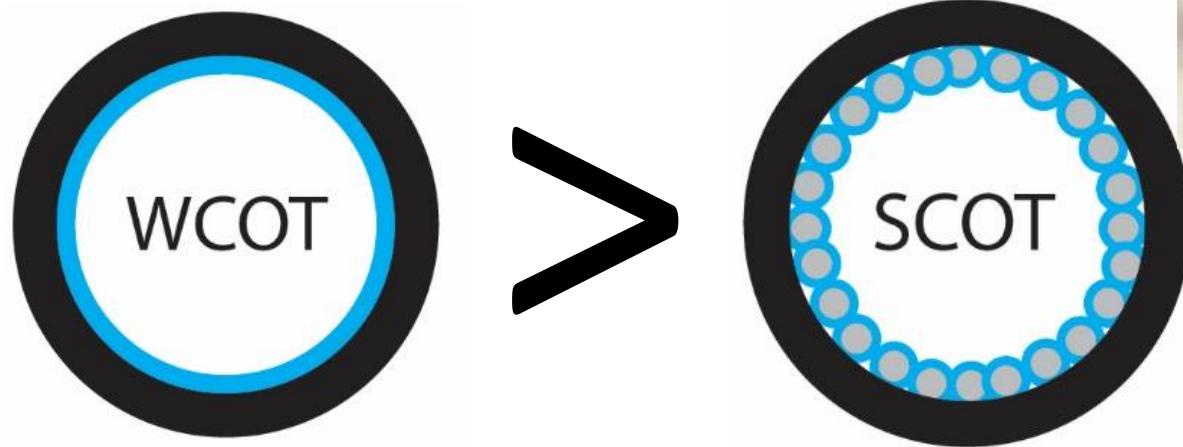
Most packed columns are 1.5 – 10 m in length  
and  
have an internal diameter of 2 – 4 mm.



# Column types

**Capillary columns** are of two types

- ✓ Wall coated open tubular (**WCOT**)
- ✓ Support coated open tubular (**SCOT**)



- The stationary phase (liquid) coated with a thin layer of *0.05 to 1  $\mu\text{m}$ .*

# Gas Chromatography - Detectors

Detectors can be grouped into *concentration dependent detectors* and *mass flow dependent detectors*

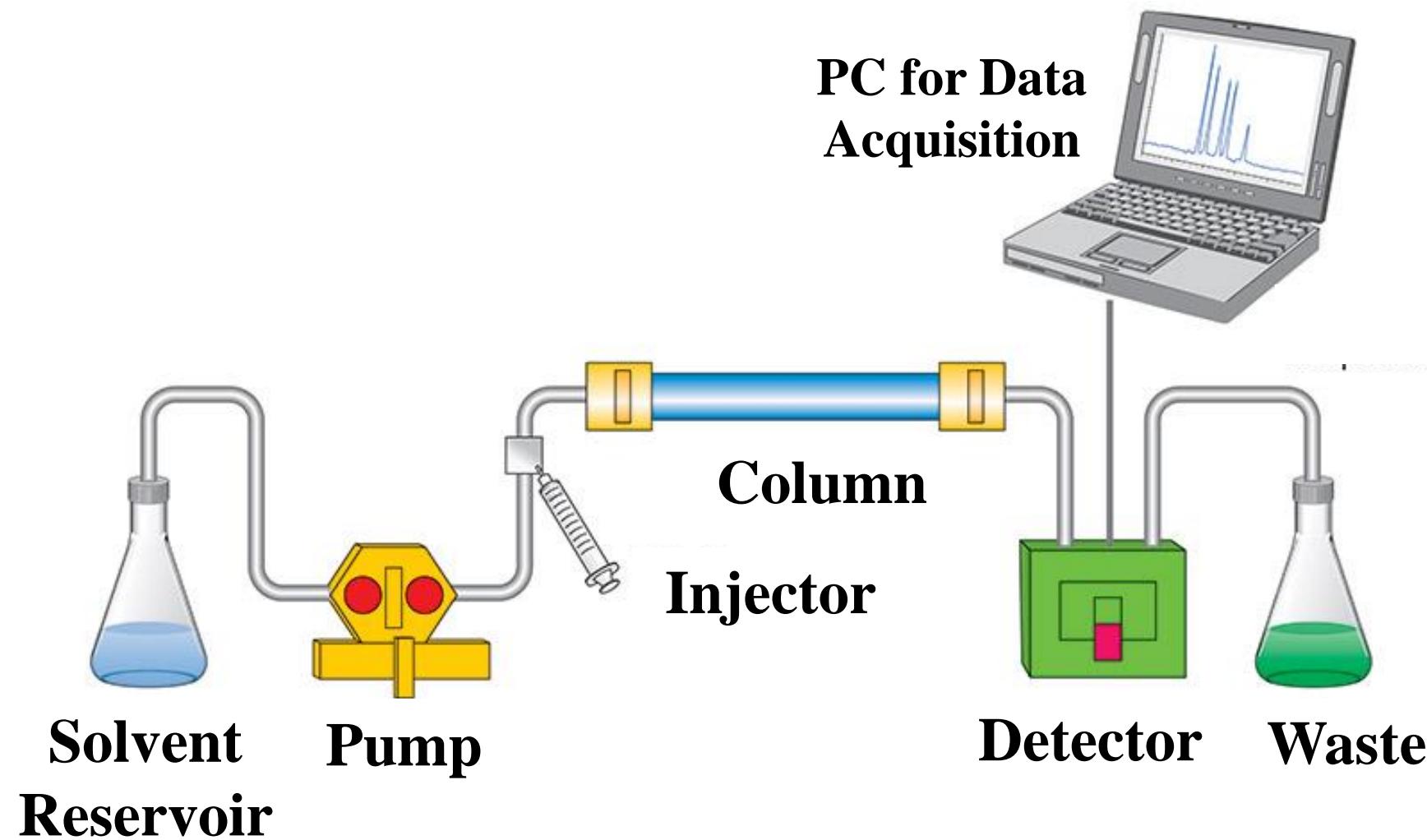
## Concentration dependent detector

- ✓ signal is related to the concentration of solute in the detector
- ✓ does not usually destroy the sample

## Mass flow dependent detectors

- ✓ signal is related to the rate at which solute molecules enter the detector
- ✓ usually destroy the sample

# High performance liquid chromatography (HPLC)



# **Components of HPLC**

## **Solvent Reservoir :**

- The mobile phase, or solvent, in HPLC is usually a mixture of polar and non-polar liquid.

## **Pump :**

- pump extracts mobile phase from the reservoir
- forces it through the system's column and detector

## **Sample Injector:**

- single injection or
- automated injection system

## **Columns :**

- usually between 50 and 300 mm long
- have an internal diameter of between 2 and 5 mm.
- commonly filled with a stationary phase with a particle size of 3–10  $\mu\text{m}$ .

## **Detectors:**

- UV or fluorescence spectroscopy
- Mass-spectrometric

# HPLC : Basic principle

Separation of a sample into its constituent parts because of the difference in the **relative affinities** of different molecules for the **mobile phase** and the **stationary phase** used in the separation.

- ✓ HPLC is basically a highly improved form of column liquid chromatography
- ✓ Instead of a solvent being allowed to drip through a column under gravity, it is forced through under high pressures of up to 400 atmospheres.
- ✓ It is much faster.

# Types of HPLC

## Normal Phase HPLC:

- ✓ NP-HPLC uses polar stationary phase and non-polar mobile phase
- ✓ the stationary phase is usually silica
- ✓ mobile phases are hexane, methylene chloride, chloroform, diethyl ether, and mixtures of these
- ✓ polar samples are retained on the polar surface of column packing longer than less polar materials.

# Types of HPLC

## Reverse Phase HPLC:

- ✓ The stationary phase is non-polar (hydrophobic) in nature
- ✓ mobile phase is a polar liquid, such as mixtures of water and methanol or acetonitrile.
- ✓ works on the principle of hydrophobic interactions hence the more nonpolar the material will be retained longer

# **Applications of HPLC**

## **Pharmaceutical Applications**

1. Pharmaceutical quality control.

## **Environmental Applications**

1. Detection of phenolic compounds in drinking water.
2. Bio-monitoring of pollutants.

## **Applications in Forensics**

1. Determination and quantification of drugs in blood, urine etc.

## **Food Safety**

1. Measurement of Quality of soft drinks and water.
2. Sugar analysis in fruit juices.

# **Thermal methods of analysis**

## Thermal methods of analysis

A group of techniques in which the **physical properties of a substance** is measured as a function of **temperature** while the substance is subjected to controlled temperature program.

The most commonly used techniques are those which measure **changes of mass or changes in energy** of a sample of a substance

# **Thermal methods of analysis**

1. Thermogravimetry Analysis (TGA)
2. Derivative Thermogravimetry (DTG)
3. Differential Thermal Analysis (DTA)
4. Differential Scanning Calorimetry (DSC)

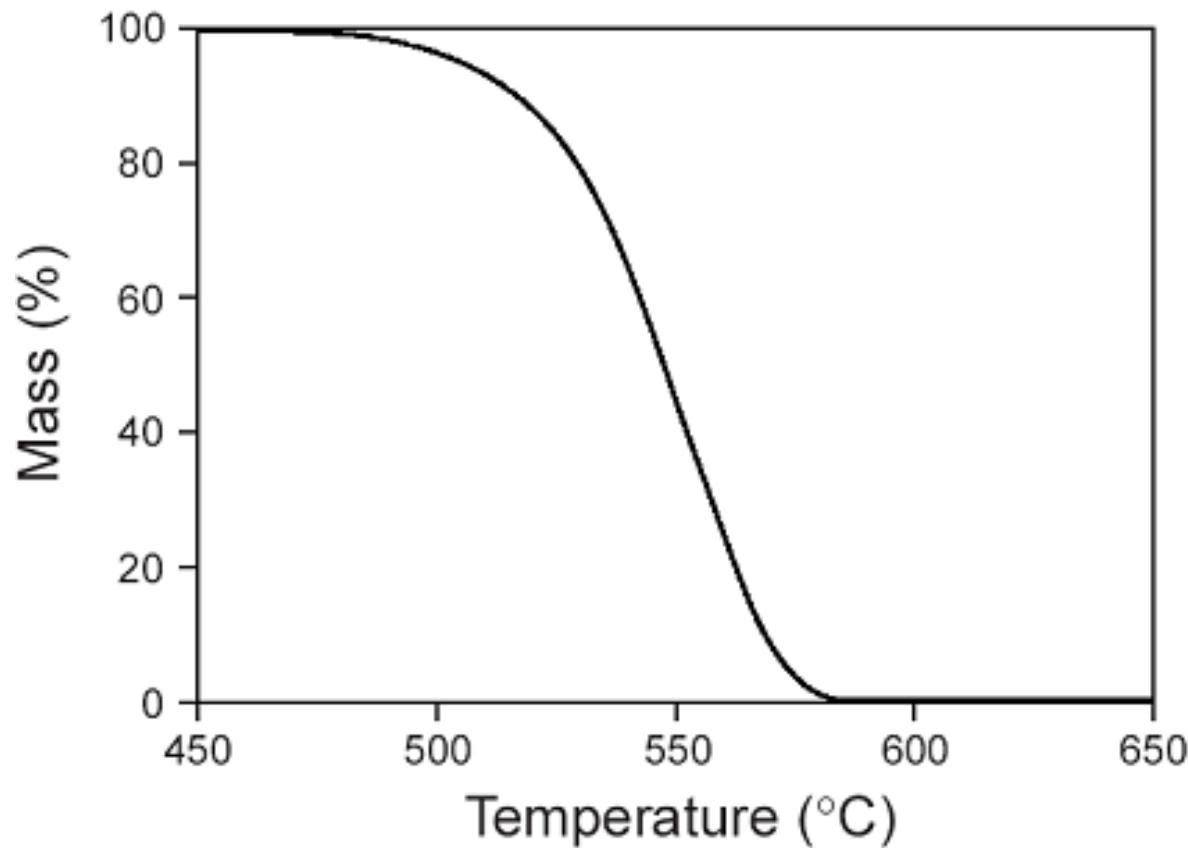
# Thermal gravimetric analysis (TGA)

A technique in which the mass of a substance is monitored as a function of temperature or time

Samples are subjected to a controlled temperature program in a controlled atmosphere



# What does a TGA thermal curve look like?



Data recorded in form of curve known as thermogram

- Change in sample composition
- Thermal stability
- Decomposition reactions and temperatures
- Absorbed moisture content
- Kinetic parameters for chemical reactions in the sample
- Purity

## Different types of TGA

***Isothermal or Static TGA:*** sample is maintained at a constant temperature for a period of time during which change in weight is recorded.

***Quasi-static TGA:*** sample is heated to a constant weight at each of a series of increasing temperature.

***Dynamic TGA:*** the sample is subjected to condition of a continuous increase in temperature at a constant heating rate, i.e., usually linear with time.

# Instrumentation

The main components of the TGA apparatus are:

**Analytical thermo balance:**

For the measurement of mass with reproducibility with the order of  $\pm 10$  micro gram

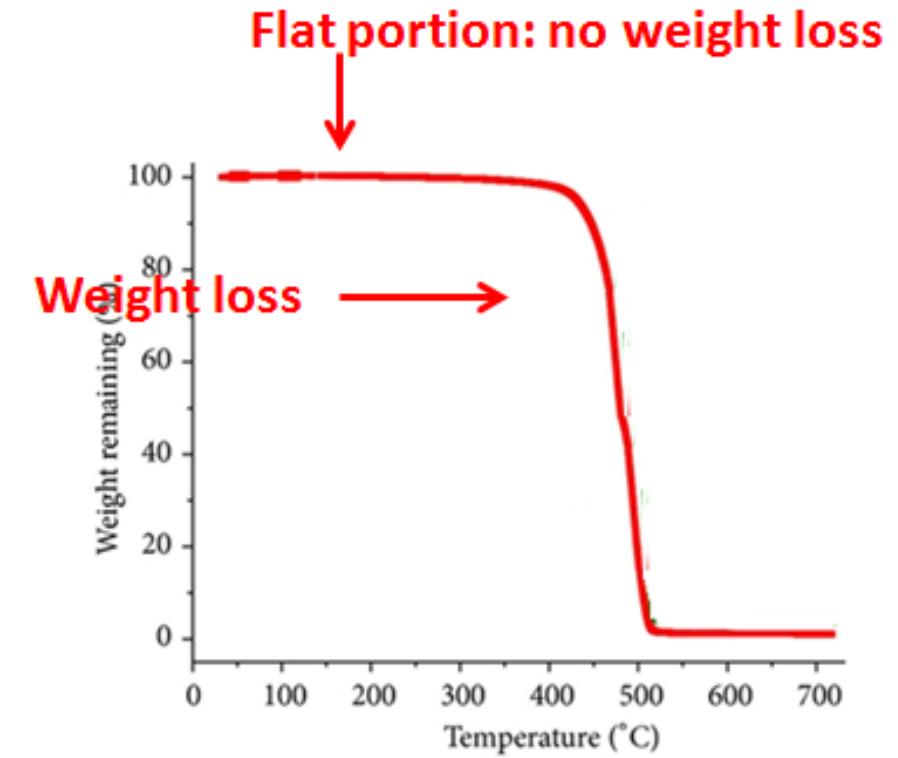
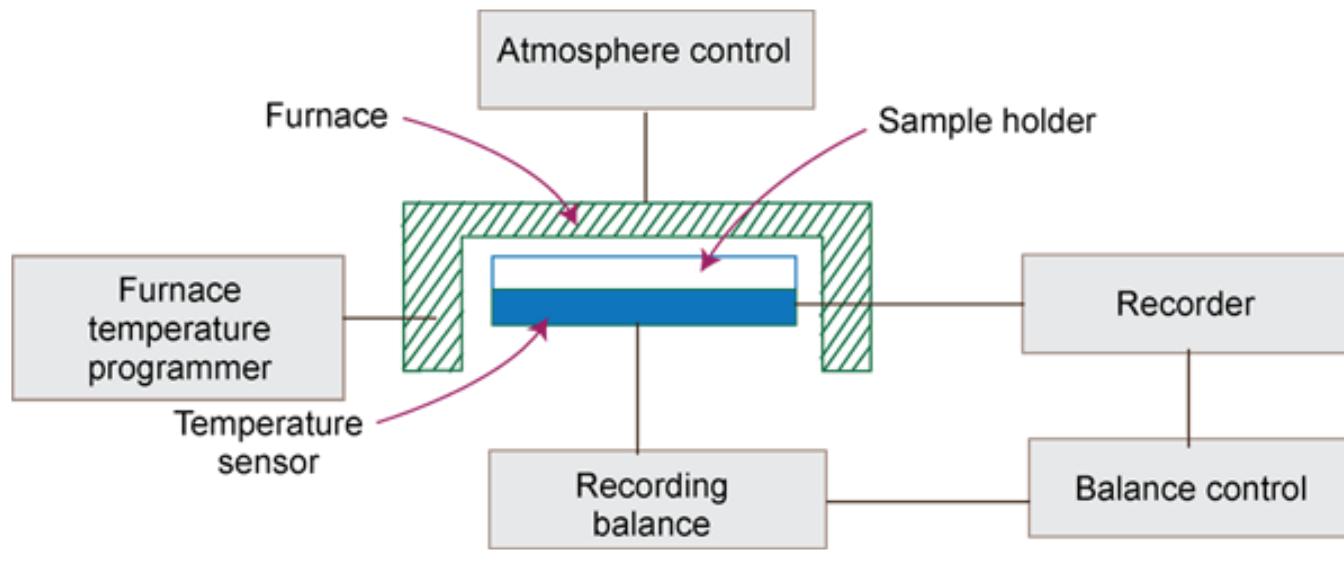
**Furnace (made up of quartz):** Programmed to increase the temperature “linearly a predetermined rate of  $0.5 - 25$  °C/min from r.t. –  $1200$  °C.

**Environment control equipment:** For providing inert atmosphere for the sample whenever desired.

**The auto sampler:** Helps to load the samples on to the microbalance.

**A recorder:** That gives a graph of ***m* (or *dm/dt*) as a function of *T*.**

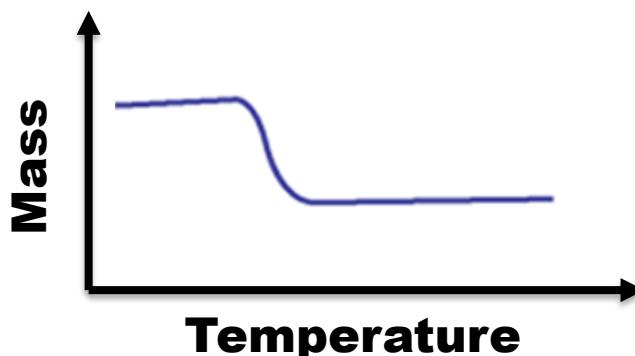
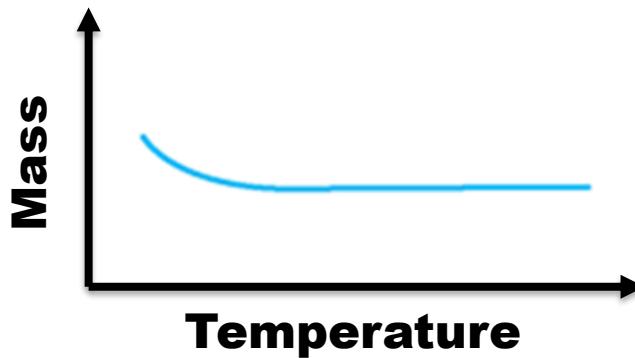
# Block diagram of TGA



**Horizontal portion** indicate there is no mass change, an indication of the thermal stability of the sample

**The slanting portion indicate** weight loss due any physical or chemical process like dehydration / formation of volatile products due to decomposition or dissociation etc.

# Types of TGA curves



## Curve 1:

No change: depicts no mass change over the entire range of temperature, the decomposition temperature is greater than the temperature range of the instrument.

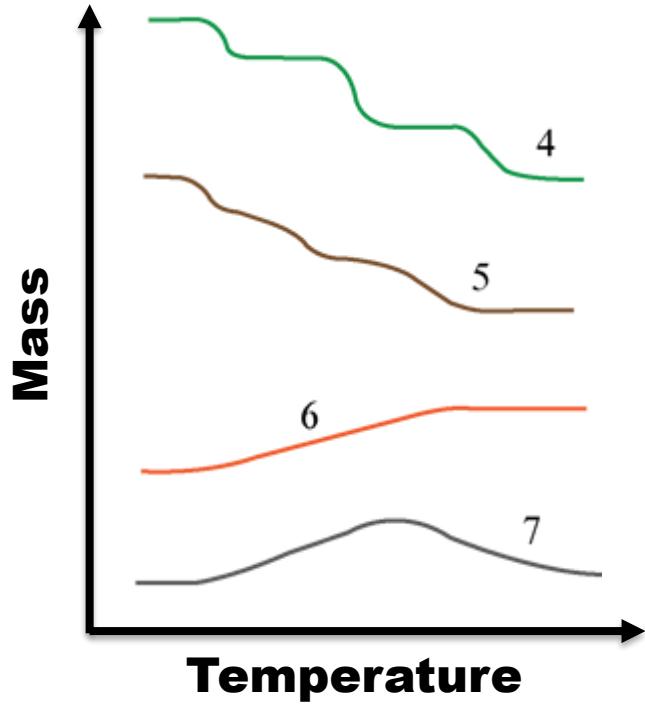
## Curve 2:

Desorption/drying: This curve shows that the mass loss is large followed by mass plateau. This is formed when evaporation of volatile product(s) during desorption, drying or polymerization takes place

## Curve 3:

Single stage decomposition: This curve is typical of single-stage decomposition temperatures having  $T_i$  and  $T_f$ .

# Types of TGA curves



**Curve 4:** Multistage decomposition: This curve reveals the multi-stage decomposition processes as a result various reactions.

**Curve 5:** Similar to 4, but either due to fast heating rate or due to no intermediates.

**Curve 6:** Atmospheric reaction: This curve shows the increase in mass. This may be due to the reactions such as surface oxidation reactions in the presence of an interacting atmosphere.

**Curve 7:** Similar to curve 6, but product decomposes at high temperatures. For example, the reaction of surface oxidation followed by decomposition of reaction product(s).

# TGA experiment: Processes that leads to weight gain and loss

Process	Weight gain	Weight loss
Adsorption or absorption	✓	
Desorption, drying		✓
Dehydration, desolvation		✓
Sublimation		✓
Vaporization		✓
Solid-state reactions (some cases)		✓
Solid-gas reactions	✓	✓
Magnetic transitions	✓	✓

# **Applications of TGA**

## **In Qualitative analysis**

Allows a **comparison of thermal stabilities** of the related materials.

**Materials Characterization/Purity:** fingerprinting of materials for identification / quality control.

## **In Quantitative analysis**

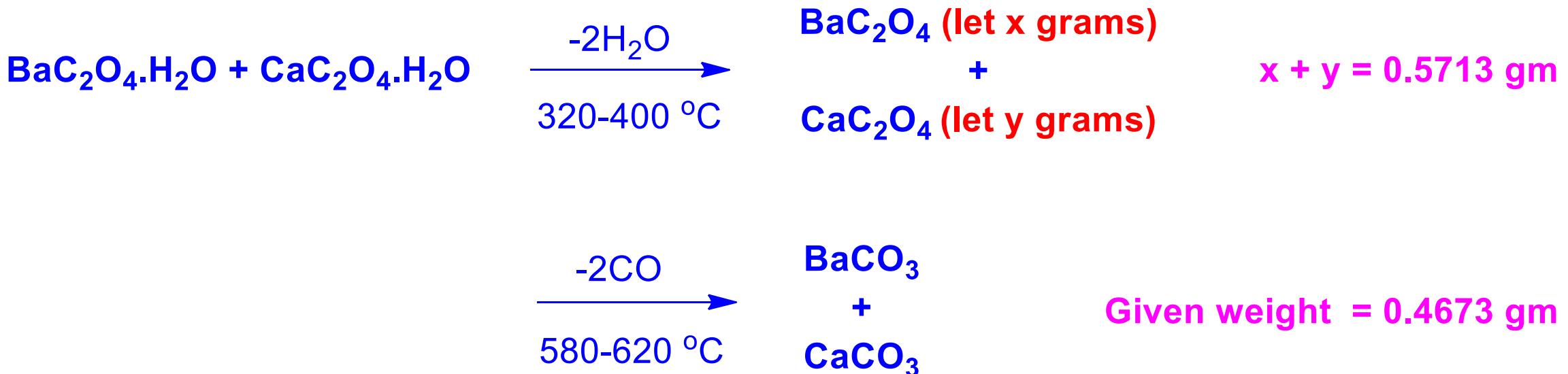
**Compositional analysis:** filler content in polymers; carbon black in oils; ash and carbon in coals, and the moisture content of many substances.

**Corrosion studies:** Study oxidation or some reactions with other reactive gases or vapors.

**It aims how much of a substance is present in the sample: e.g. how much  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  is present in a mixture.**

Q. Calcium and Barium ions were precipitated as monohydrated oxalates ( $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ). 0.6025 sample was taken and subjected to heating rate of 5 °C/min. They left a residue that weighed 0.5713 gm in 320-400 °C range and mass loss in this temperature range corresponds to the combined loss of water by monohydrated oxalate of Ca and Ba. A further loss in mass was observed in the temperature range of 580-620 °C and the left residue of  $\text{BaCO}_3$  and  $\text{CaCO}_3$  weighed 0.4673 gm.

Calculate the percentage of  $\text{Ca}^{+2}$  and  $\text{Ba}^{+2}$  ions in the sample?



We know that the molecular weight of

$$\text{BaC}_2\text{O}_4 = 225.35$$

$$\text{CaC}_2\text{O}_4 = 128.09$$

$$\text{BaCO}_3 = 197.35$$

$$\text{CaCO}_3 = 100.09$$

**no. of moles of  $\text{BaC}_2\text{O}_4$  = no. of moles of  $\text{BaCO}_3$**   
**and no. of moles of  $\text{CaC}_2\text{O}_4$  = no. of moles of  $\text{CaCO}_3$**

Thus,

$$(x/225.35) \times 197.35 + (y/128.09) \times 100.09 = 0.4673 \quad \dots \dots \rightarrow (1)$$

$$x + y = 0.5713 \text{ qm} \quad \dots \rightarrow (2)$$

## From 1 and 2;

x = 0.221389 gm of BaC<sub>2</sub>O<sub>4</sub>

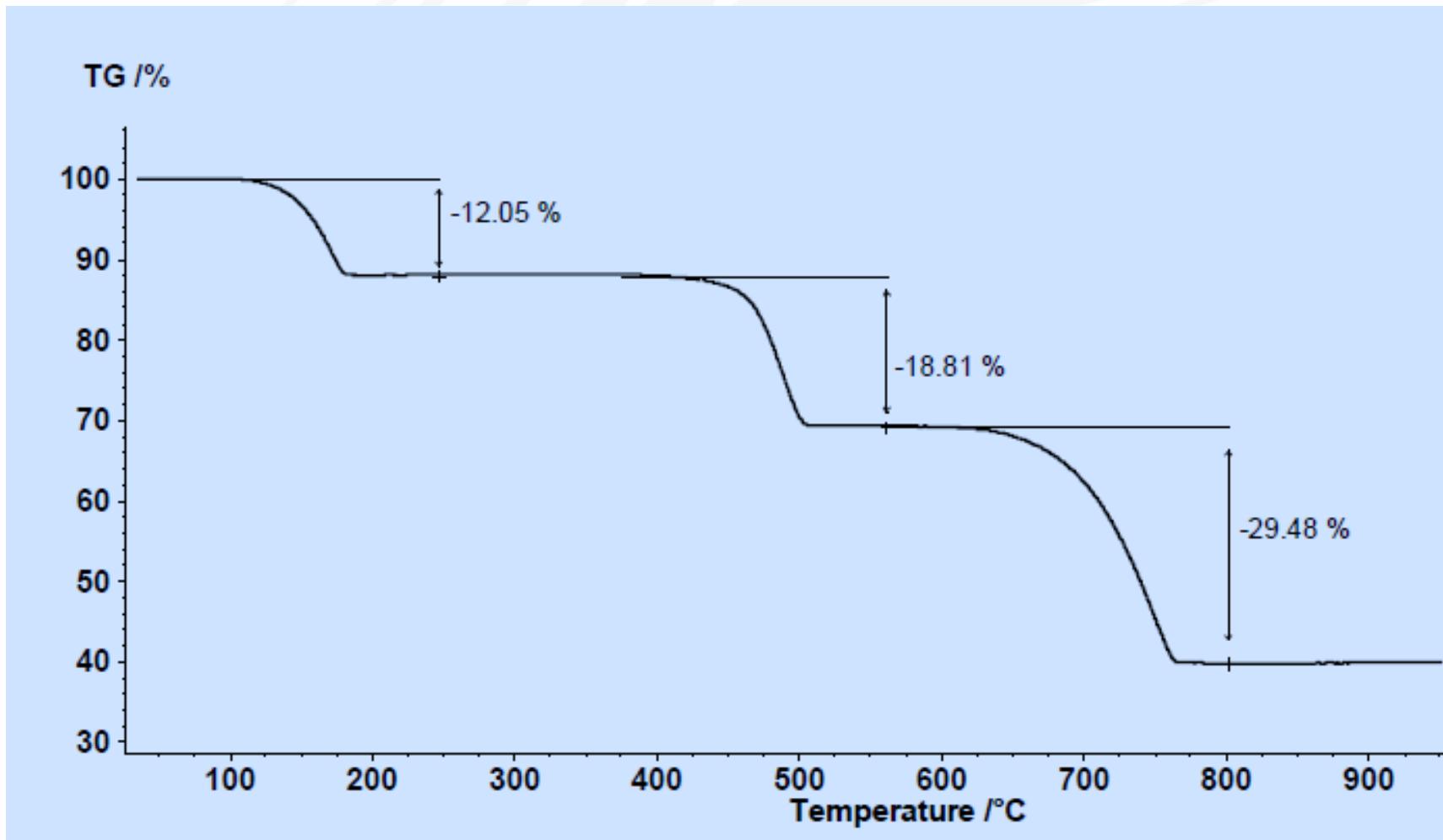
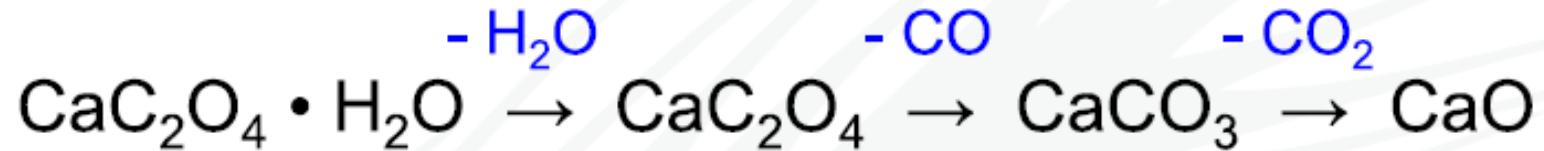
y = 0.34993 gm of CaC<sub>2</sub>O<sub>4</sub>

**Now,**

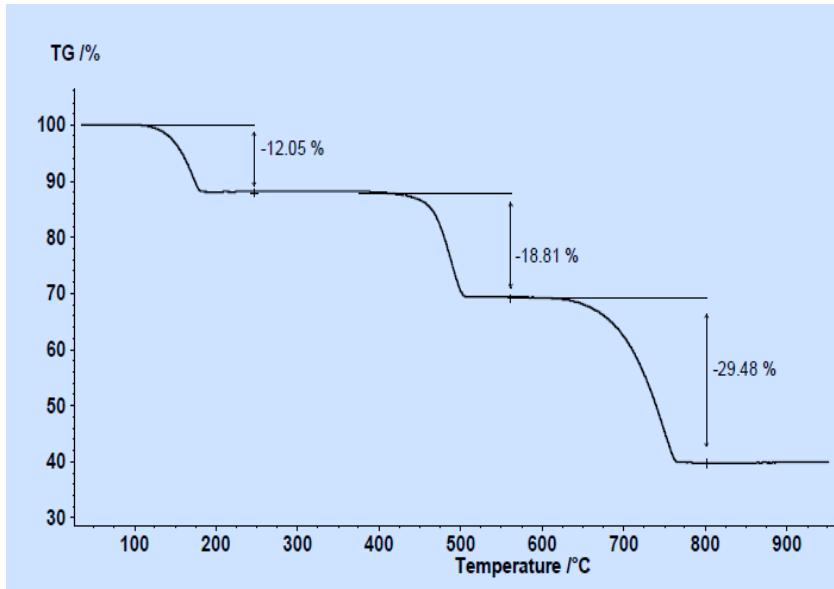
$$\begin{aligned}\text{grams of Ba} &= (137.35 \text{ (m.wt. of Ba)}) / \text{m.wt. of BaC}_2\text{O}_4) \times 0.221389 \\ &= 0.13492 \text{ gm}\end{aligned}$$

Hence the percentage of Ba =  $(0.13492/0.6025) \times 100 = 22.39\%$

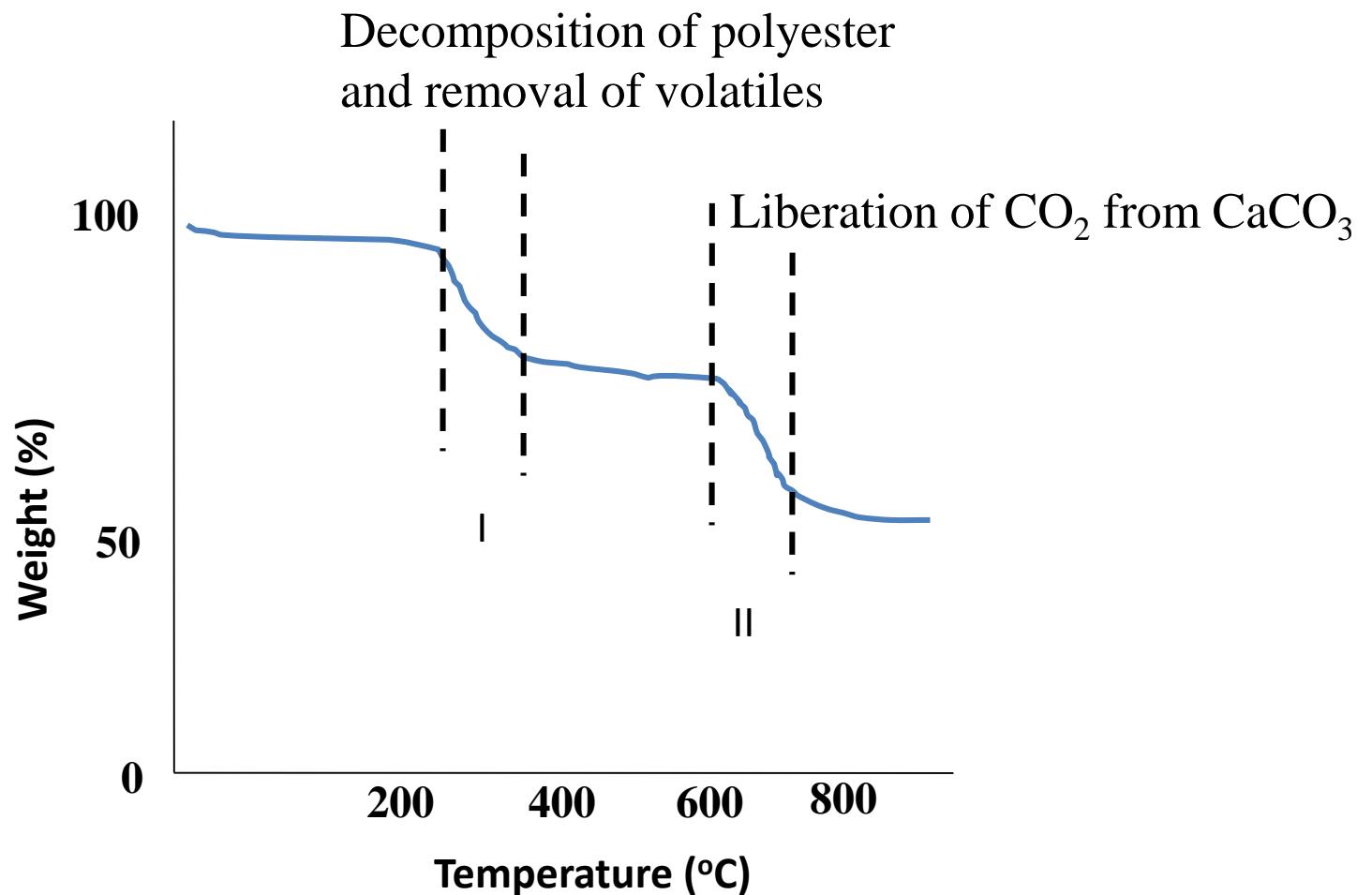
## Calcium oxalate monohydrate display three weight loss when heated



# Thermogram of calcium oxalate monohydrate



# **CaCO<sub>3</sub> in polyester can be determined by TGA curve as follows:**



$$\% \text{ of } \text{CaCO}_3 = \% \text{ of } \text{CO}_2 \frac{\text{molecular weight of } \text{CaCO}_3}{\text{molecular weight of } \text{CO}_2}$$

## **Limitations of TGA**

For TGA to be useful, only when temperature variation must bring about a change in the mass of analyte.

Thus TGA method is largely limited to decomposition and oxidation reactions and to such physical processes as vaporization, sublimation and desorption.

### **TGA method cannot be used for**

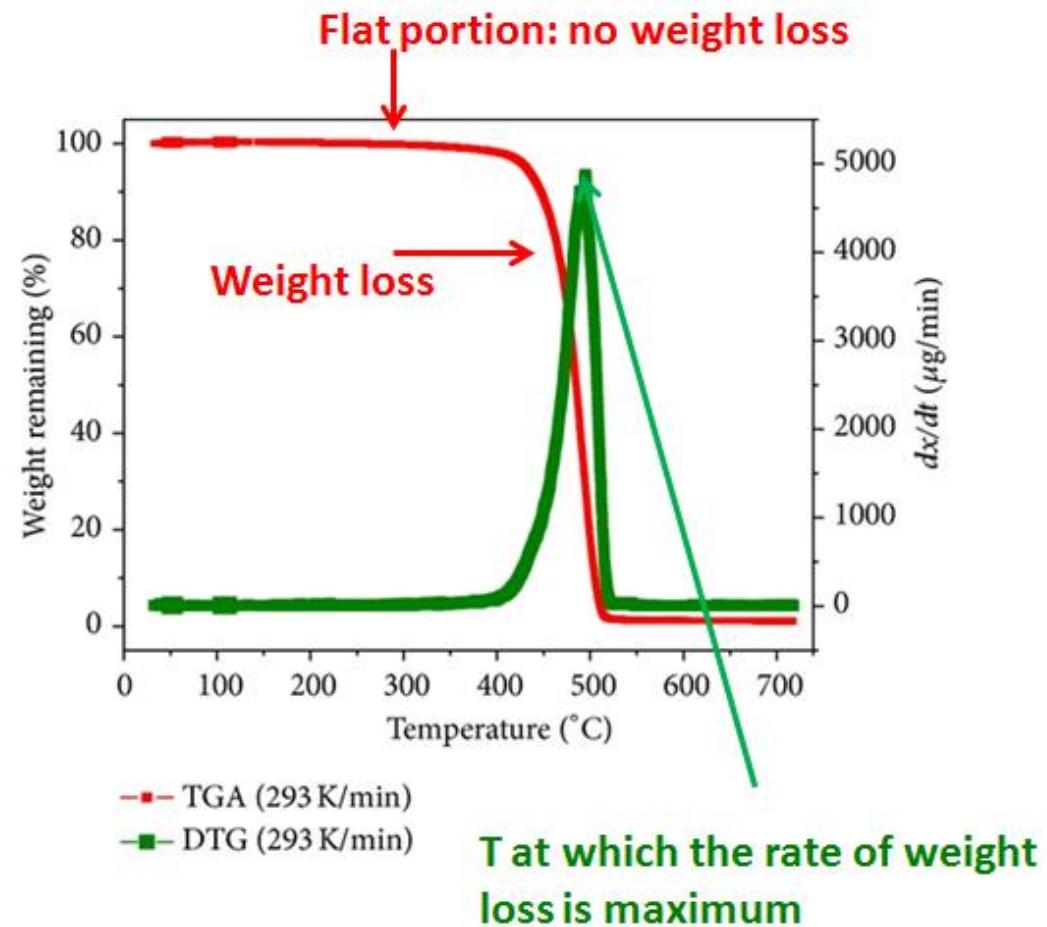
- Pure fusion reactions
- Crystalline transitions
- Glass transition and crystalline temperature of polymer
- Solid state reactions with no volatile products

### **Rhombic Sulphur ⇌ Monoclinic Sulphur**

Where there is no weight change but absorption or evolution of heat

# *Derivative Thermogravimetry (DTG)*

Plots change in mass with temperature,  $dm/dt$ , and resolves changes more clearly



# Factors that affect the results

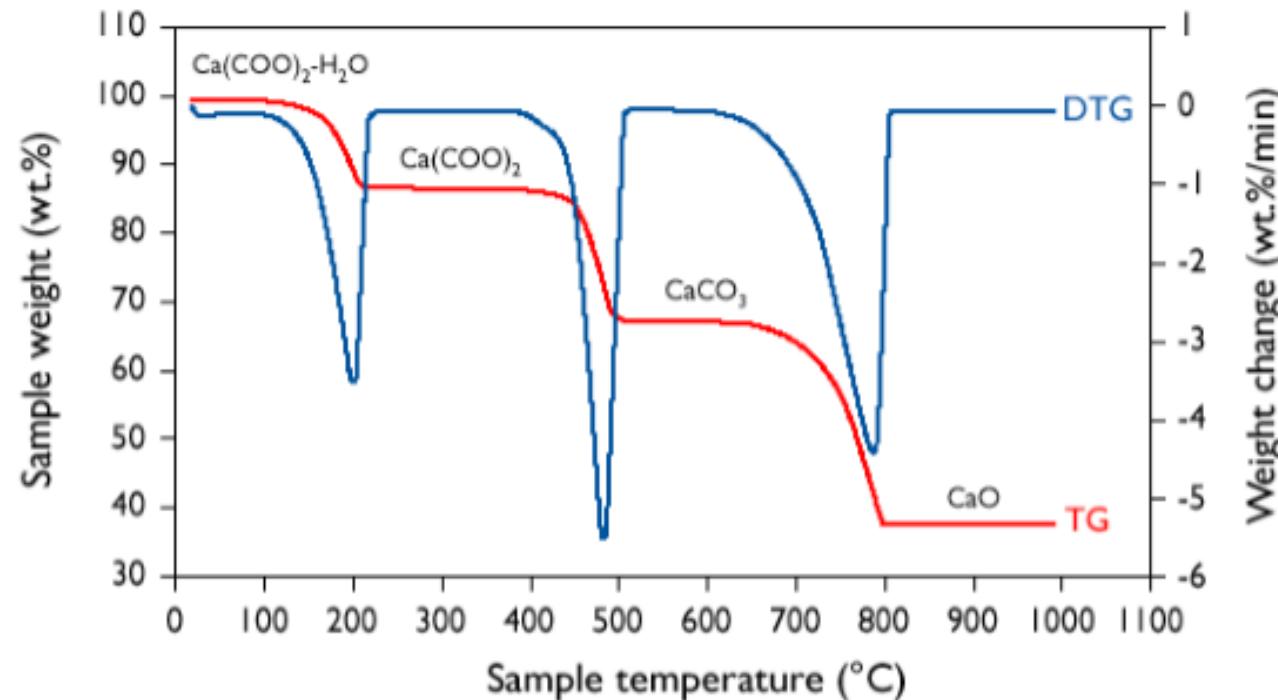
## A) INSTRUMENTAL

- Heating rate
- Furnace atmosphere and flow-rate
- Geometry of pan and material

## B) SAMPLE-RELATED

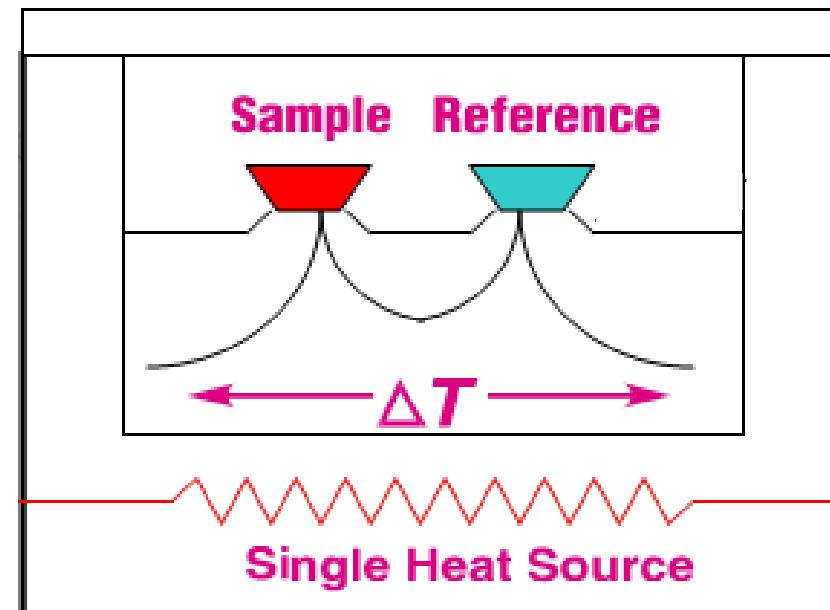
- Mass
- Particle size
- Sample history

## TGA & DTG

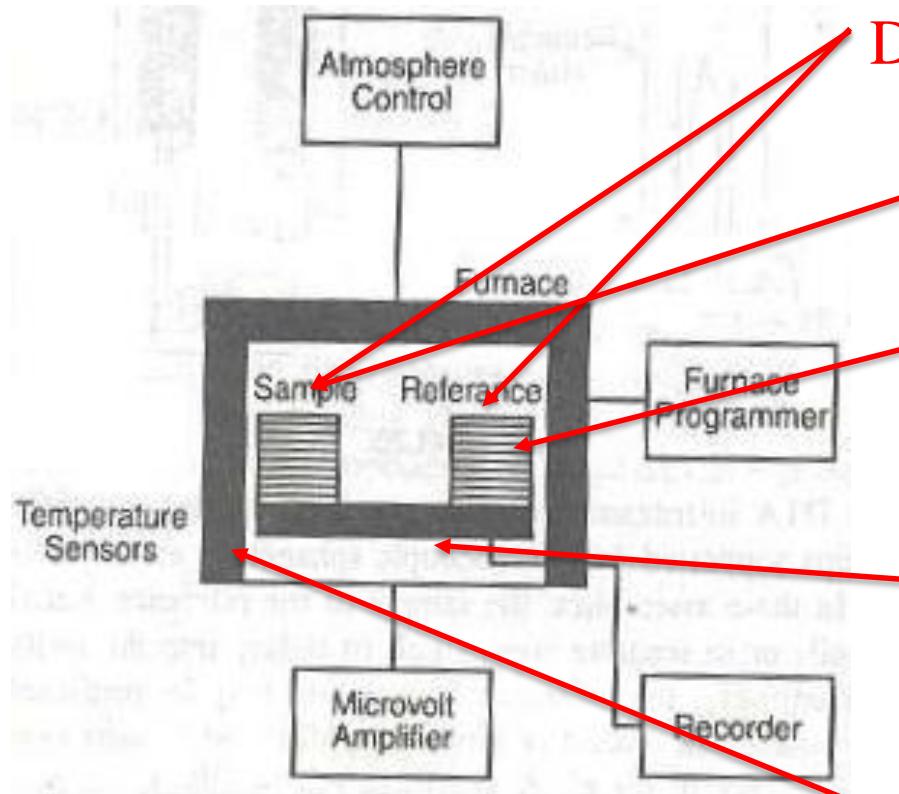


# Differential Thermal Analysis (DTA)

Measures the temperature difference between a sample and an inert reference as a function of temperature while the sample and reference is heated at a constant rate.



Glass transitions, phase changes, and melting points can be measured.



Schematic diagram of a typical DTA system

DTA contain two chambers which are ideal and symmetrical

Sample is placed in one chamber

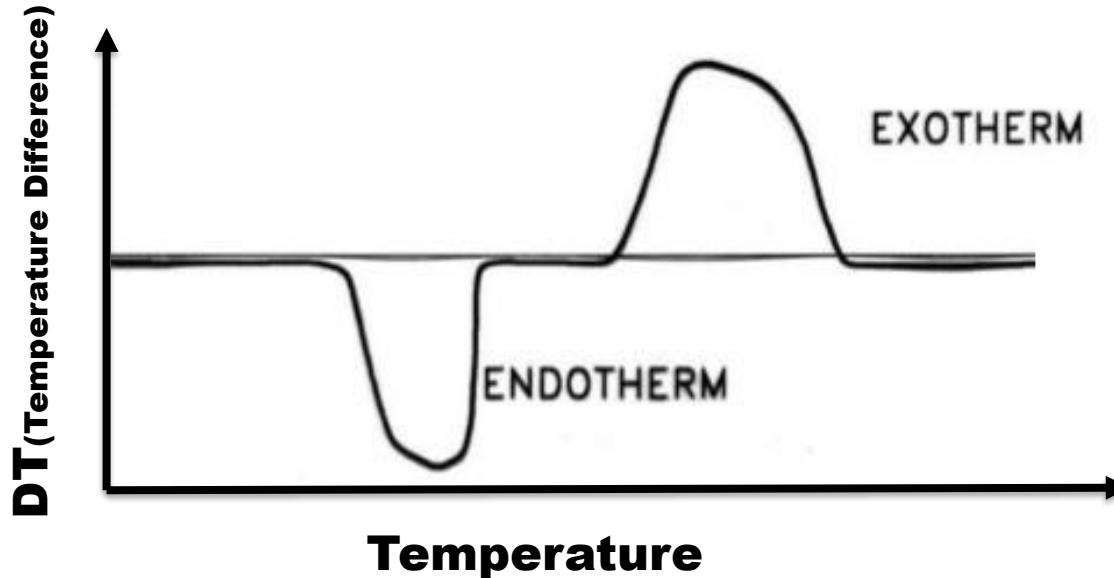
Thermally inert reference in other ( $\alpha$ -alumina)

Two chambers are controlled and connected to the same temperature sensor (usually thermocouple)

The temperature of the furnace and the two chambers are increased linearly at a rate of 5 - 12 degree per min.

Temperature difference ( $DT = Ts - Tr$ ) between the sample and reference will be recorded and plotted as a function of Temperature ( $T/Tr$ )

# Differential Thermogram: A graph with DT vs. Temp.(T)

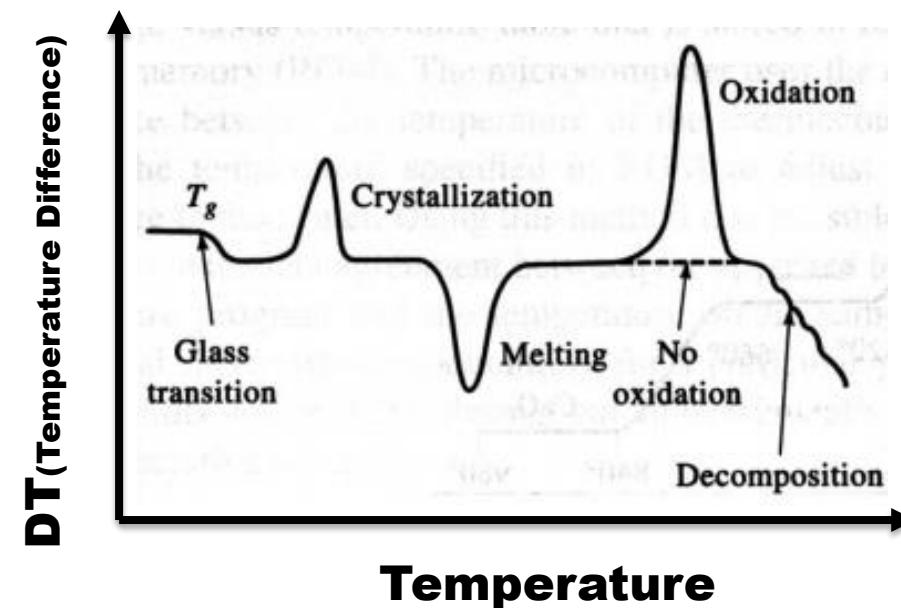


*Endothermic changes*, the peaks are below zero; eg: absorption, desorption, sublimation, fusion, vaporization

A good information can be obtained about the nature of the test sample from the **shape and sizes** of these peaks

Sharp endothermic peaks: Fusion processes or changes in crystallinity

Broad endothermic peak: Dehydration reactions



# **Applications**

## **In Analytical chemistry**

- Melting and boiling points and effect of pressure on it
- Identification of the substances (Identification of clays)

## **In Inorganic chemistry**

**Thermal stability** of inorganic compounds and complexes

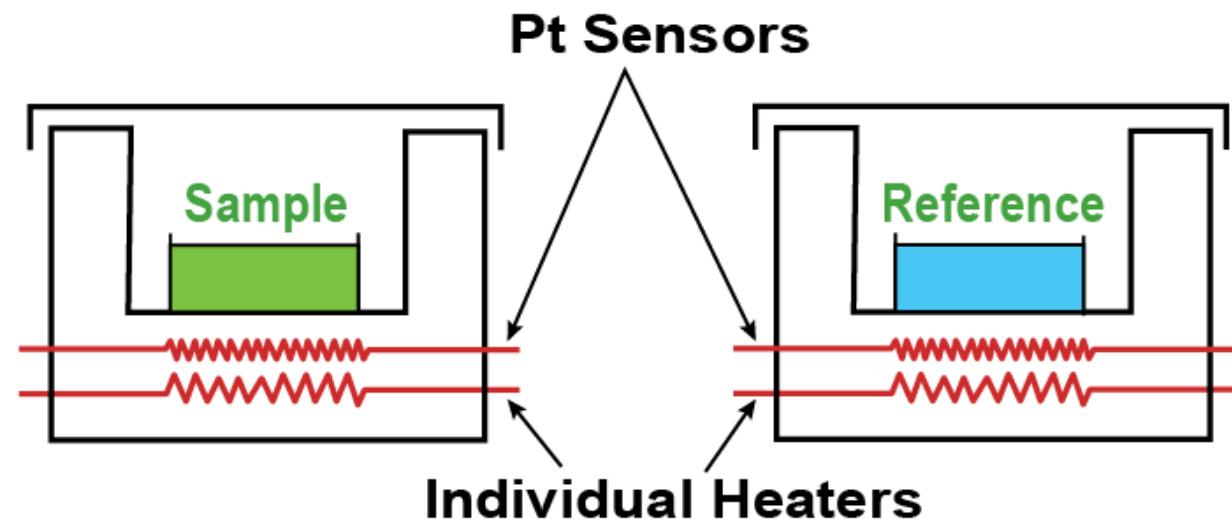
## **In Organic chemistry**

**Qualitative analysis of polymer**

mixture by analyzing the characteristic melting point of each polymer

# Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis method where **differences in heat flow into a substance and a reference** are measured as a function of sample **temperature**, while both are subjected to a controlled temperature program.



DSC measures the energy (heat) absorbed or released by a sample as a function of temperature or time

$$Q = C \Delta T \text{ where } c \text{ is the specific heat of the sample}$$

The differences in the amount of heat ( $Q$ ) required to increase the temperature ( $\Delta T$ ) of a sample and reference are measured as a function of temperature.

The reference sample should have a well defined heat capacity over the range of temperatures to be scanned and analyzed.

## The underlying principle of DSC

Both the sample and reference are maintained at nearly the same temperature throughout the experiment.

“When the sample undergoes a physical transformation (phase transitions, etc), more or less heat will be needed to flow to it as compared to the reference to maintain both of them at the same temperature”

Depends on whether the process is exothermic or endothermic

Generally the heat energy supplied to the sample is given a +ve sign.

The heat lost due to endothermic reaction is compensated by this supply

The heat energy supplied to the reference is given –ve sign

The heat gain as a consequence of exothermic reaction in the sample

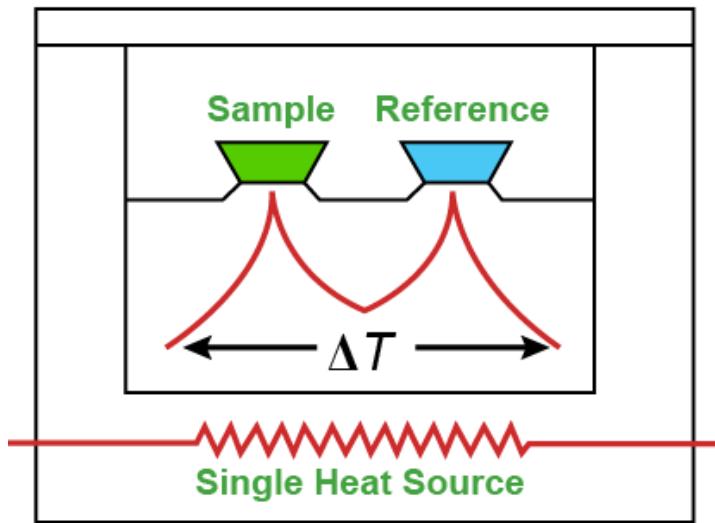
## When a solid sample melts into a liquid

It requires more heat flowing in to the sample to increase its temperature at the same rate as the reference

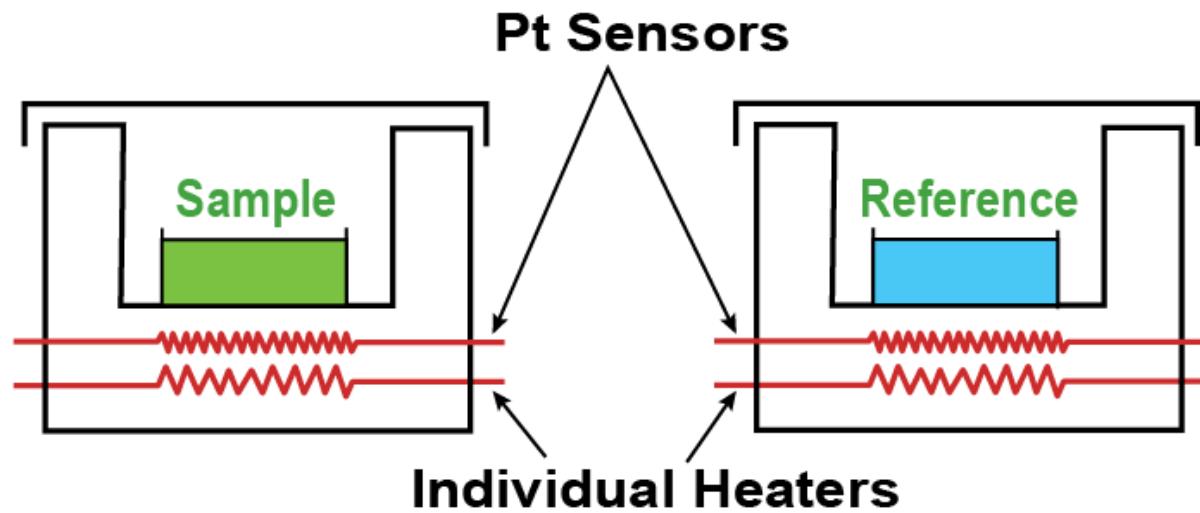
This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid

Similarly, when the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature

During a phase transition, a temperature difference (heat flux difference) between the sample and reference can be measured by means of a thermocouple



**DTA**

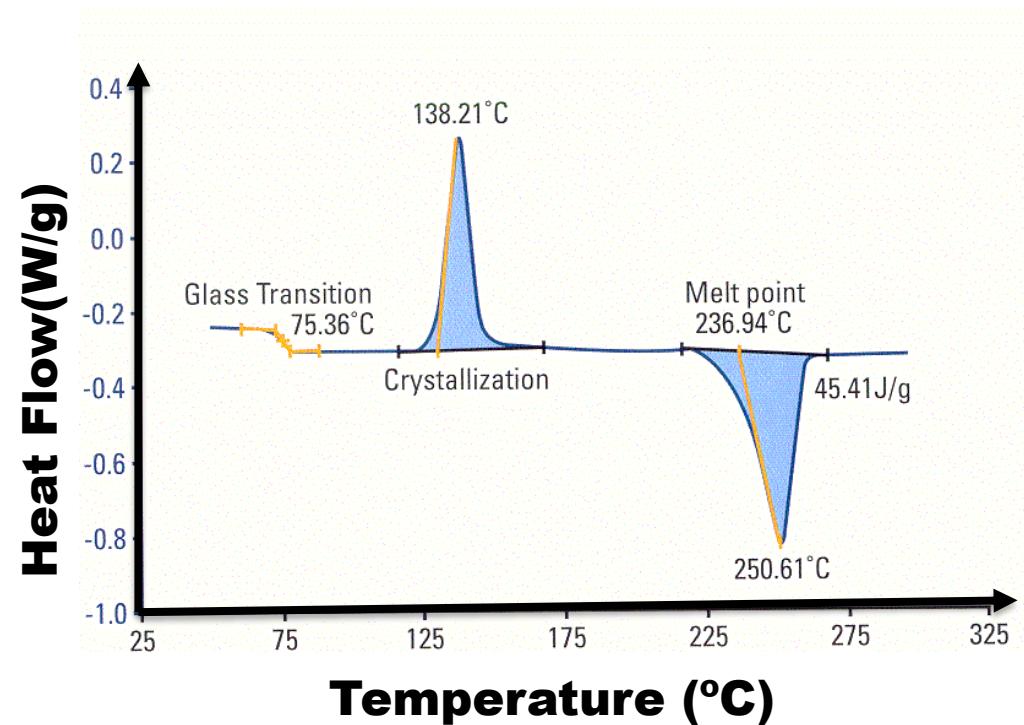


**DSC**

# DSC thermogram

DSC thermogram is similar to DTA

The differences is only with the y axis *i.e.*,  $dQ/dt$  is plotted Vs temperature



- The enthalpy change can be calculated by integrating the area under the curve.

# Applications of DSC

1. Glass transitions
2. Crystallisation time and temperature
3. Percent crystallinity
4. Heats of fusion and reactions
5. Specific heat capacity
6. Oxidative/thermal stability
7. Rate and degree of cure
8. Reaction kinetics

<b>DTA</b>	<b>DSC</b>
<ol style="list-style-type: none"> <li>1. Graph : <math>\Delta T</math> and <math>T</math></li> <li>2. Sample size= 5-20 mg</li> <li>3. Specific heat measurements are <b>not</b> accurate</li> <li>4. Calorimetric accuracy in the temperature range of 190-1000 deg c.</li> <li>5. Secondary power source is <b>not required</b></li> <li>6. The area of DTA peak is complex function of sample geometry, heat capacity and heat loses</li> <li>7. Sensitivity of measurement of heat of transition is 0.5kJ/mole</li> </ol>	<ol style="list-style-type: none"> <li>1. Graph: <math>dH/dt</math> vs <math>T</math></li> <li>2. Sample size= 2-10 mg</li> <li>3. Specific heat measurements are accurate</li> <li>4. Calorimetric accuracy in the temperature range of 170-750 deg c.</li> <li>5. Secondary power source is required</li> <li>6. The area of DSC peak is directly related to the enthalpy change occurring.</li> <li>7. Sensitivity of measurement of heat of transition is few J/mole</li> </ol>

# Basic Principle

Technique	Instrument	Parameter Measured	Drawing of the curve
Thermogravimetric Analysis (TGA)	Thermobalance	Mass	Mass <b>vs</b> temperature
Derivative Thermogravimetry (DTG)	Thermobalance	$dm/dT$	$dm/dT$ <b>vs</b> temperature
Differential Thermal Analysis (DTA)	DTA Apparatus	$\Delta T$	$\Delta T$ <b>vs</b> temperature
Differential Scanning Calorimetry (DSC)	Calorimeter	$dH/dt$	$dH/dt$ <b>vs</b> temperature

# CY1001D: Chemistry: Module 3

## Organometallic chemistry and Catalysis

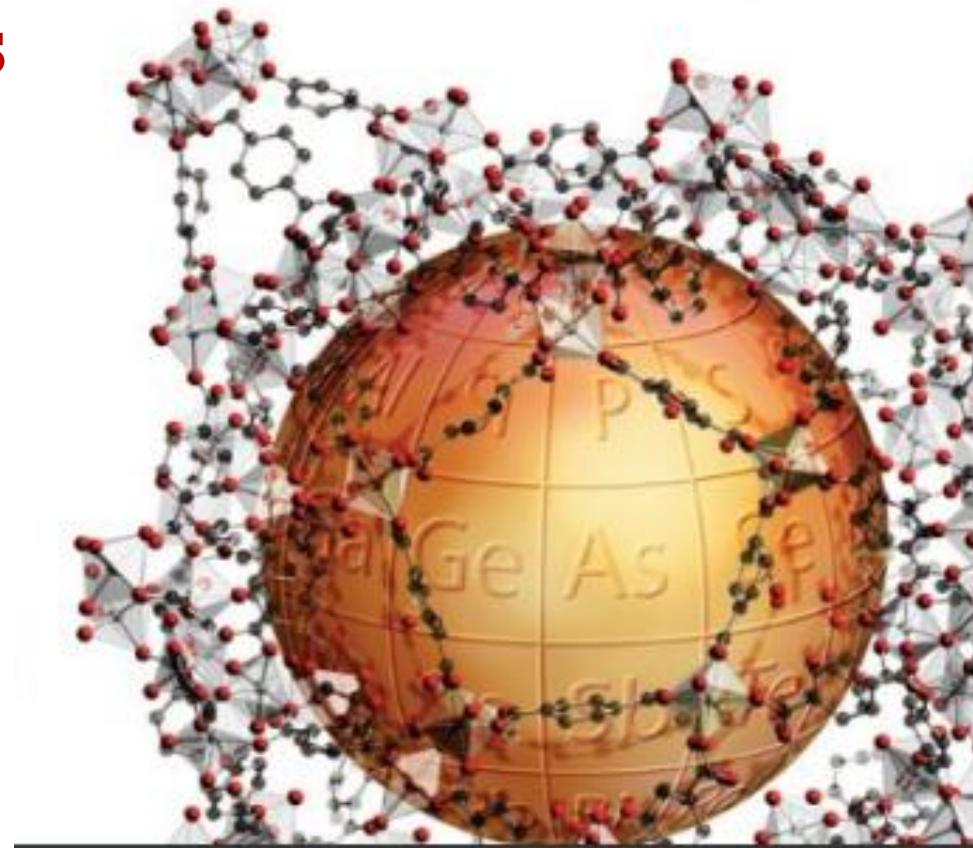
18-electron rule

Fifth Edition

Shriver & Atkins'

# Inorganic Chemistry

Atkins • Overton • Rourke • Weller • Armstrong • Hagerman



Inorganic Chemistry  
Shriver and Atkins

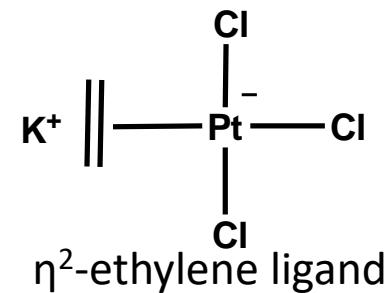
# Organometallic Chemistry

## Chemistry of Metal-Carbon bonds

- Organometallic compounds: The compounds contain one or multiples **metal-carbon bond(s)**
- The metal center in such a compound is bonded to carbon of an organic molecule  
**R-Mg-X, R-Li, Cp-Fe-Cp**

### Zeise's salt

Potassium trichloro(ethene)platinate(II)



Zeise's salt was one of the first organometallic compounds reported in the **1827** by W. C. Zeise

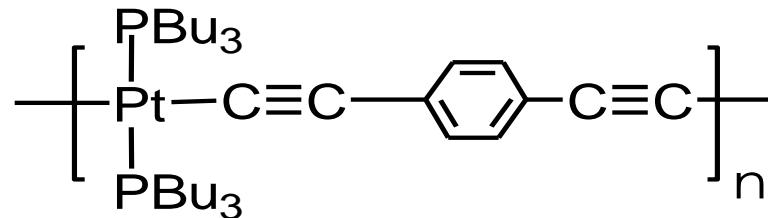
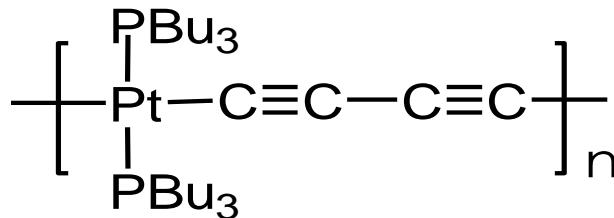
# Why Organometallic Chemistry ?

1. Useful for chemical synthesis, especially for catalytic processes  
e.g. production of fine chemicals

2. Application in material sciences

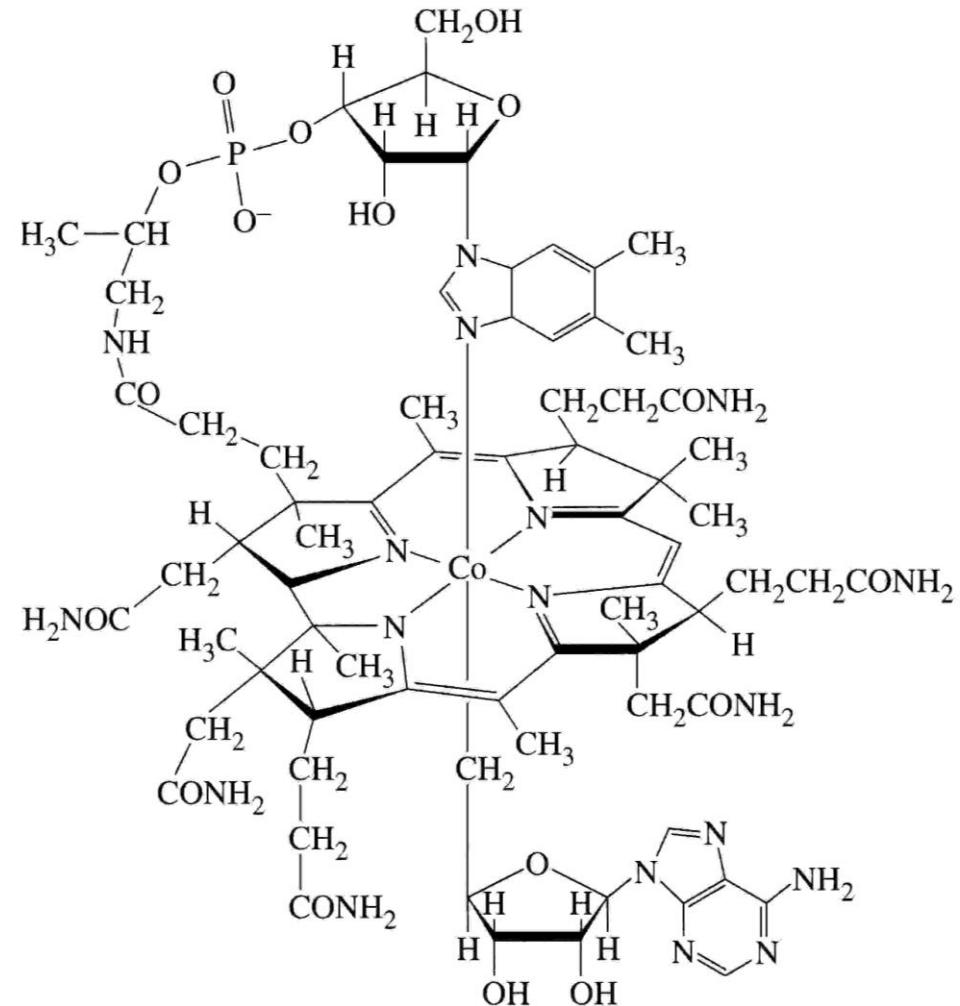
e.g. organometallic polymers

Precursors to films for coating, Luminescent materials



### 3. Biological Science

Organometallic chemistry may help us to understand some enzyme-catalyzed reactions

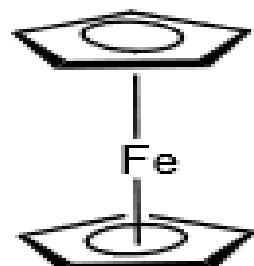


*Vitamin B<sub>12</sub>*

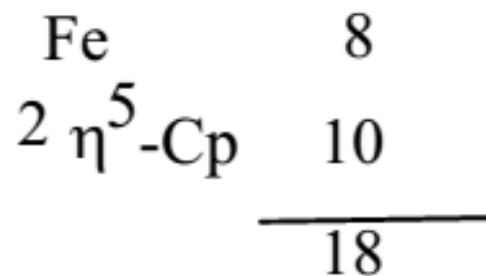
# Organometallic compounds: Bond between Metal & Carbon

## The 18-Electron rule:

Thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d electrons and the electrons supplied by the surrounding ligands equals to 18



Fe: [Ar]3d<sup>6</sup> 4s<sup>2</sup>



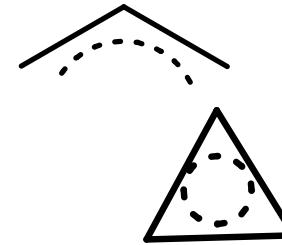
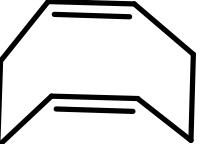
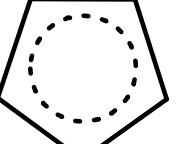
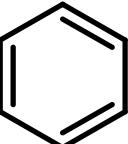
# Periodic Table of the Elements

Periodic Table of the Elements																		
1 IA 1A	2 IIA 2A	3 IIIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIIB 7B	8 VIII 8	9 VII 7A	10 VIA 6A	11 VA 5A	12 IVA 4A	13 III 3A	14 IIA 2A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A	
1 H Hydrogen $1s^1$ 1.008	2 Be Beryllium $[He]2s^2$ 9.012	3 Li Lithium $[He]2s^1$ 6.941	4 Be Beryllium $[He]2s^2$ 9.012	5 Mg Magnesium $[Ne]3s^2$ 24.305	6 V Vanadium $[Ar]3d^34s^2$ 50.942	7 Cr Chromium $[Ar]3d^54s^1$ 51.996	8 Mn Manganese $[Ar]3d^54s^2$ 54.938	9 Fe Iron $[Ar]3d^64s^2$ 55.845	10 Co Cobalt $[Ar]3d^74s^2$ 58.933	11 Ni Nickel $[Ar]3d^84s^2$ 58.693	12 Cu Copper $[Ar]3d^104s^1$ 63.546	13 Zn Zinc $[Ar]3d^104s^2$ 65.38	14 B Boron $[He]2s^22p^1$ 10.811	15 C Carbon $[He]2s^22p^2$ 12.011	16 N Nitrogen $[He]2s^22p^3$ 14.007	17 O Oxygen $[He]2s^22p^4$ 15.999	18 F Fluorine $[He]2s^22p^5$ 18.998	19 Ne Neon $[He]2s^22p^6$ 20.18
20 K Potassium $[Ar]4s^1$ 39.098	21 Ca Calcium $[Ar]3d^14s^2$ 40.078	22 Sc Scandium $[Ar]3d^14s^2$ 44.956	23 Ti Titanium $[Ar]3d^24s^2$ 47.88	24 V Vanadium $[Ar]3d^34s^2$ 50.942	25 Cr Chromium $[Ar]3d^54s^1$ 51.996	26 Mn Manganese $[Ar]3d^54s^2$ 54.938	27 Fe Iron $[Ar]3d^64s^2$ 55.845	28 Co Cobalt $[Ar]3d^74s^2$ 58.933	29 Ni Nickel $[Ar]3d^84s^2$ 58.693	30 Cu Copper $[Ar]3d^104s^1$ 63.546	31 Zn Zinc $[Ar]3d^104s^2$ 65.38	32 Ga Gallium $[Ar]3d^104s^24p^1$ 69.723	33 Ge Germanium $[Ar]3d^104s^24p^2$ 72.031	34 As Arsenic $[Ar]3d^104s^24p^3$ 74.922	35 Se Selenium $[Ar]3d^104s^24p^4$ 78.971	36 Br Bromine $[Ar]3d^104s^24p^5$ 79.904	37 Kr Krypton $[Ar]3d^104s^24p^6$ 84.79	
38 Rb Rubidium $[Kr]5s^1$ 84.468	39 Sr Strontium $[Kr]4d^15s^2$ 87.62	40 Y Yttrium $[Kr]4d^25s^2$ 88.906	41 Zr Zirconium $[Kr]4d^25s^1$ 91.224	42 Nb Niobium $[Kr]4d^55s^1$ 92.908	43 Mo Molybdenum $[Kr]4d^55s^2$ 95.95	44 Tc Technetium $[Kr]4d^55s^2$ 98.907	45 Ru Ruthenium $[Kr]4d^75s^1$ 101.07	46 Rh Rhodium $[Kr]4d^9$ 102.908	47 Pd Palladium $[Kr]4d^10$ 106.42	48 Ag Silver $[Kr]4d^105s^1$ 107.868	49 Cd Cadmium $[Kr]4d^105s^2$ 112.414	50 In Indium $[Kr]4d^105s^25p^1$ 114.818	51 Sn Tin $[Kr]4d^105s^25p^3$ 118.711	52 Te Tellurium $[Kr]4d^105s^25p^4$ 121.760	53 I Iodine $[Kr]4d^105s^25p^5$ 126.904	54 Xe Xenon $[Kr]4d^105s^25p^6$ 131.24		
55 Cs Cesium $[Xe]6s^1$ 132.905	56 Ba Barium $[Xe]6s^2$ 137.328	57-71 Hf Hafnium $[Xe]4f^145d^26s^2$ 178.49	72 Ta Tantalum $[Xe]4f^145d^46s^2$ 180.948	73 W Tungsten $[Xe]4f^145d^66s^2$ 183.84	74 Re Rhenium $[Xe]4f^145d^66s^2$ 186.207	75 Os Osmium $[Xe]4f^145d^96s^2$ 190.23	76 Ir Iridium $[Xe]4f^145d^96s^2$ 192.217	77 Pt Platinum $[Xe]4f^145d^106s^1$ 195.085	78 Au Gold $[Xe]4f^145d^106s^1$ 196.967	79 Hg Mercury $[Xe]4f^145d^106s^2$ 200.592	80 Tl Thallium $[Xe]4f^145d^106s^25p^1$ 204.383	82 Pb Lead $[Xe]4f^145d^106s^25p^3$ 207.2	83 Bi Bismuth $[Xe]4f^145d^106s^26p^3$ 208.980	84 Po Polonium $[Xe]4f^145d^106s^26p^4$ 209.987	85 At Astatine $[Xe]4f^145d^106s^26p^5$ 222.01			
87 Fr Francium $[Xe]6s^1$ 223.020	88 Ra Radium $[Xe]6s^2$ 226.025	89-103 Rf Rutherfordium $[261]$ 104 Db Dubnium $[262]$ 105 Sg Seaborgium $[266]$ 106 Bh Bohrium $[264]$ 107 Hs Hassium $[269]$ 108 Mt Meitnerium $[268]$ 109 Ds Darmstadtium $[269]$ 110 Rg Roentgenium $[272]$ 111 Cn Copernicium $[277]$ 112 Uut Ununtrium $[289]$ 113 Fl Flerovium $[289]$ 114 Uup Ununpentium $[289]$ 115 Lv Livermorium $[288]$ 116 Uus Ununoctium $[288]$ 117 Uuo Ununseptium $[288]$ 118 Uuo Ununoctium $[288]$	13 III 3A	14 IV 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A										

## Lanthanide Series

## Actinide Series

# Electron counting for common ligands: Neutral ligand method

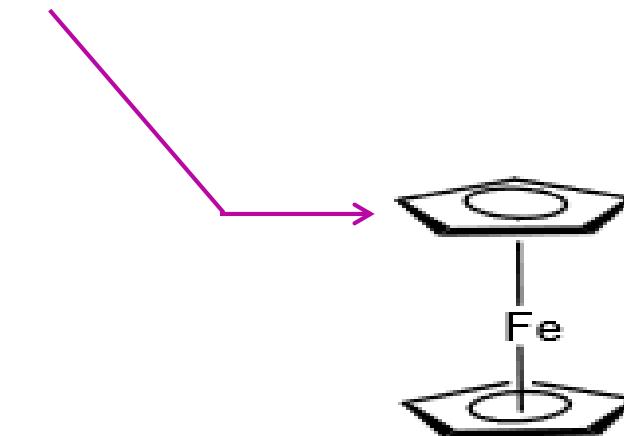
<u>Ligand</u>	<u>Name</u>	<u>e<sup>-</sup> count</u>	
CO	Carbonyl	2	
H <sub>2</sub> C=CH <sub>2</sub>	Ethylene	2	
$\eta^3\text{-C}_3\text{H}_5 \equiv$		$\pi$ -allyl	3
		Cyclopropenyl	3
		Butadiene	4
		1,3-cyclooctadiene(COD)	4
		Cyclobutadiene	4
$\eta^5\text{-C}_5\text{H}_5 \equiv$		Cyclopentadienyl	5
$\eta^6\text{-C}_6\text{H}_6 \equiv$		Benzene	6

## Hapticity ( $\eta$ ):

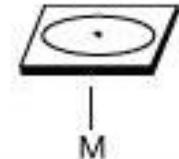
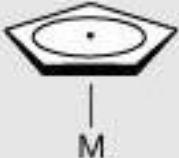
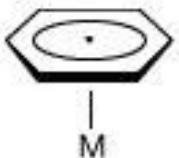
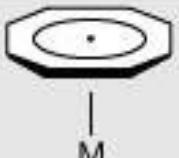
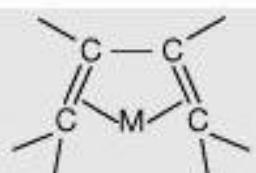
Hapticity is the coordination of a ligand to a metal center via an uninterrupted and contiguous series of atoms

The hapticity of a ligand is described with the Greek letter  $\eta$  ('eta').

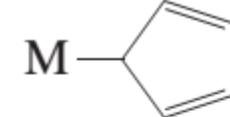
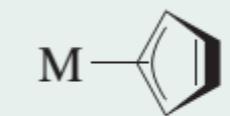
**$\eta^5$  describes a ligand** that coordinates through **5 neighboring atoms**

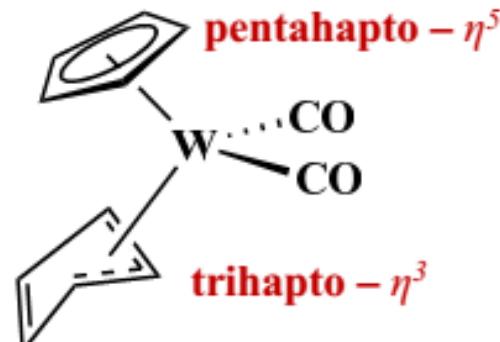


# Common organic ligands and their heptacyt

available electrons*	hapticity†	ligand	metal-ligand‡, § structure	available electrons*	hapticity†	ligand	metal-ligand‡, § structure	
1	$\eta^1$	methyl, alkyl $\text{CH}_3, \text{CH}_2\text{R}$	$\text{M}-\text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$	4	$\eta^4$	cyclobutadiene $\text{C}_4\text{H}_4$		
2	$\eta^1$	alkylidene (carbene)	$\text{M}=\text{C} \begin{array}{l} \diagup \\ \diagdown \\ \text{R} \end{array}$	5 (3) (1)	$\eta^5$ $\eta^3$ $\eta^1$	cyclopentadienyl $\text{C}_5\text{H}_5 (\text{Cp})$		
2	$\eta^2$	alkene $\text{H}_2\text{C}=\text{CH}_2$	$>\text{C}=\text{C}< \begin{array}{l} \\ \diagup \\ \text{M} \end{array}$	6	$\eta^6$	benzene $\text{C}_6\text{H}_6$		
3	$\eta^3$	$\pi$ -allyl $\text{C}_3\text{H}_5$	$\begin{array}{c}   \\ >\text{C}=\text{C}< \\   \\ \text{M} \end{array}$	8 (6) (4)	$\eta^8$ $\eta^6$ $\eta^4$	cyclooctatetraene $\text{C}_8\text{H}_8 (\text{cot})$		
3	$\eta^1$	alkylidyne (carbyne) $\text{C}-\text{R}$	$\text{M}\equiv\text{C}-\text{R}$	*For neutral ligands. †The number of carbon atoms attached to a metal. ‡For the first six entries hydrogen atoms are indicated by —, R is an organic group such as $\text{CH}_3$ . §For the cyclic ligands (the last four entries) each vertex represents a $\text{C}-\text{H}$ .				
4	$\eta^4$	1,3-butadiene $\text{C}_4\text{H}_6$						

# Variable Hapticity

1	$\eta^1\text{-C}_5\text{H}_5$	Monohaptocyclopentadienyl	
3	$\eta^3\text{-C}_5\text{H}_5$	Trihaptocyclopentadienyl	
5	$\eta^5\text{-C}_5\text{H}_5$	Pentahaptocyclopentadienyl	

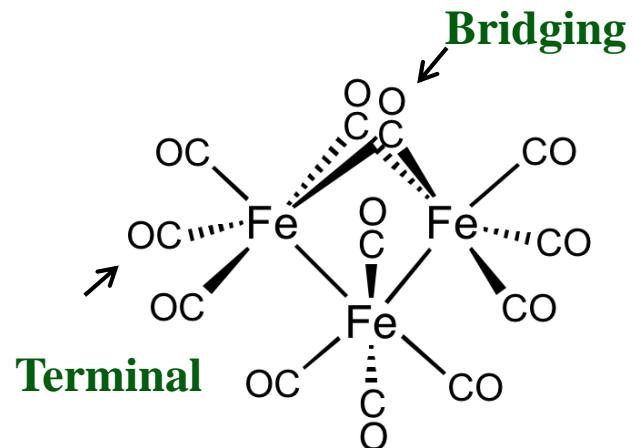


W:	<b>6</b>
2CO:	<b>4</b>
$\eta^5\text{-Cp}:$	<b>5</b>
$\eta^3\text{-Cp}:$	<b>3</b>
<b>Total :</b>	
	<b>18</b>

W: [Xe] 4f<sup>14</sup> 5d<sup>4</sup> 6s<sup>2</sup>

## Bridging ligands:

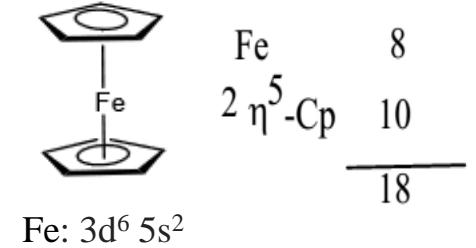
A ligand that connects two or more atoms, usually metal ions is considered as bridging ligand and described with the Greek letter (' $\mu$ ').



Carbonyl group can also bridge between two metals  
Where they can be seen as one electron each to the two metals

## 18 electron counting: neutral-ligand method

Each metal atom and ligand is treated as neutral



Count all valence electrons of the metal atom and all the electrons donated by the ligands

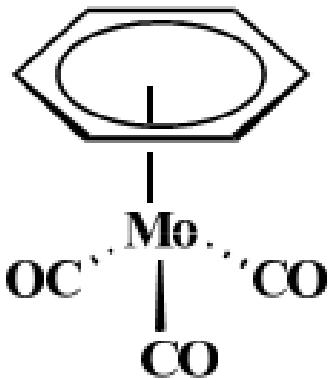
If the complex is charged, simply add or subtract the appropriate number of electrons to the total.

**Key point:** All ligands are treated as neutral and are categorized according to how many electrons they are considered to donate.

# 18 electron counting for common ligands: neutral ligand method

-H, -Cl, -Br, -I, -OH, -OR, -CN, -CH <sub>3</sub> , -CR <sub>3</sub>	1
CO, PR <sub>3</sub> , NH <sub>3</sub> , H <sub>2</sub> O	2
=O, =S,	2
=CRR' (carbene), H <sub>2</sub> C=CH <sub>2</sub>	2
≡CR (carbyne)	3
η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> (π-allyl)	3
Ethylenediamine(en)	4
Bipyridine(bipy)	4
Butadiene, cyclobutadiene, 1,3-cyclooctadiene(COD)	4
η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> (Cyclopentadienyl)	5
η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> (Benzene)	6
η <sup>7</sup> -C <sub>7</sub> H <sub>7</sub> (cycloheptatrienyl)	7

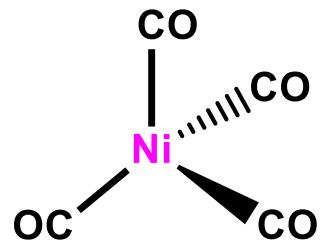
Mo: [Kr]4d<sup>5</sup> 5s<sup>1</sup>



Mo : 6  
3CO: 6  
 $1(C_6H_6):$  6  

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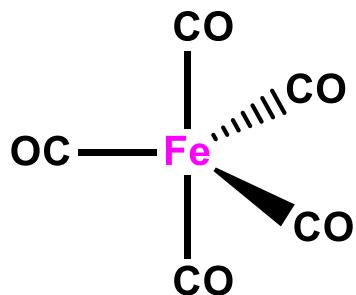
Total : 18



Ni : 10  
4CO: 8  

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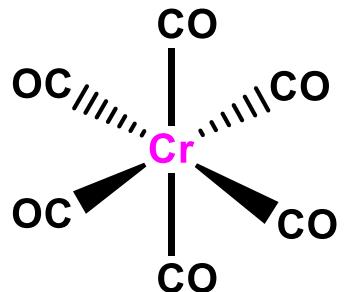
Total : 18



Fe : 8  
5CO: 10  

---

Total : 18

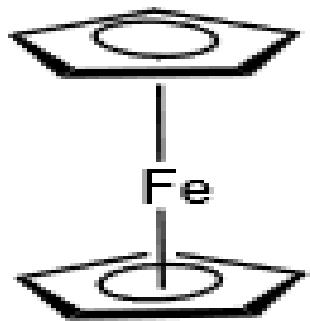


Cr : 6  
6CO: 12  

---

Total : 18

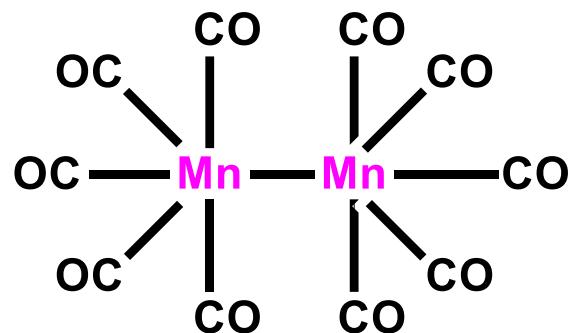
Ni: [Ar]3d<sup>8</sup> 5s<sup>2</sup>  
Fe: [Ar]3d<sup>6</sup> 4s<sup>2</sup>  
Cr: [Ar]3d<sup>5</sup> 4s<sup>1</sup>



$$\begin{array}{rcl}
 \text{Fe} & : & 8 \\
 2 \times \eta^5\text{Cp} & : & 10 \\
 \hline
 \text{Total} & : & 18
 \end{array}$$

Fe: [Ar]3d<sup>6</sup> 4s<sup>2</sup>

**Ferrocene:** Iron is sandwich between two  $\eta^5$ cyclopentadienyl ligand



Mn: 3d<sup>5</sup> 4s<sup>2</sup>

$$\begin{array}{rcl}
 \text{Mn} & : & 7 \\
 5\text{CO} & : & 10 \\
 1\text{M-M} & : & 1 \\
 \hline
 \text{Total} & : & 18
 \end{array}$$

$$\begin{array}{rcl}
 2 \times \text{Mn} & : & 14 \\
 2 \times 5 \text{ CO} & : & 20 \\
 2 \times \text{M-M} & : & 2 \\
 \hline
 \text{Total} & : & 36
 \end{array}$$

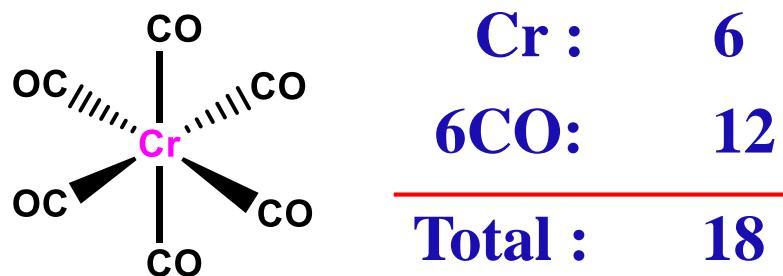
e count for each metal =  $\frac{36}{2} = 18$

# 18-electrons rule: Stability of metal complex

Cr: [Ar]3d<sup>5</sup> 4s<sup>1</sup>



A Cr atom has 6 electrons outside its Noble gas core. Each CO is considered to act as a donor of 2 electrons. The total electrons count is therefore:



Cr(CO)<sub>6</sub> is therefore considered an 18 electron complex thermally stable and can be sublimed without decomposition

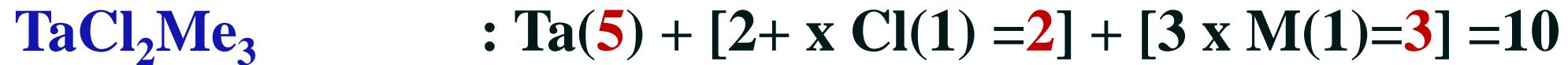
On the other hand, Cr(CO)<sub>5</sub>, a 16-electron species and Cr(CO)<sub>7</sub>, a 20-electron species, are much less stable and are known only as transient species.

Similarly, Cr(CO)<sub>6</sub><sup>+</sup> having 17 electrons and Cr(CO)<sub>6</sub><sup>-</sup> having 19-electrons are far less stable than the 18-electron Cr(CO)<sub>6</sub>.

## Scope of 18 electron rule for d-block organometallic compounds

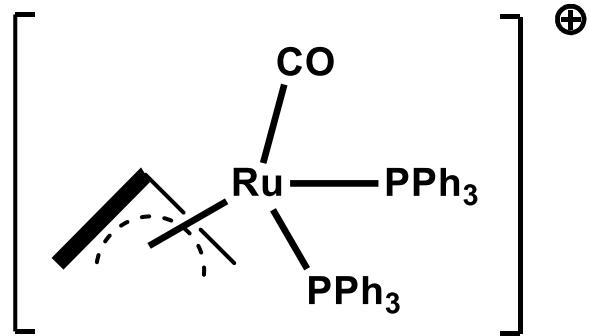
Usually less than 18 electrons			Usually 18 electrons			16 or 18	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

## Exceptions to the 18 electron rule



Zr: [Kr]4d<sup>2</sup>5s<sup>2</sup>    Ta: 4f<sup>14</sup>5d<sup>3</sup>6s<sup>2</sup>    W: [Xe] 4f<sup>14</sup> 5d<sup>4</sup>6s<sup>2</sup>    Pt: [Xe] 4f<sup>14</sup> 5d<sup>9</sup> 6s<sup>1</sup>    Ir: 4f<sup>14</sup> 5d<sup>7</sup> 6s<sup>2</sup>    Rh: [Kr]4d<sup>8</sup>5s<sup>1</sup>

# Electron counting for ionic complex



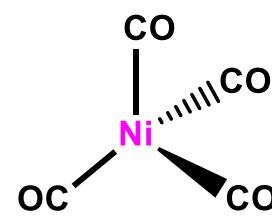
Ru:	8
$\eta^3\text{-allyl}$ :	3
2x PPh <sub>3</sub> :	4
CO:	2
Charge:	-1
<hr/>	
Total :	16

Ru: [Kr]4d<sup>7</sup> 5s<sup>1</sup>

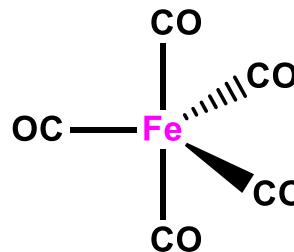
## Exception to 18 electron rule

- Square planar organometallic complexes of the late transition metals (16e)
- Some organometallic complexes of early transition metals (e.g.  
 $\text{Cp}_2\text{TiCl}_2$ ,  $\text{WMe}_6$ ,  $\text{Me}_2\text{NbCl}_3$ ,  $\text{CpW}(=\text{O})\text{Cl}_3$ )
- Sterically demanding bulky ligands force complexes to have less than 18 e

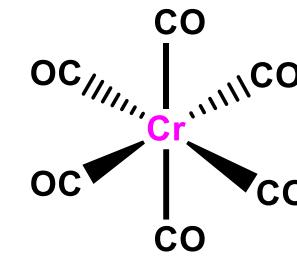
# Structure of metal carbonyl



$$\begin{array}{rcl} \text{Ni :} & 10 \\ \text{4CO:} & 8 \\ \hline \text{Total :} & 18 \end{array}$$



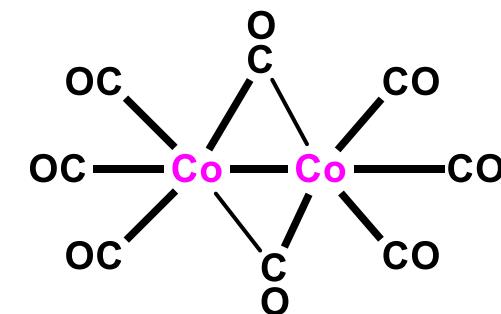
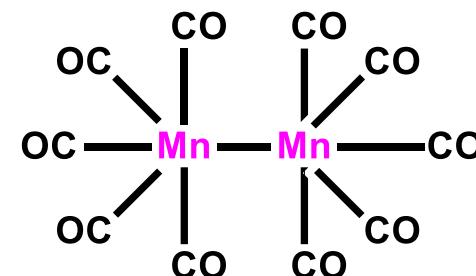
$$\begin{array}{rcl} \text{Fe :} & 8 \\ \text{5CO:} & 10 \\ \hline \text{Total :} & 18 \end{array}$$



$$\begin{array}{rcl} \text{Cr :} & 6 \\ \text{6CO:} & 12 \\ \hline \text{Total :} & 18 \end{array}$$

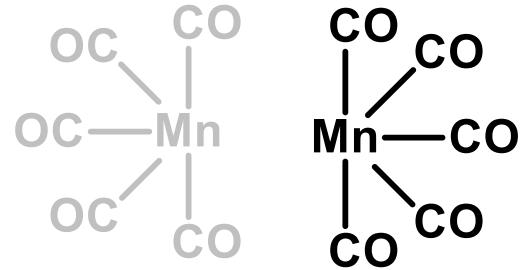
Ni: [Ar]3d<sup>8</sup> 4s<sup>2</sup>  
Fe: [Ar]3d<sup>6</sup> 4s<sup>2</sup>  
Cr: [Ar]3d<sup>5</sup> 4s<sup>1</sup>

Q. Ni(CO)<sub>4</sub>, Fe(CO)<sub>5</sub> and Cr(CO)<sub>6</sub> exist as monomeric form. However Mn(CO)<sub>5</sub>, Co(CO)<sub>4</sub> exist as dimer, why?

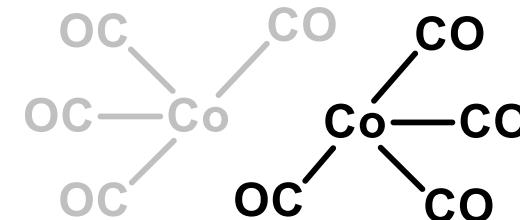


## Mn(CO)<sub>5</sub>, Co(CO)<sub>4</sub> dimerize to form stable 18 electrons complex

**Monomer**

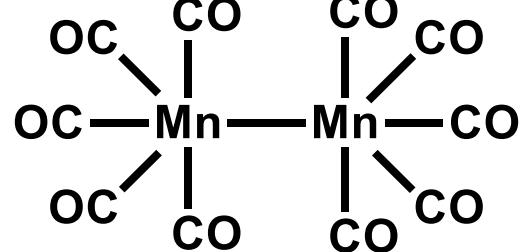


Mn :	7
5CO:	10
<b>Total :</b>	<b>17</b>

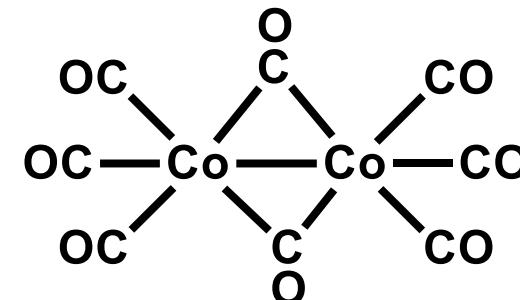


Co :	9
4CO:	8
<b>Total :</b>	<b>17</b>

**Dimer**



Mn :	7
5CO:	10
1M-M :	1
<b>Total :</b>	<b>18</b>



Co :	9
3CO:	6
2μ2-CO:	2
1M-M :	1
<b>Total :</b>	<b>18</b>

Mn: [Ar]3d<sup>5</sup> 4s<sup>2</sup>

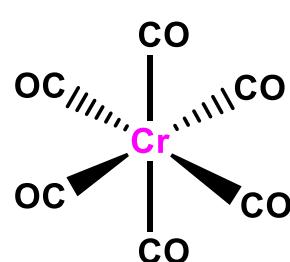
Co: [Ar]3d<sup>7</sup> 4s<sup>2</sup>

# 18-electrons rule: Stability of metal complex

Cr: [Ar]3d<sup>5</sup> 4s<sup>1</sup>



A Cr atom has 6 electrons outside its Noble gas core. Each CO is considered to act as a donor of 2 electrons. The total electrons count is therefore:



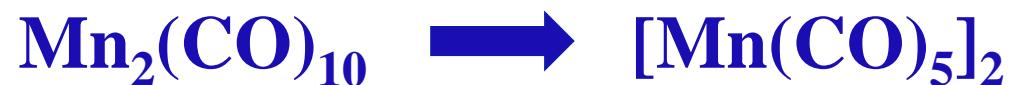
Cr :	6
6CO:	12
Total :	18

Cr(CO)<sub>6</sub> is therefore considered an 18 electron complex thermally stable and can be sublimed without decomposition

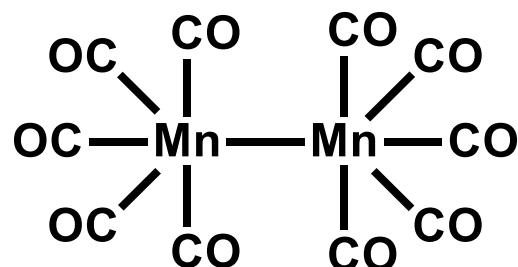
On the other hand, Cr(CO)<sub>5</sub>, a 16-electron species and Cr(CO)<sub>7</sub>, a 20-electron species, are much less stable and are known only as transient species.

Similarly, Cr(CO)<sub>6</sub><sup>+</sup> having 17 electrons and Cr(CO)<sub>6</sub><sup>-</sup> having 19-electrons are far less stable than the 18-electron Cr(CO)<sub>6</sub>.

# Calculation for number of metal-metal bond



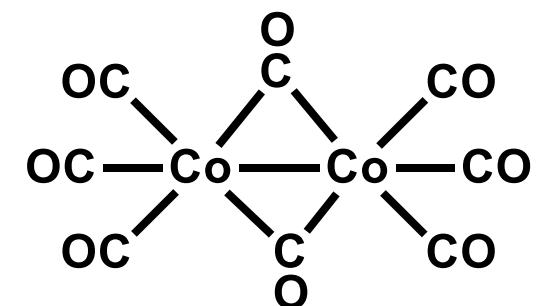
$$\begin{array}{rcl}
 \text{Mn :} & 7 \\
 5\text{CO:} & 10 \\
 \text{M-M :} & X \\
 \hline
 \text{Total :} & 17+X = 18 \\
 & X = 1
 \end{array}$$



Mn: [Ar]3d<sup>5</sup> 4s<sup>2</sup>



$$\begin{array}{rcl}
 \text{Co :} & 9 \\
 4\text{CO:} & 8 \\
 \text{M-M :} & X \\
 \hline
 \text{Total :} & 17+X = 18 \\
 & X = 1
 \end{array}$$



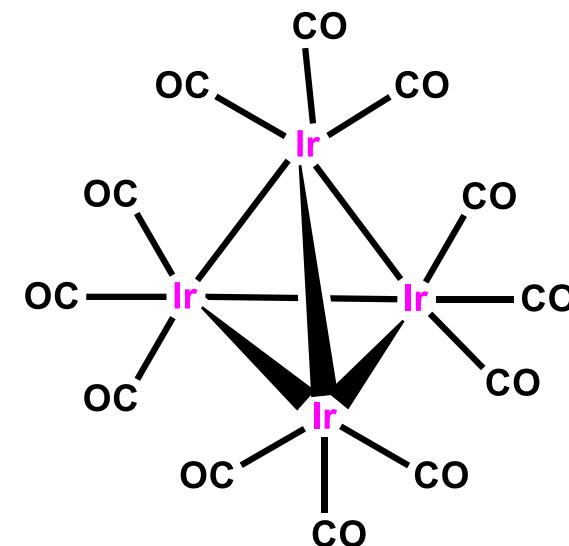
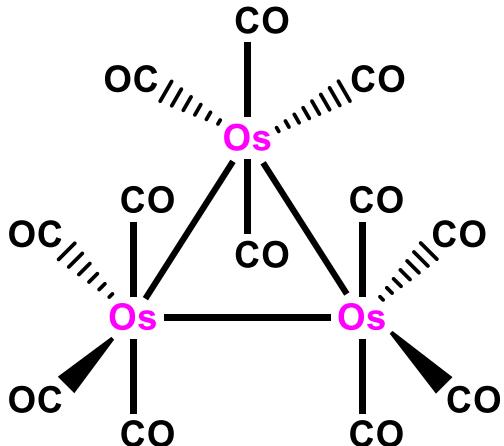
Co: [Ar]3d<sup>7</sup> 5s<sup>2</sup>

# Calculation for number of metal-metal bond



$\text{Os} :$ 8 $4\text{CO}:$ 8 $\text{M-M :}$ X <hr style="border-top: 1px solid black; margin: 5px 0;"/> $\text{Total :} \quad 16 + X \quad = 18$	$\text{Ir} = [\text{Xe}] 4f^{14} 5d^7 6s^2$ $3\text{CO:}$ 6 $\text{M-M :}$ X <hr style="border-top: 1px solid black; margin: 5px 0;"/> $\text{Total :} \quad 15 + X \quad = 18$
--	--

**X = 2**



## **18 electron counting: donor pair method**

Account the **charge on each ligand** and determine the formal **oxidation state of the metal**.

Common organometallic ligands are assigned an electron count and charge.

The charge on ligands helps determine d-electron count of metal.

**Add up all electrons** from Metal d orbitals and ligands to find total e- count.  
The donor-pair method requires a calculation of the oxidation number

**Key point:** Ligands are considered to donate electrons in pairs (eg.Lewis base), resulting in the need to treat some ligands as neutral and others as charged.

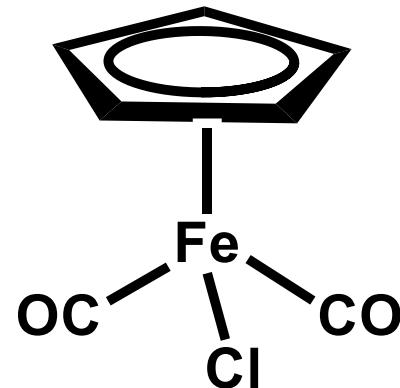
The **oxidation number** of the metal atom is the total charge of the complex minus the charges of any ligands

The **number of d electrons** the metal provides is its **group number minus its oxidation number**

The total electron count is the sum of the number of electrons on the metal atom and the number of electrons provided by the ligands

## Electron counting for common ligands

Name of the Ligand	Neutral ligand	Donor pair
-H, -Cl, -Br, -I, -OH, -OR, -CN, -CH <sub>3</sub> , -CR <sub>3</sub>	1	2
CO, PR <sub>3</sub> , NH <sub>3</sub> , H <sub>2</sub> O, H <sub>2</sub> C=CH <sub>2</sub>	2	2
=O, =S,	2	4
≡CR (carbyne)	3	3
η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> (p-allyl)	3	4
Ethylenediamine(en)	4	4
Bipyridine(bipy)	4	4
Butadiene, cyclobutadiene, 1,3-cyclooctadiene(COD)	4	4
η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> (Cyclopentadienyl) <sup>-</sup>	5	6
η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> (Benzene)	6	6
η <sup>7</sup> -C <sub>7</sub> H <sub>7</sub> (cycloheptatrienyl) <sup>+</sup>	7	6



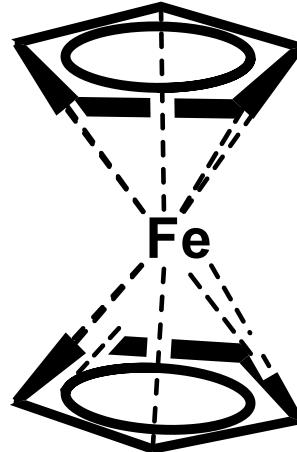
Fe: [Ar]3d<sup>6</sup> 4s<sup>2</sup>

### Neutral –ligand method

Fe :	8
$\eta^5\text{-Cp}$ :	5
2x CO :	4
Cl :	1
<hr/>	
Total :	18

### Donor Pair method

Fe(+2) :	6
$\eta^5\text{-Cp}$ :	6
2x CO :	4
Cl :	2
<hr/>	
Total :	18



### Neutral –ligand method

$$\begin{array}{rcl} \text{Fe :} & 8 \\ 2x \eta^5\text{-Cp :} & 10 \\ \hline \text{Total :} & 18 \end{array}$$

### Donor Pair method

$$\begin{array}{rcl} \text{Fe(+2) :} & 6 \\ 2x \eta^5\text{-Cp :} & 12 \\ \hline \text{Total :} & 18 \end{array}$$



Mn: [Ar]3d<sup>5</sup> 4s<sup>2</sup>



Co: [Ar]3d<sup>7</sup> 4s<sup>2</sup>

### Neutral ligand method

Mn :	7
5x CO :	10
Cl :	1
Total :	18

### Donor pair method

Mn(+1) :	6
5x CO :	10
Cl :	2
Total :	18

Co :	9
$\eta^4\text{-C}_4\text{H}_6$ :	4
$\eta^3\text{-C}_3\text{H}_5$ :	3
Total :	16

Co(+1) :	8
$\eta^4\text{-C}_4\text{H}_6$ :	4
$\eta^3\text{-C}_3\text{H}_5$ :	4
Total :	16

**Ta(Me)<sub>5</sub>**

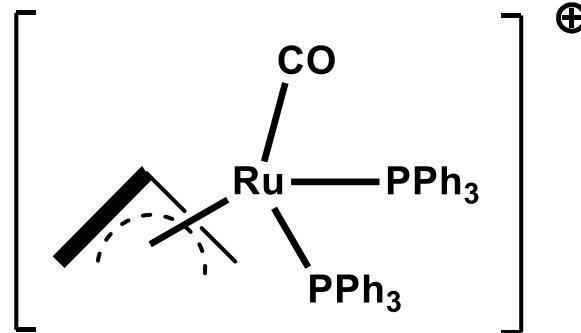
Ta: [Xe]4f<sup>14</sup> 5d<sup>3</sup> 6s<sup>2</sup>

## Neutral ligand method

$$\begin{array}{rcl} \text{Ta :} & 5 \\ \text{5x Me :} & 5 \\ \hline \text{Total :} & 10 \end{array}$$

## Donor pair method

$$\begin{array}{rcl} \text{Ta(+5) :} & 0 \\ \text{5x Me :} & 10 \\ \hline \text{Total :} & 10 \end{array}$$



Ru: [Kr]4d<sup>7</sup> 5s<sup>1</sup>

## Neutral ligand method

Ru :	8
CO :	2
2x PPh <sub>3</sub> :	4
η <sup>3</sup> -allyl:	3
Charge :	-1
<hr/>	
Total :	16

## Donor pair method

Ru (+2) :	6
CO :	2
2x PPh <sub>3</sub> :	4
η <sup>3</sup> -allyl:	4
<hr/>	
Total :	16



Re: [Xe]4f<sup>14</sup> 5d<sup>5</sup> 6s<sup>2</sup>

Re :	7
5x CO :	10
PF <sub>3</sub> :	2
Charge :	-1
<hr/>	
Total :	18

Re(+1) :	6
5x CO :	10
PF <sub>3</sub> :	2
<hr/>	
Total :	18

## Chemistry of Metal Carbonyls



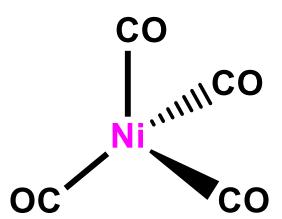
Sample of iron pentacarbonyl  
 $\text{Fe}(\text{CO})_5$ :an air-stable liquid

**Metal carbonyls are coordination complexes** of transition metals with **carbon monoxide ligands**.

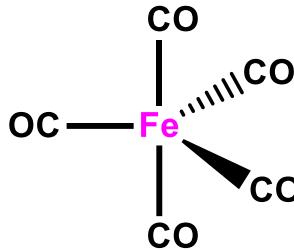
Its primary mode of attachment to metal atom is through the C atom

Metal carbonyls are useful in organic synthesis and as **catalysts** or catalyst precursors in homogeneous catalysis, such as **hydroformylation reaction**. In Mond process, **nickel carbonyl is used to produce pure nickel**.

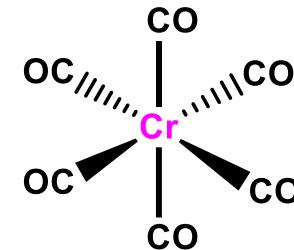
**Metal carbonyls are toxic** by skin contact, inhalation or ingestion because of their ability to **carbonylate hemoglobin to carboxyhemoglobin**, which prevents the binding of O<sub>2</sub>



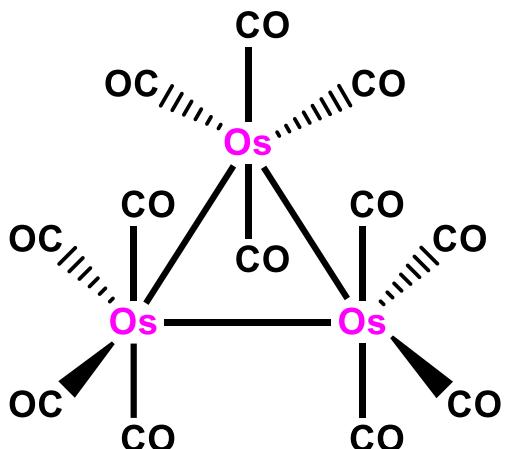
$\text{Ni}(\text{CO})_4$



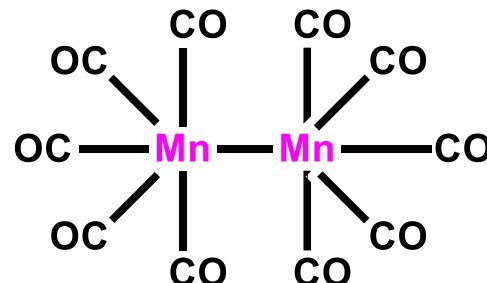
$\text{Fe}(\text{CO})_5$



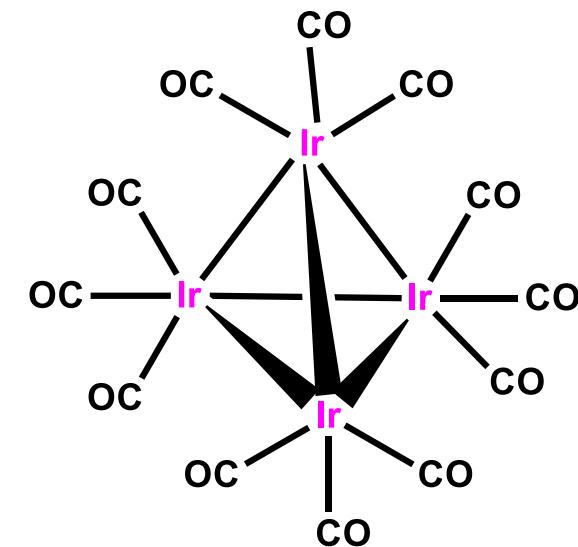
$\text{Cr}(\text{CO})_6$



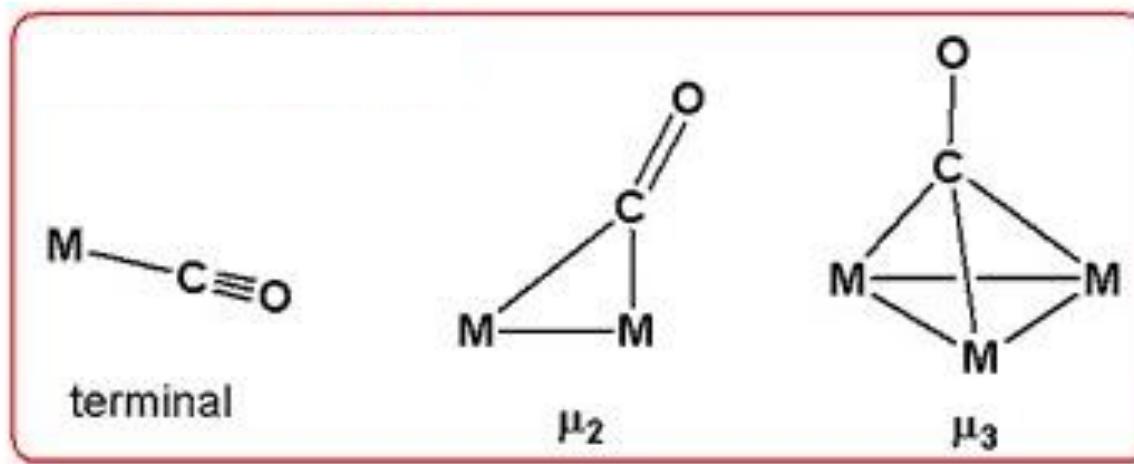
$\text{Os}_3(\text{CO})_{12}$



$\text{Mn}_2(\text{CO})_{10}$



$\text{Ir}_4(\text{CO})_8$

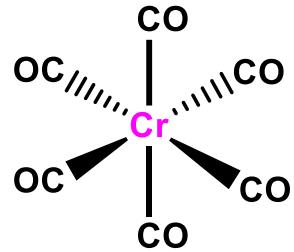


Most common bridging mode, the **CO ligand bridges a pair of metals**. This bonding mode is observed in the commonly available metal carbonyls:  $\text{Co}_2(\text{CO})_8$ ,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Fe}_3(\text{CO})_{12}$ , and  $\text{Co}_4(\text{CO})_{12}$ .

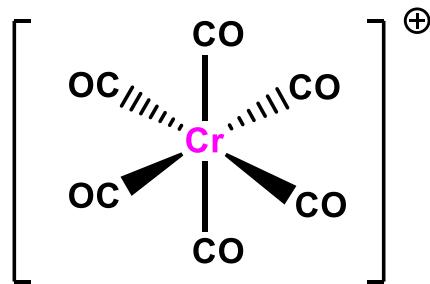
In certain higher nuclearity clusters, CO bridges between three or even four metals. These ligands are denoted  $\mu_3\text{-CO}$  and  $\mu_4\text{-CO}$ .

# Electron density on the metal centre influence on CO stretching frequency

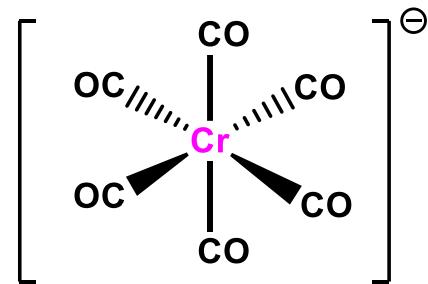
Cr: [Ar]3d<sup>5</sup> 4s<sup>1</sup>



Cr :	6
6CO:	12
Total :	18



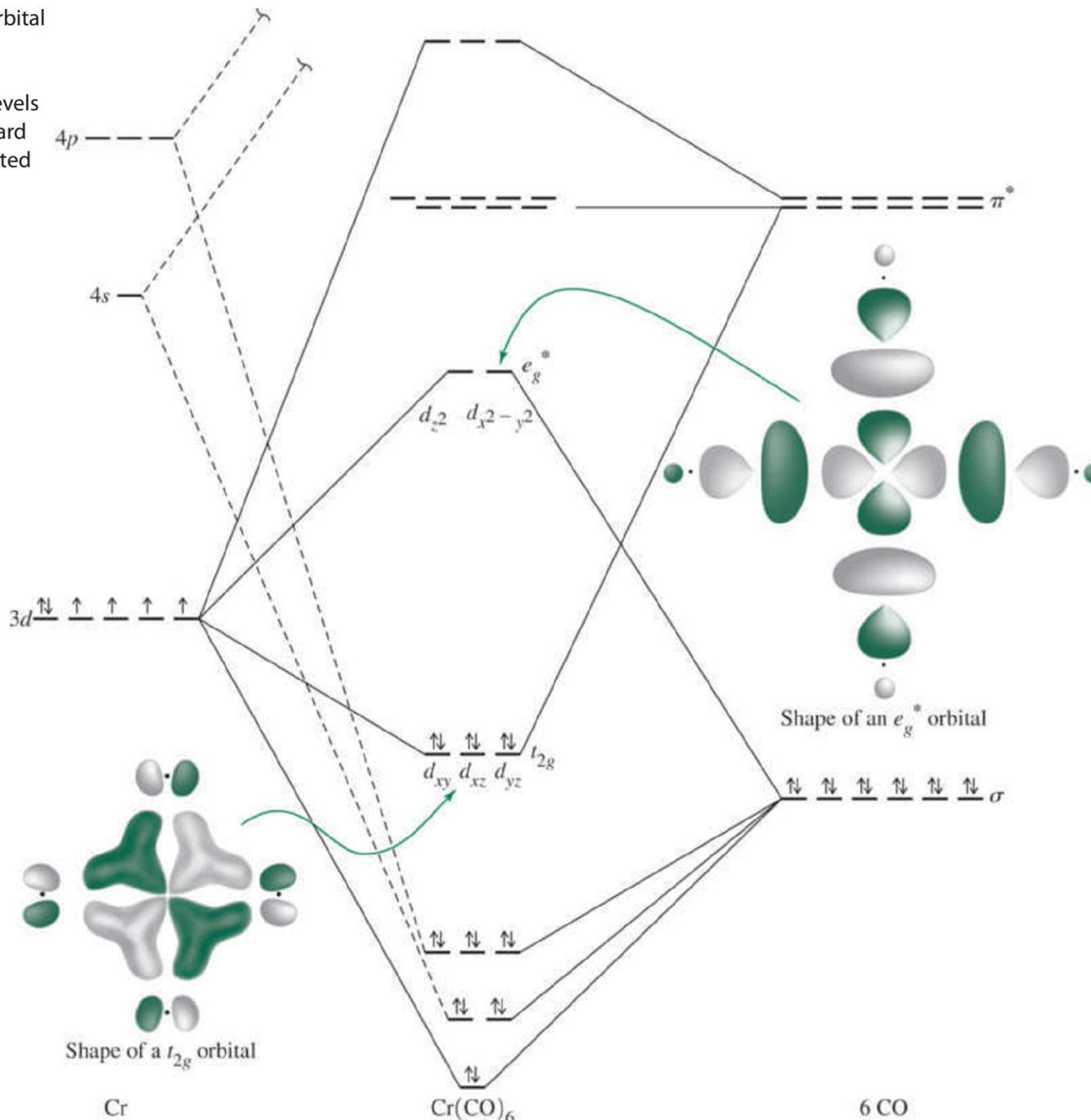
Cr :	6
6CO:	12
Charge :	-1
Total :	17

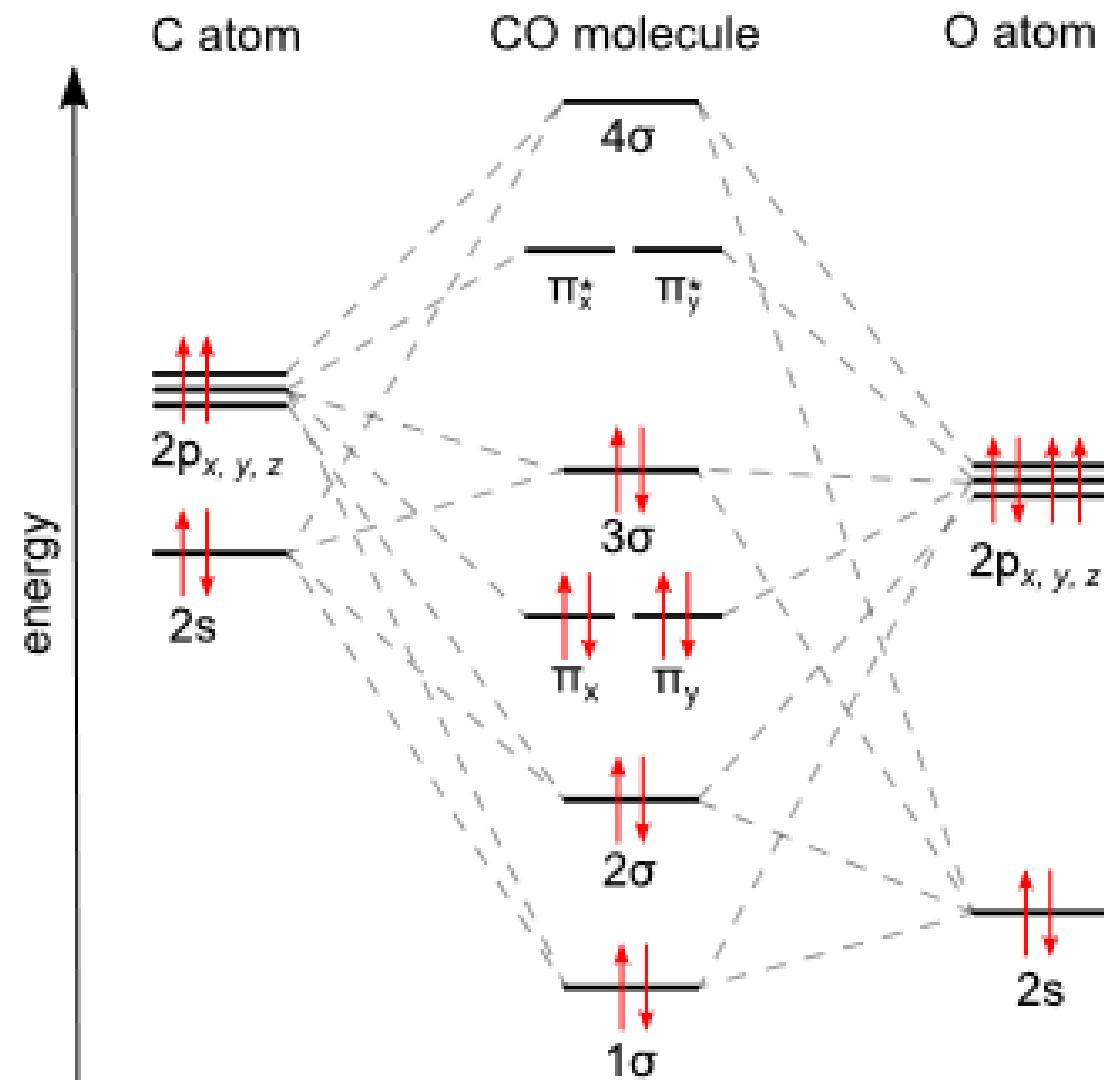


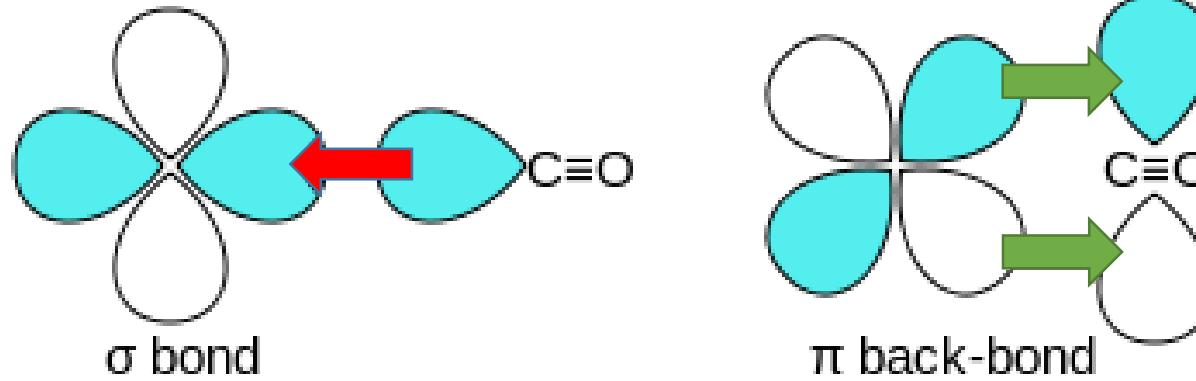
Cr :	6
6CO:	12
Charge :	1
Total :	19

**FIGURE 13.8** Molecular Orbital Energy Levels of  $\text{Cr}(\text{CO})_6$ .

Molecular Orbital Energy Levels of  $\text{Cr}(\text{CO})_6$  by Gary O. Spessard and Gary L. Miessler. Reprinted by permission.







**A sigma bond** arises from overlap of the **nonbonding electron pair on carbon with a blend of metal d orbital (s bonding)**

A pair of  $\pi$  bonds arises from overlap of **filled d-orbitals on the metal with a pair of  $\pi$ -antibonding orbitals of carbon atom in CO ( $\pi$  anti bonding or back bonding)**

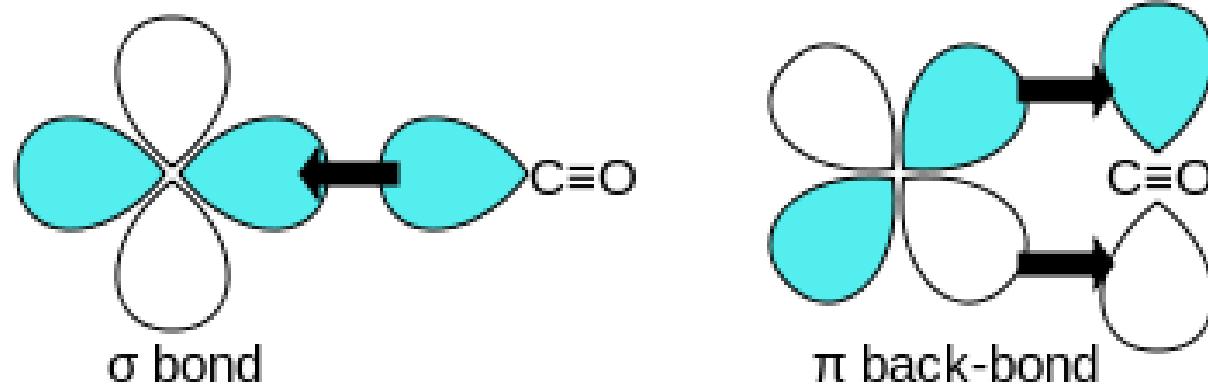
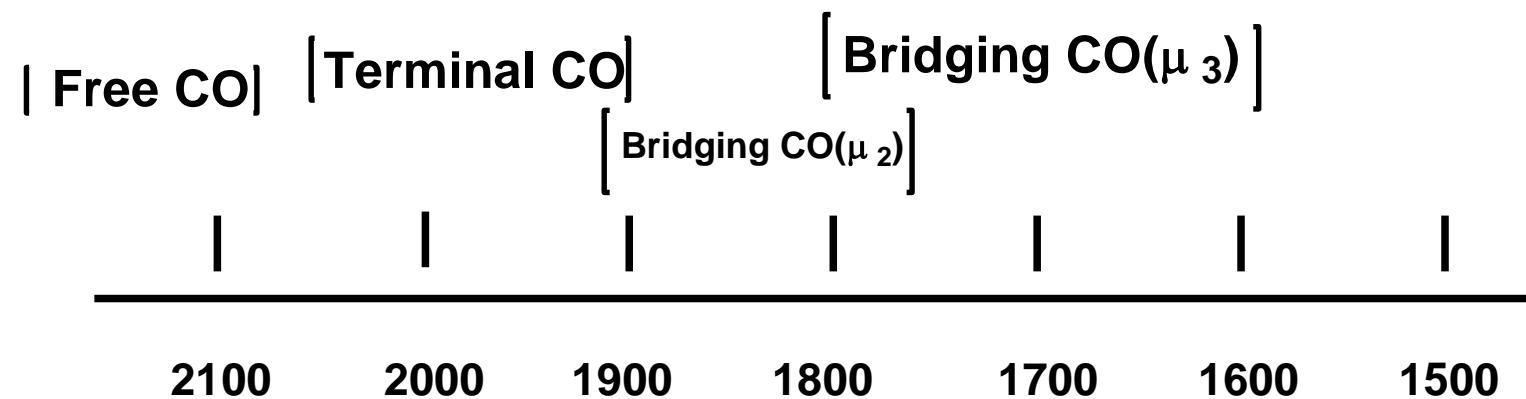
As electrons from the metal fill the  $\pi$ -antibonding orbital of CO, they weaken the carbon-oxygen bond compared with free carbon monoxide, while the metal-carbon bond is strengthened

**Infrared (IR) spectroscopy** is very useful technique for identification of the presence of carbonyl ligands.

IR can also help to determine the bridging/terminal carbonyl group

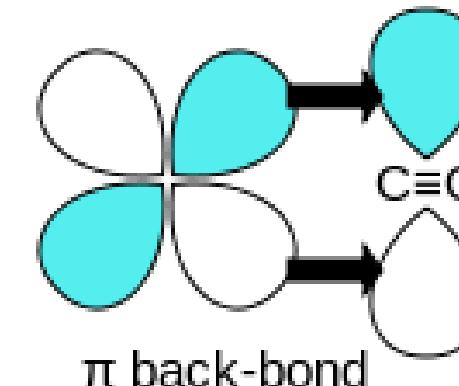
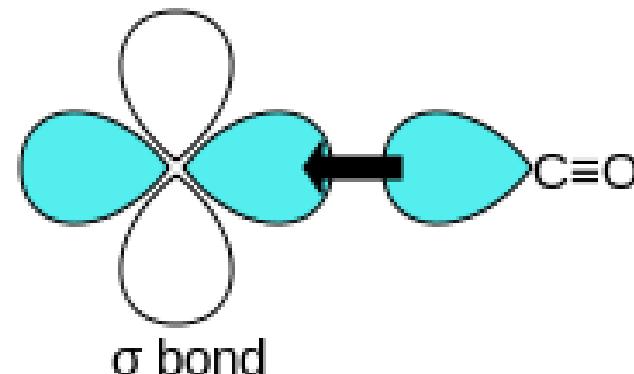
For compounds with doubly bridging CO ligands, denoted  $\mu_2\text{-CO}$   $\nu_{\text{CO}}$  is usually shifted by 100–200  $\text{cm}^{-1}$  to lower energy compared to the signatures of terminal CO, i.e. in the region  $1800 \text{ cm}^{-1}$ .

Bands for face capping ( $\mu_3$ ) CO ligands appear at even lower energies.

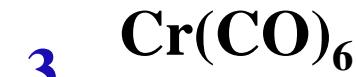
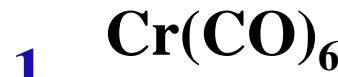


# Influence of coordination and charge on CO stretching frequencies

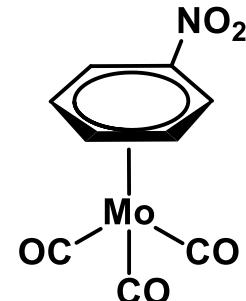
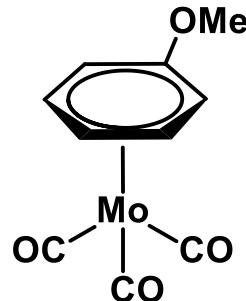
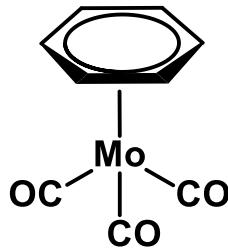
<u>Compound</u>	<u>Wave number (cm<sup>-1</sup>)</u>
CO(g)	2143
[Mn(CO) <sub>6</sub> ] <sup>+</sup>	2090
Cr(CO) <sub>6</sub>	2000
[V(CO) <sub>6</sub> ] <sup>-</sup>	1860
[Ti(CO) <sub>6</sub> ] <sup>2-</sup>	1750



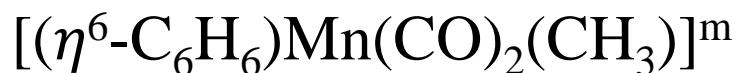
Q. Arrange the given carbonyl complexes in the increasing order of CO stretching frequencies and justify your answer



2.



Q. Following the  $18e^-$  rule as a guide; determine charge ‘m’ in the given complex



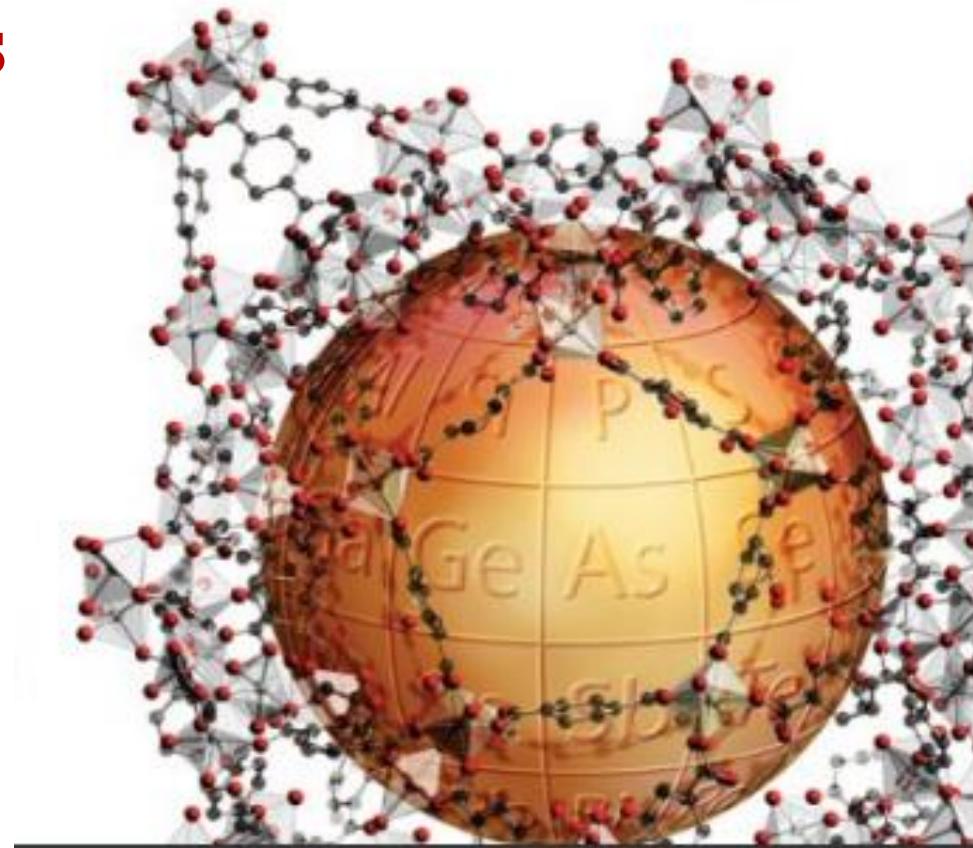
Mn :	7
2CO :	4
$\eta^6\text{-C}_6\text{H}_6$ :	6
CH <sub>3</sub> :	1
Charge :	-m
<hr/>	
Total :	18-m = 18
	m = 0

**After Mid-Sem**

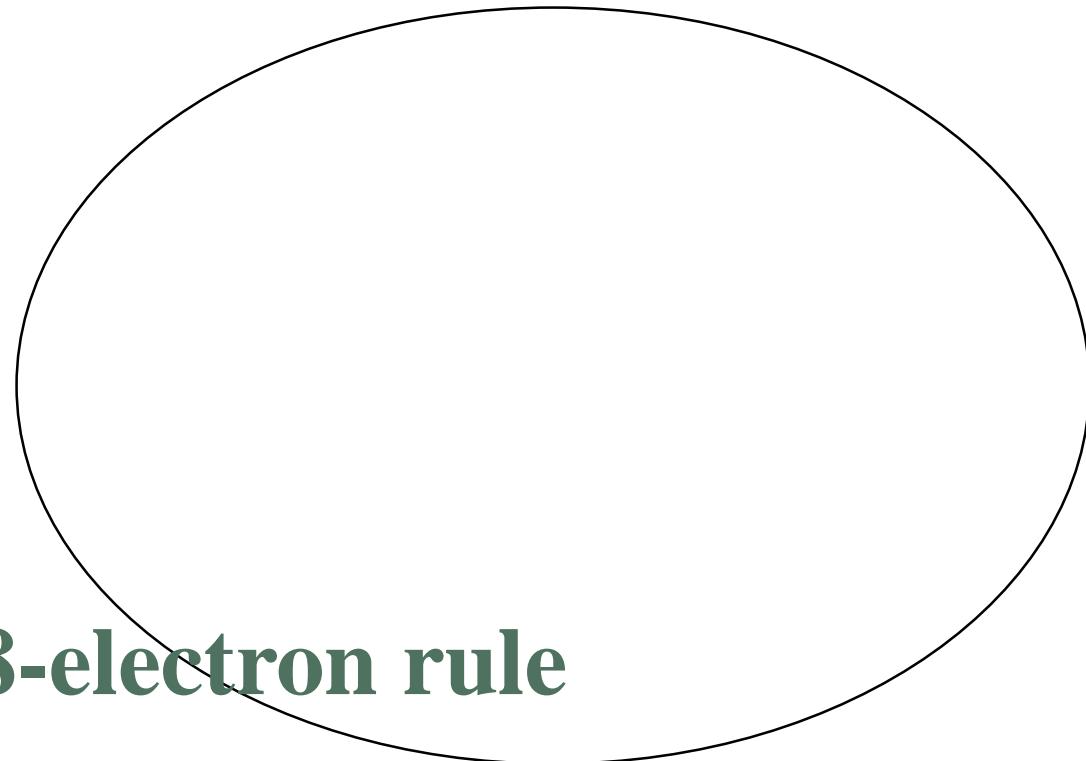
Shriver & Atkins'

# Inorganic Chemistry

Atkins • Overton • Rourke • Weller • Armstrong • Hagerman



## CY1001D: Chemistry: Module 3 Organometallic chemistry and Catalysis



18-electron rule

Inorganic Chemistry  
Shriver and Atkins

# **Nobel -Prize related to Organometallic Chemistry:**

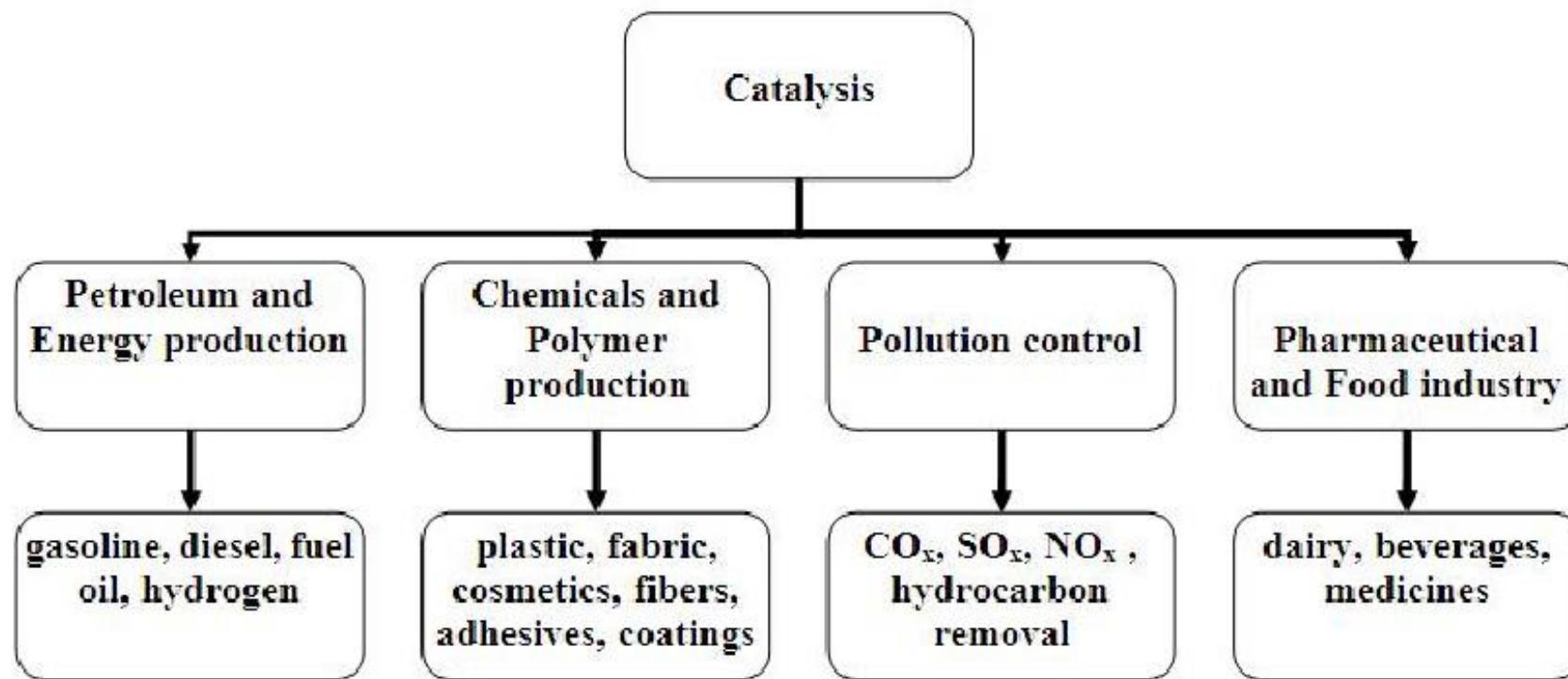
<b>Victor Grignard (1912)</b>	<b>Grignard reagent</b>
<b>K. Ziegler, G. Natta (1963)</b>	<b>Ziegler-Natta catalyst</b>
<b>E. O. Fisher, G. Wilkinson (1973)</b>	<b>Sandwich compounds</b>
<b>K. B. Sharpless, R. Noyori (2001)</b>	<b>Asymmetric oxidation and hydrogenation reaction</b>
<b>Yves Chauvin, Robert H. Grubbs, Richard R. Schrock (2005)</b>	<b>Alkene metathesis reaction</b>
<b>Akira Suzuki, Ei-ichi Negishi, Richard F. Heck (2010)</b>	<b>C-C cross coupling reaction</b>

## Catalyst :

- A catalyst is a substance that increases the rate of a reaction
  - The chemical composition for the catalyst remain same even after the reaction
- 

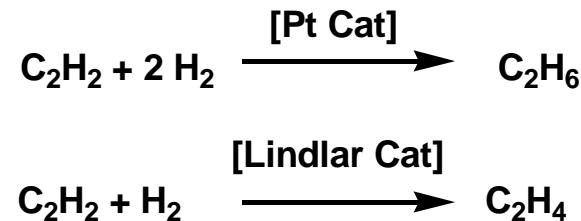
Catalysts are widely used in industry, and in the laboratory

Contribute to one-sixth of the value of all manufactured goods in industrialized countries



# Properties of Catalyst

- Small quantity of catalyst is enough to catalyze a large quantity of reaction
- Catalyst is highly selective
- Though reactants are same in a reaction, but product varies depending on the catalyst



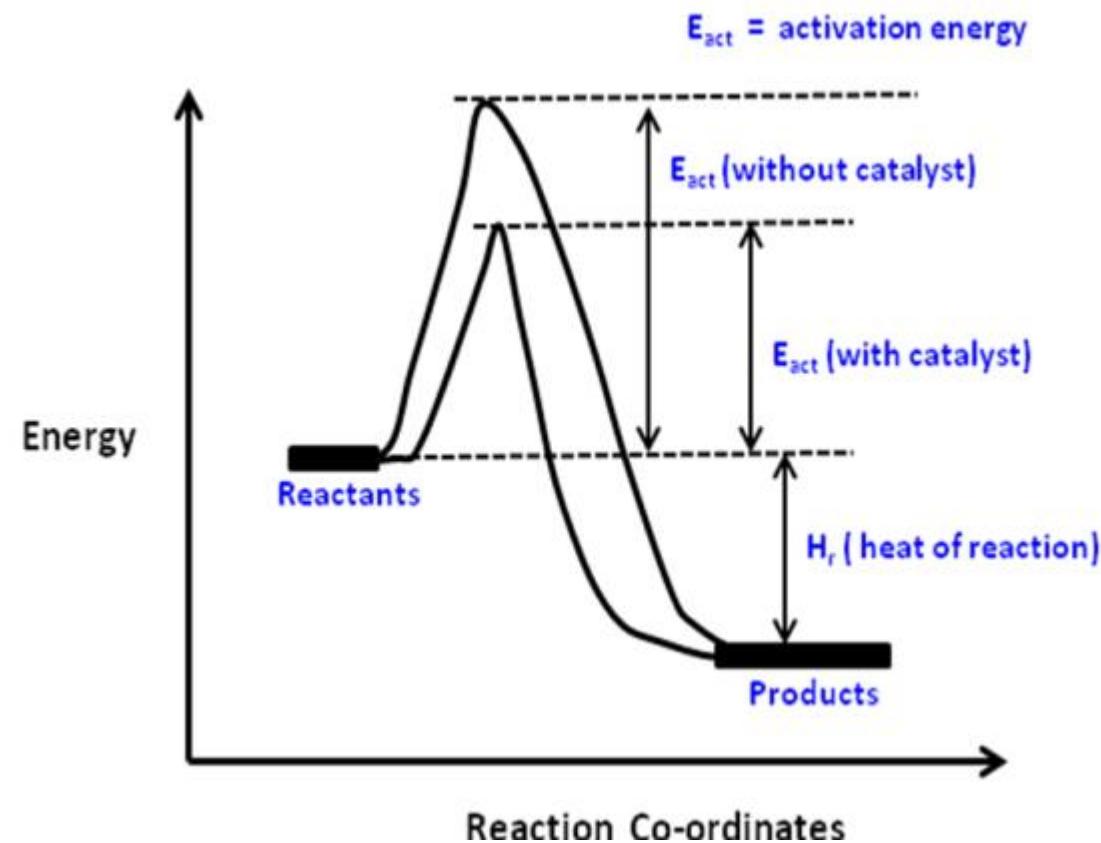
- Catalyst can not start the reaction by itself. Also doesn't alter the position of equilibrium, but helps in achieving the equilibrium faster
- Catalytic activity increases as surface area of catalyst increases
- Catalytic activity is maximum at optimum temperature

**Promoter (catalyst of a catalyst):**  
**increases the catalytic active by increase in no. of active sites**

**Catalytic poison:**  
**stops or decreases by blocking the active sites of the catalysts**

Catalysis involves understanding of the thermodynamics, kinetics, electronic interaction, crystal structure, reactor design and process development for a catalytic process.

□ Catalysts can be atoms, molecules, enzymes and solid surfaces



Catalysis increases the rate of reactions

# **Types of Catalytic reaction**

## → **I. Homogeneous**

**Homogeneous catalytic reaction**, the catalyst is in the same phase as the reactants

Typically, all the reactants and catalysts either are in liquid or gas phase

## → **II. Heterogeneous**

In **heterogeneous catalytic reaction**, the catalyst and the reactants are in different phases

Reactions of liquid or gases in the presence of solid catalysts are the typical examples

e.g. Hydrogenation of alkene/alkyne over Raney Ni catalyst

# Heterogeneous solid catalysis is strongly associated with adsorption phenomenon

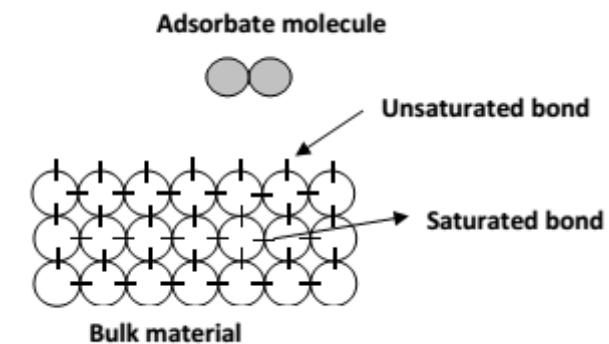
- In solid catalysis, at least one of the reactant needs to be **adsorbed on the surface of the catalyst.**
- Adsorption of a component ‘A’ on surface of material ‘B’ : component ‘A’ is called **adsorbate** and surface ‘B’ is called **adsorbent**.
- The surfaces include both **external surface and internal surface** due to the pores. For highly porous material, the internal surface area due to the pores is much higher than the external surface area.

# **Types of adsorption**

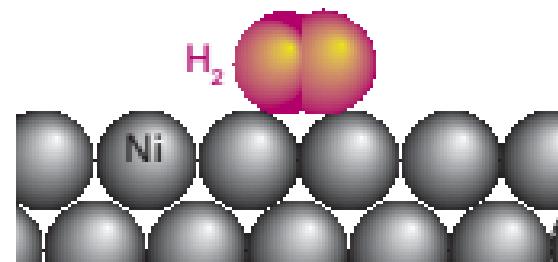
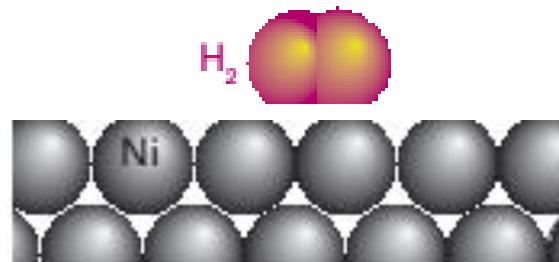
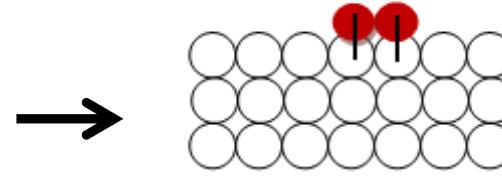
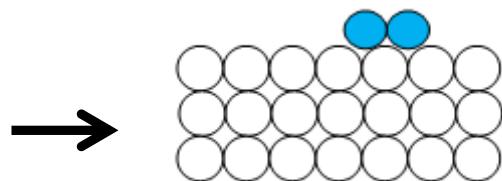
Depending on the nature of interaction, the adsorption can be of two types

**Physisorptions**

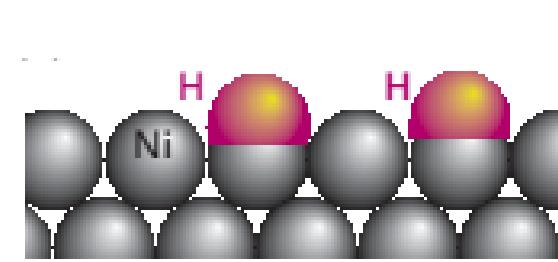
**Chemisorptions**



**at the beginning of adsorption**

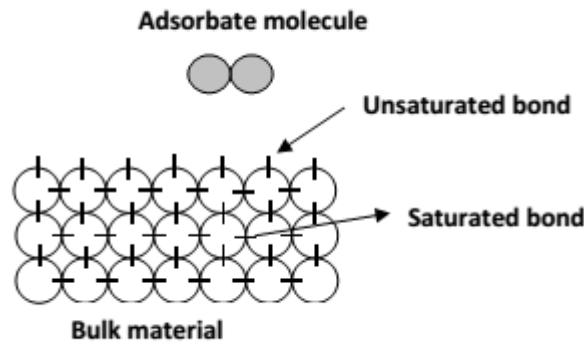


Physisorption of hydrogen on nickel surface

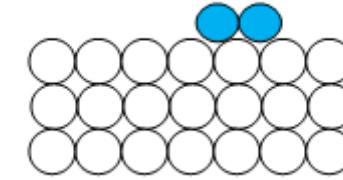


Chemisorption of hydrogen on nickel surface

# Physisorptions



at the beginning of adsorption



physisorbed condition

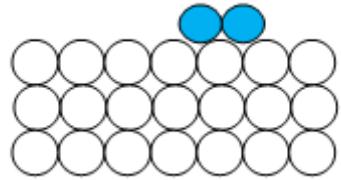
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The phenomenon of adsorbate molecules attaching themselves to adsorbent surface under the influence of van der Waals forces is called **physisorption or physical adsorption**.

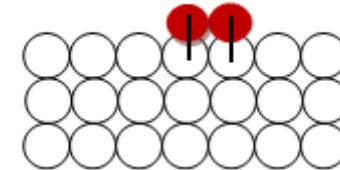
The van der Waals forces mainly consist of dipole-dipole interactions (exothermic process). (10 to 40 kJ /mol)

Adsorption of nitrogen on carbon or alumina

# Chemisorptions



**physisorbed condition**



**chemisorbed condition**

---

After physisorption, the adsorbed molecules can undergo electronic rearrangement with the surface atoms. This phenomenon is called **chemisorption**

Chemisorption is associated with formation and breaking of chemical bonds (80-400 kJ/mol) and often required higher temperature

Chemisorption process is selective and an adsorbed molecule will chemisorbed only on selected adsorbent.

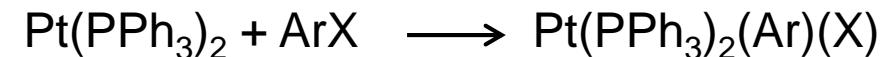
**Chemisorption of hydrogen on Raney Ni, Pd, Pt etc**

# Oxidative-Addition Reactions



Oxidation state:    0    2+

Reactions involve the metal atom increase coordination number by two units and also increase in oxidation state by 2.

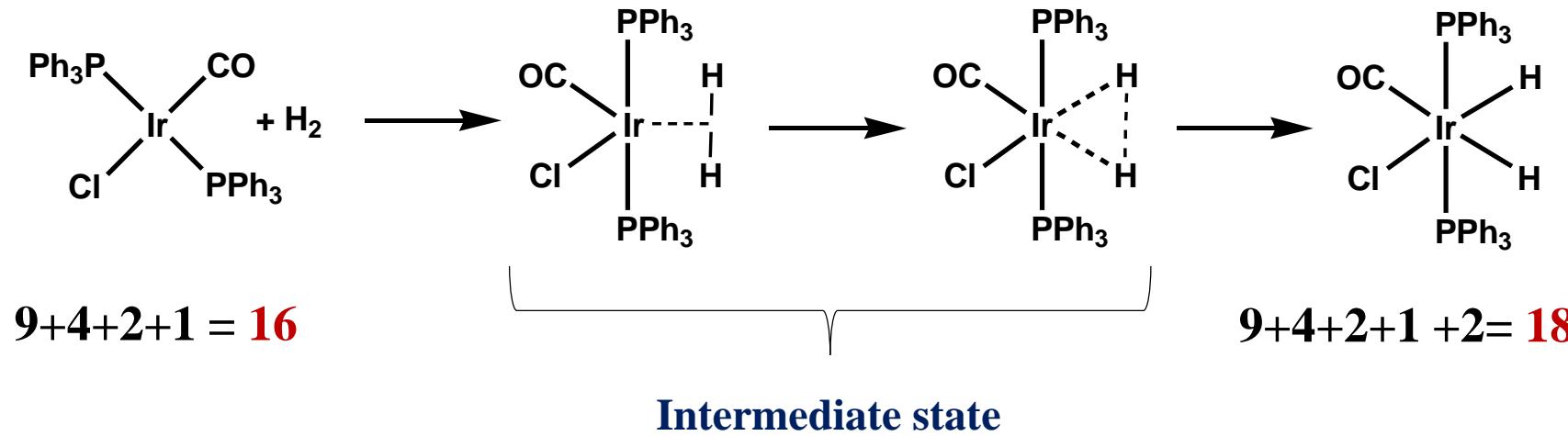


## Criteria to exhibit oxidative addition reaction:

- Vacant coordination site
- Suitable orbitals be available for bond formation.  
e.g.  $[\text{Fe}(\text{CO})_4]^{2-}$  has 4 L, but addition of X-Y requires antibonding orbitals which isn't favorable
- Ease of oxidation

$\text{Ir} = [\text{Xe}] \ 4\text{f}^{14} \ 5\text{d}^7 \ 6\text{s}^2$

# Mechanism of oxidative addition reaction



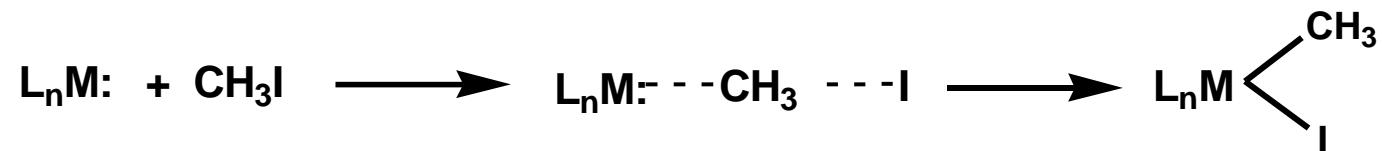
Concerted reaction-

3 centered transition state (i.e. bond break and formation occur simultaneously)

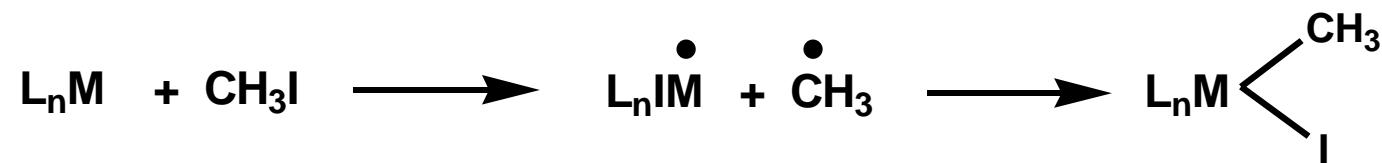
# Mechanism for oxidative addition reaction

## For electrophilic polar molecule

Electrophile: charge or neutral species have vacant orbitals attracted to an  $e^-$  rich center

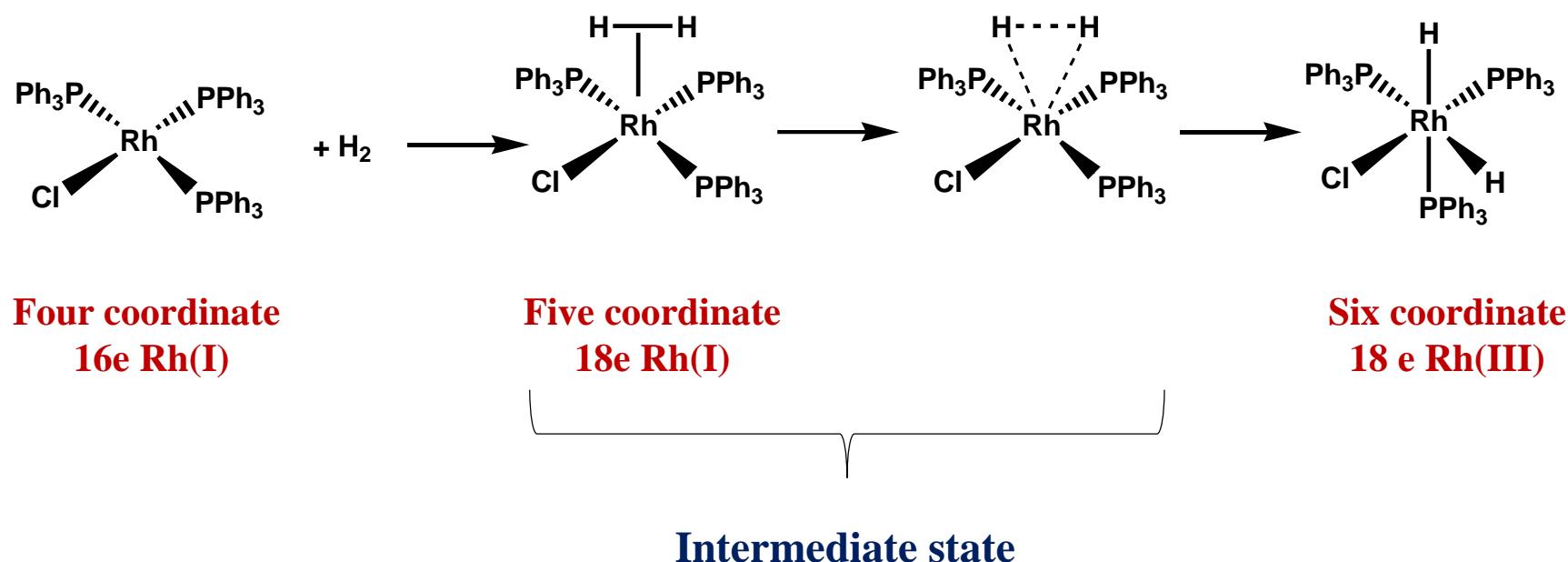


Radical or one electron transfer mechanism



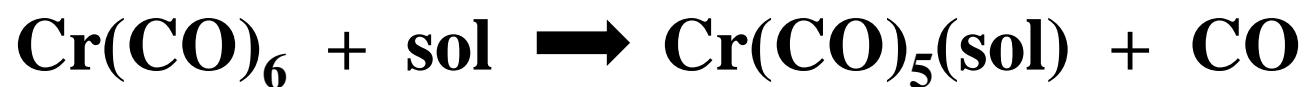
# Oxidative addition reactions

The oxidative addition of hydrogen is a concerted reaction: dihydrogen coordinates to form a  $\sigma$ -bonded  $\text{H}_2$  ligand, and then back bonding from the metal results in cleavage of the H-H bond and the formation of *cis* dihydrides

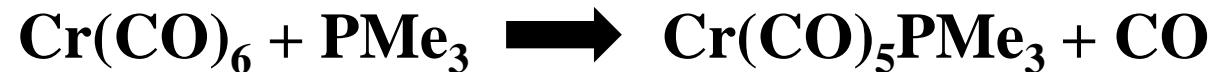


# Substitution Reaction

Replacement of one ligand by another in organometallic complexes.



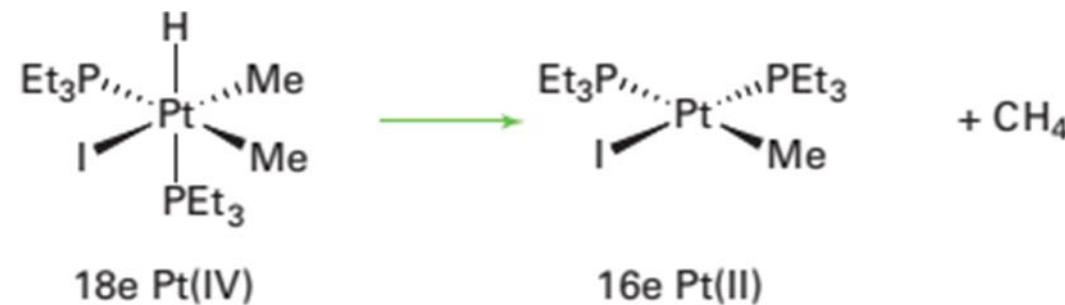
Sol = any solvated molecule e.g. THF



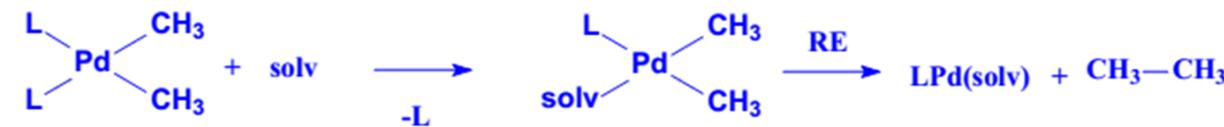
# Reductive-Elimination reactions

The opposite of oxidative addition, where two ligands couple and eliminate from a metal centre, is known as reductive elimination.

e.g. 1



e.g. 2



- Oxidative addition and reductive elimination reactions are in principle reversible  
However, one direction is normally thermodynamically favored over the other

## Insertion reactions

Insertion reactions do not involve changes in metal oxidation state.

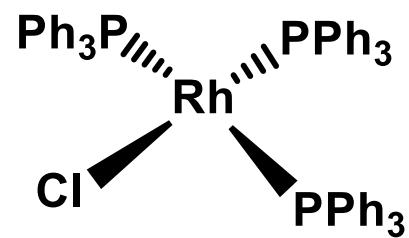
Insertion of Carbon monoxide (**CO**) into metal-carbon bond **Mn-CH<sub>3</sub>** bond called **carbonylation**



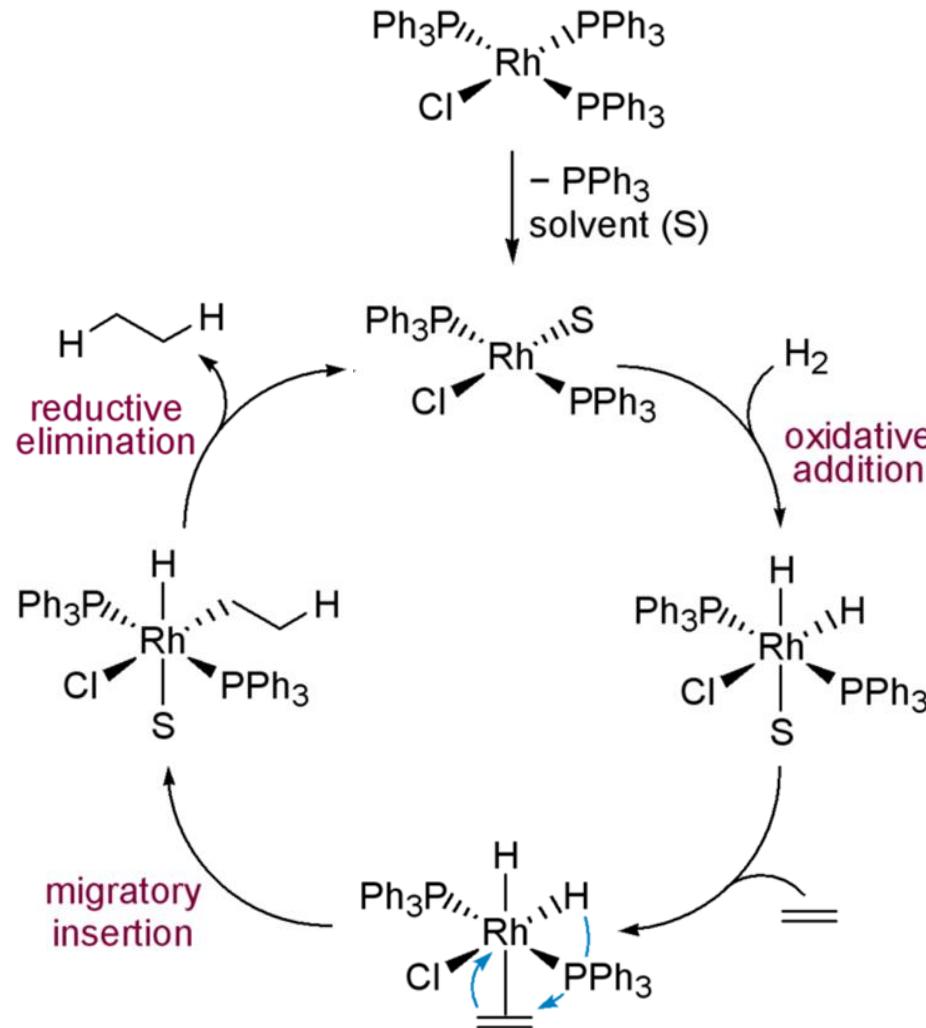
Reverse of above insertion reaction called **decarbonylation reaction**

## Wilkinson's catalyst

- Cholorotris(triphenylphosphine)rhodium(I)  $[\text{Rh}(\text{Cl})(\text{PPh}_3)_3]$  is known as Wilkinsons catalyst
- Wilkinson's catalyst is an effective homogeneous catalyst for double bond hydrogenation

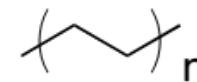
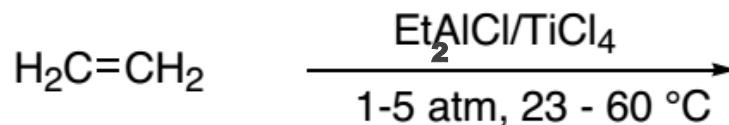


# Mechanism: Hydrogenation by Wilkinson catalyst



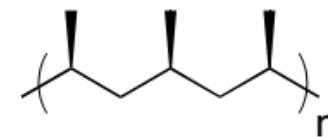
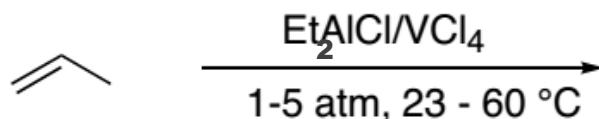
# Historical work of Ziegler and Natta

## Polymerization of ethylene



-high molecular weight, Linear PE  
-low pressures and temperatures

## Polymerization of propylene

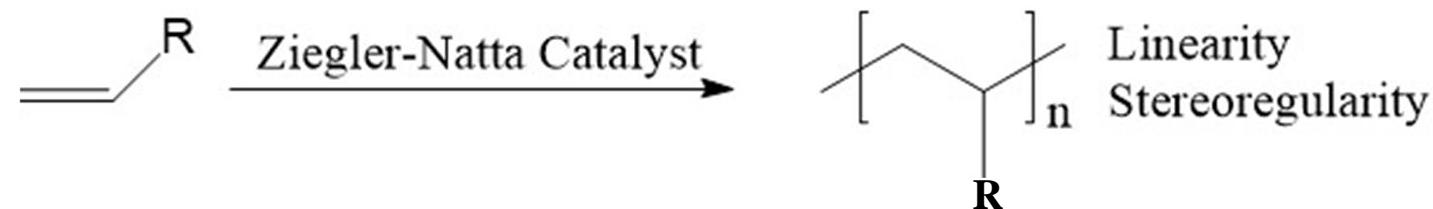


-1st example of a crystalline  
isotactic polypropylene

Nobel prize in chemistry in 1963

# Ziegler-Natta Catalyst

- Ziegler –Natta(ZN) catalyst is used in polymerization of olefins with high linearity and stereoselectivity
- The Ziegler-Natta (ZN) catalyst, named after two chemists: **Karl Ziegler** and **Giulio Natta**, and considered as powerful tool for polymerization of  $\alpha$ -olefins



# Ziegler-Natta Catalyst

A typical Ziegler-Natta catalyst system usually contains two parts:

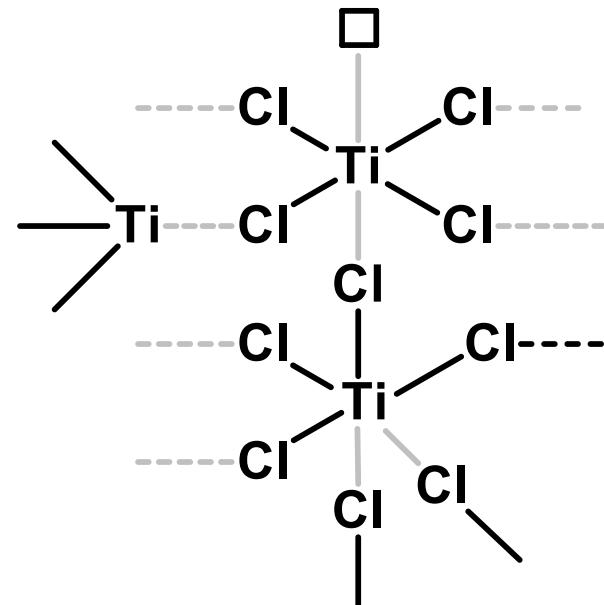
- Transition metal (Group IV metals, like Ti, Zr, Hf) compound
- Organoaluminum compound (co-catalyst)

e.g.  $\text{TiCl}_4 + \text{Et}_3\text{Al}$  or  $\text{TiCl}_4 + \text{AlEt}_2\text{Cl}$

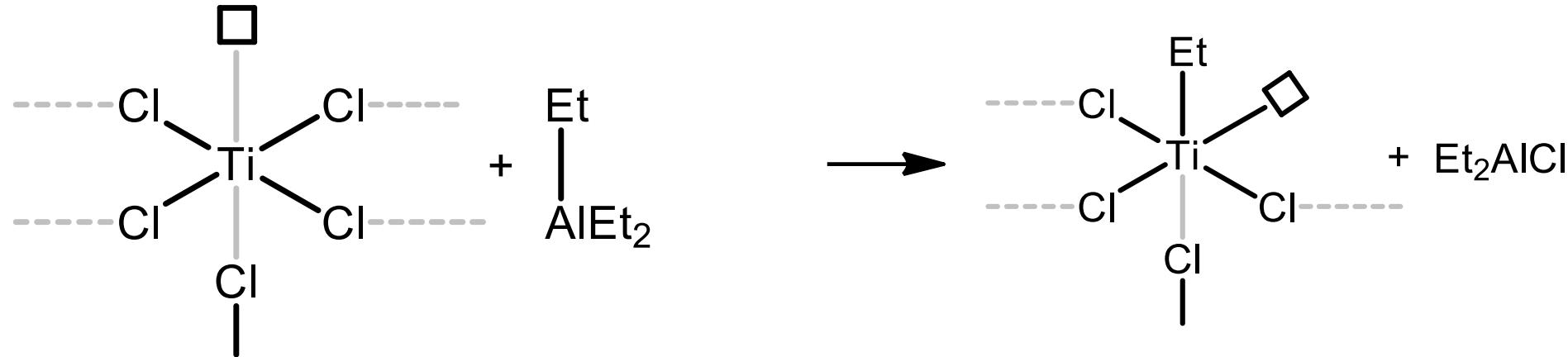
# **TiCl<sub>4</sub>**

The titanium chloride compound has a crystal structure in which each Ti atom is coordinated to 6 chlorine atoms

On the crystal surface, a Ti atom is surrounded by 5 chlorine atoms with one empty orbital to be filled.

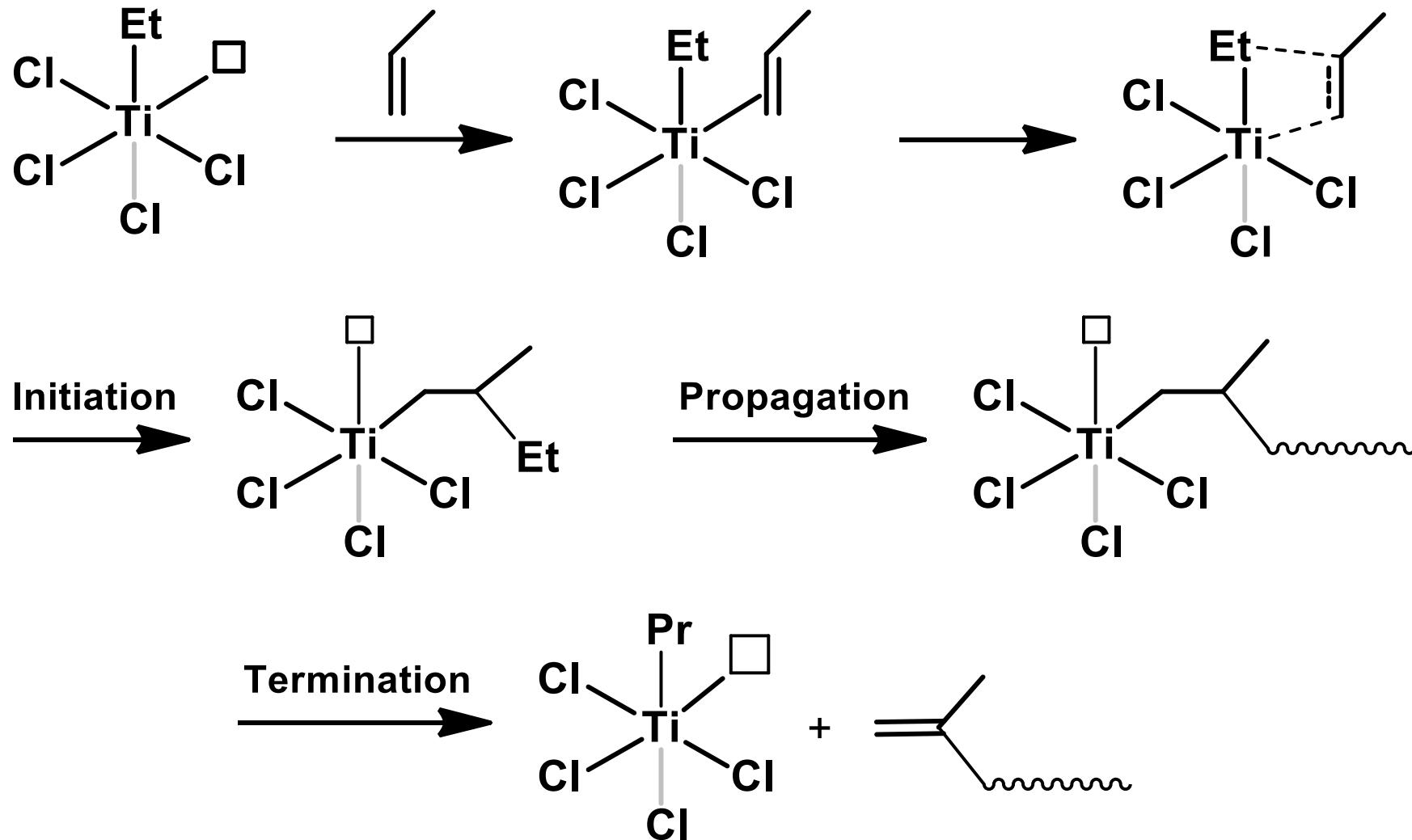


## $\text{TiCl}_4 + \text{AlEt}_3$ catalyst



- $\text{Et}_3\text{Al}$  donates an ethyl group to  $\text{Ti}$  atom and the  $\text{Al}$  atom is coordinated to one of the chlorine atoms
- One chlorine atom from titanium is kicked out during this process

# Steps involved in polymerization reactions



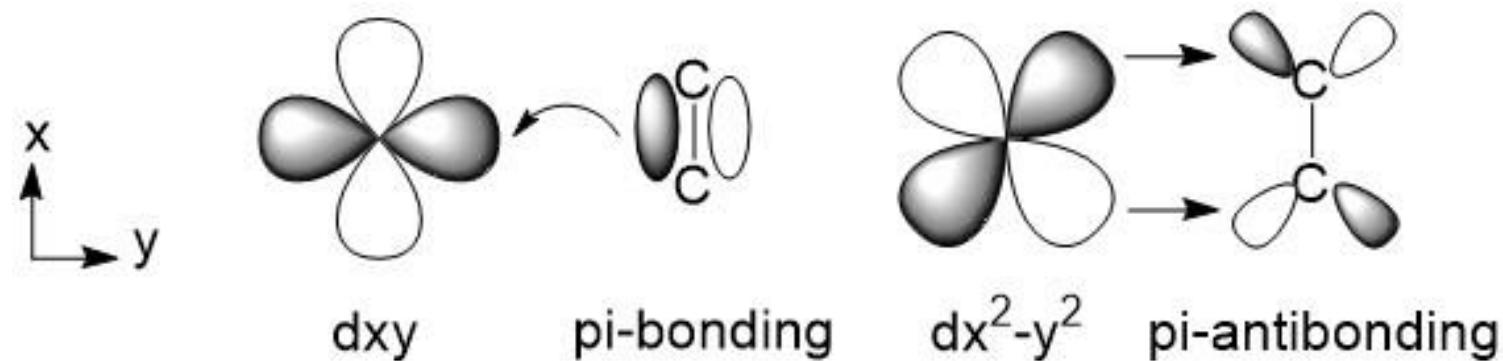
# Mechanism of Ziegler-Natta catalytic polymerization

1. Initiation, 2. Propagation 3. Termination

## Initiation step

The polymerization reaction is initiated by forming alkene-metal complex

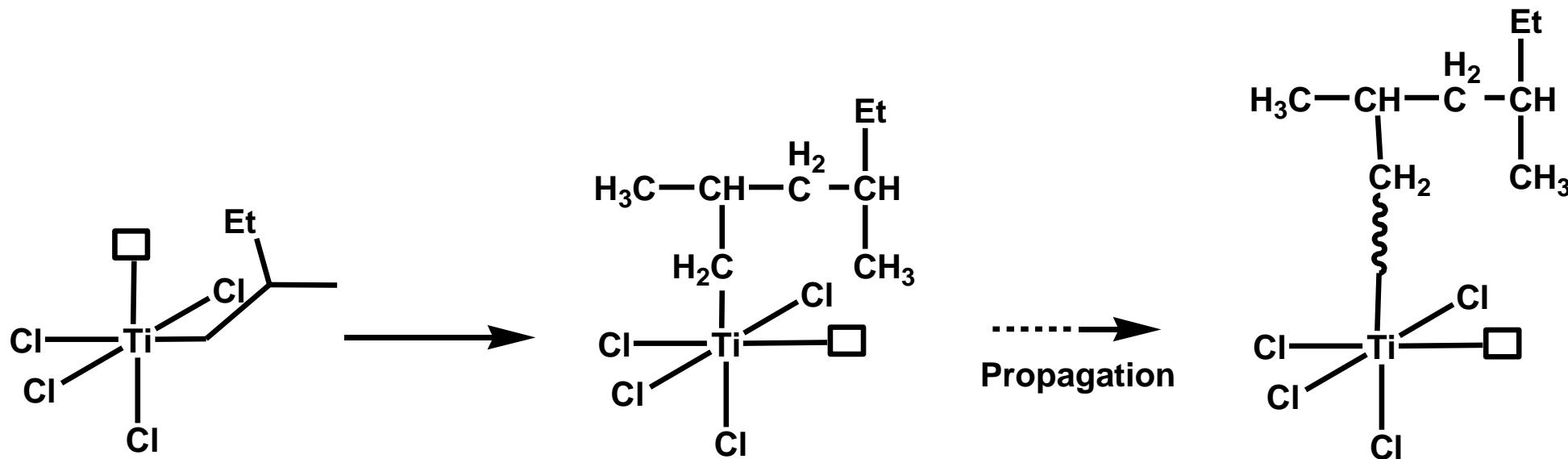
When a vinyl monomer like propylene comes to the active metal center, it can be coordinated to Ti atom by overlapping their orbitals



Interaction between metal-d orbital with  $\pi$ -bonding alkene

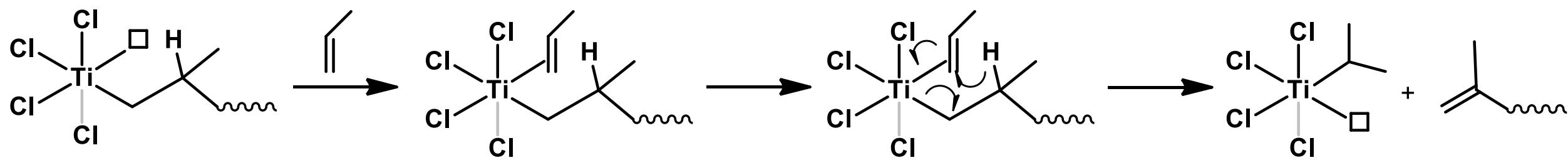
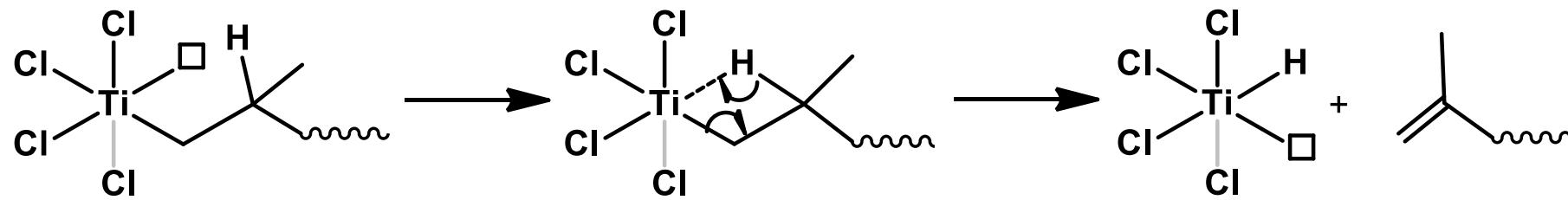
## Propagation step

When other propylene molecules come in, this process starts over and over, giving linear polypropylene



## Termination step

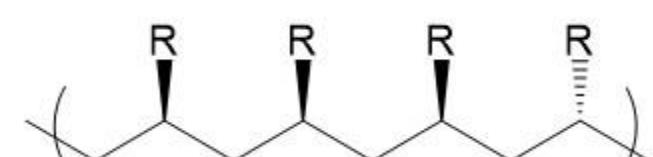
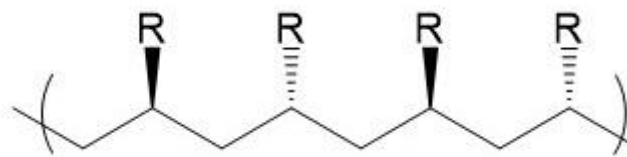
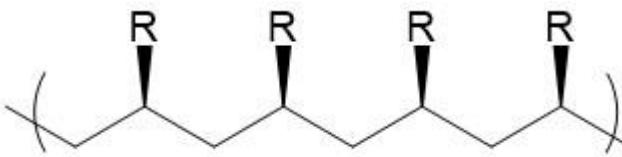
Termination is the final step of a chain-growth polymerization, forming desired polymers products.



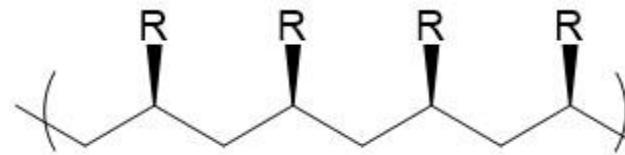
## Stereo-selectivity

Stereochemistry of polymers made from ZN-catalyst can be well regulated by rational design of ligands. By using different ligand system, either syndiotactic or isotactic polymers can be obtained.

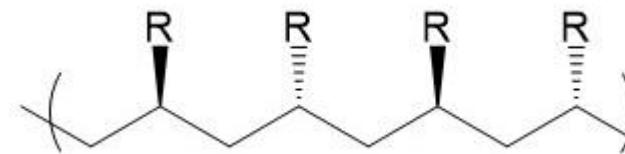
The relative stereochemistry of adjacent chiral centers within a macromolecule is defined as **tacticity**.



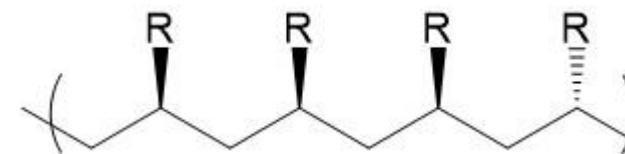
# Isotactic, Syndiotactic and Atactic Polymer



Isotactic polymers: substituents are located on the same side of the polymer backbone



Syndiotactic polymers: substituents located on alternative positions

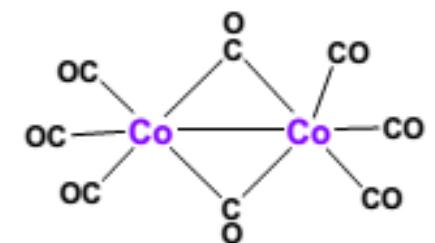


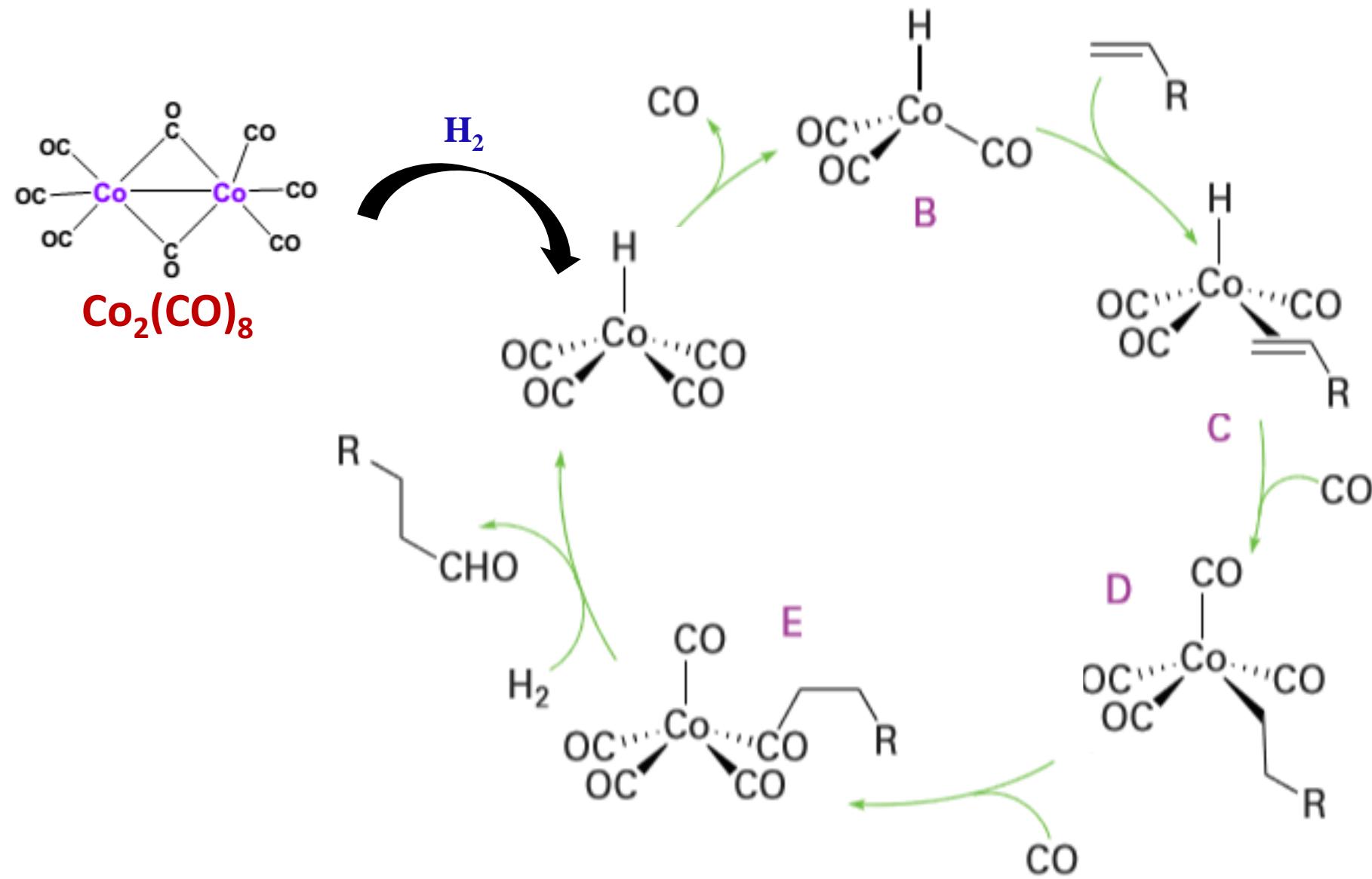
Atactic polymers: substituents located randomly along the chain

# Catalysis : Carbonylation reactions

## Oxo process

In the oxo process, **an olefin** (e.g. propylene), **dihydrogen**, and **carbon monoxide** react together in presence of dicobalt-octacarbonyl to give butyraldehydes.





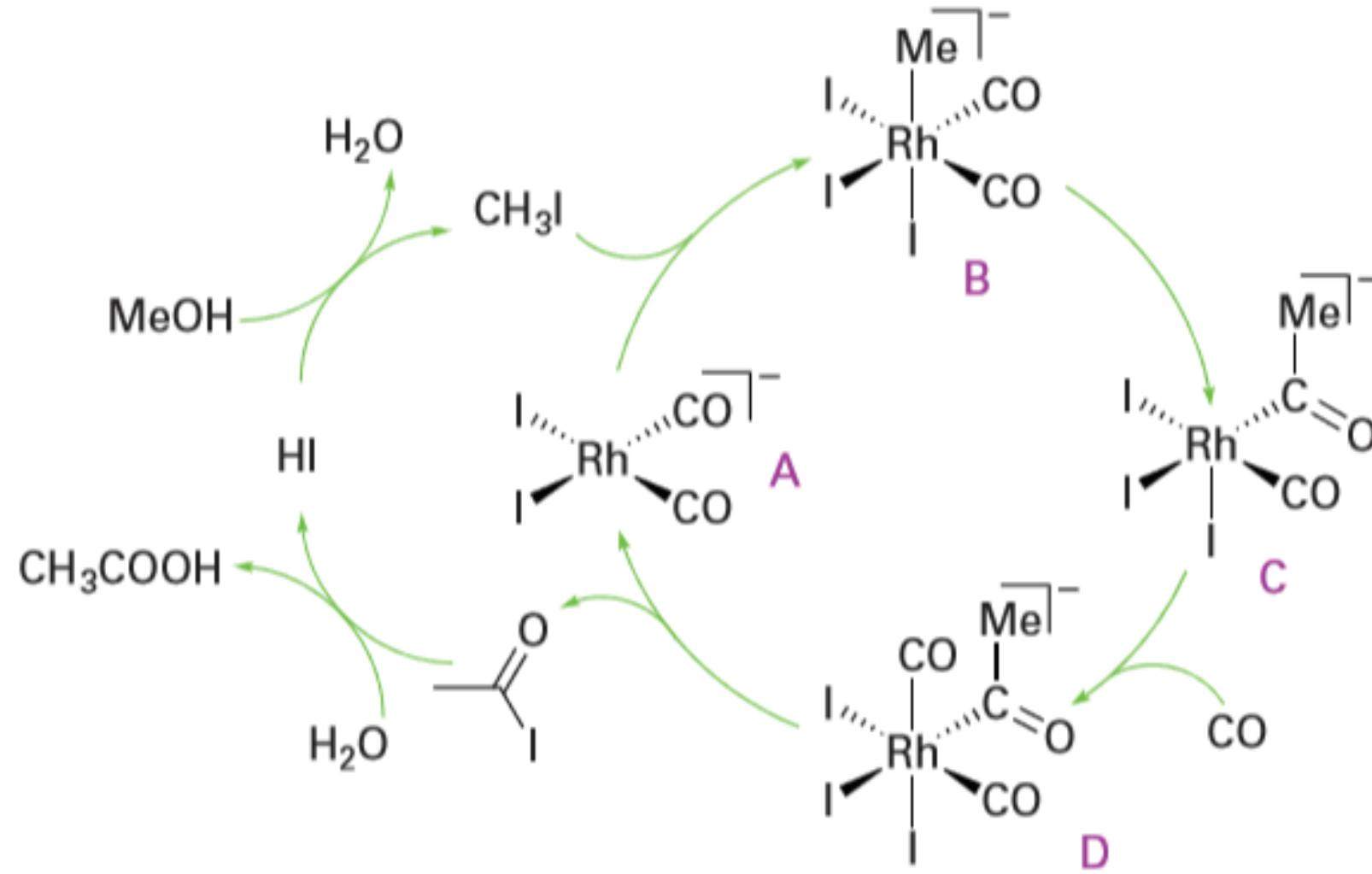
## Monsanto process

A highly successful industrial method for the manufacture of acetic acid by catalytic **carbonylation of methanol**

The reaction is catalyzed by a **Rh catalyst developed at Monsanto**

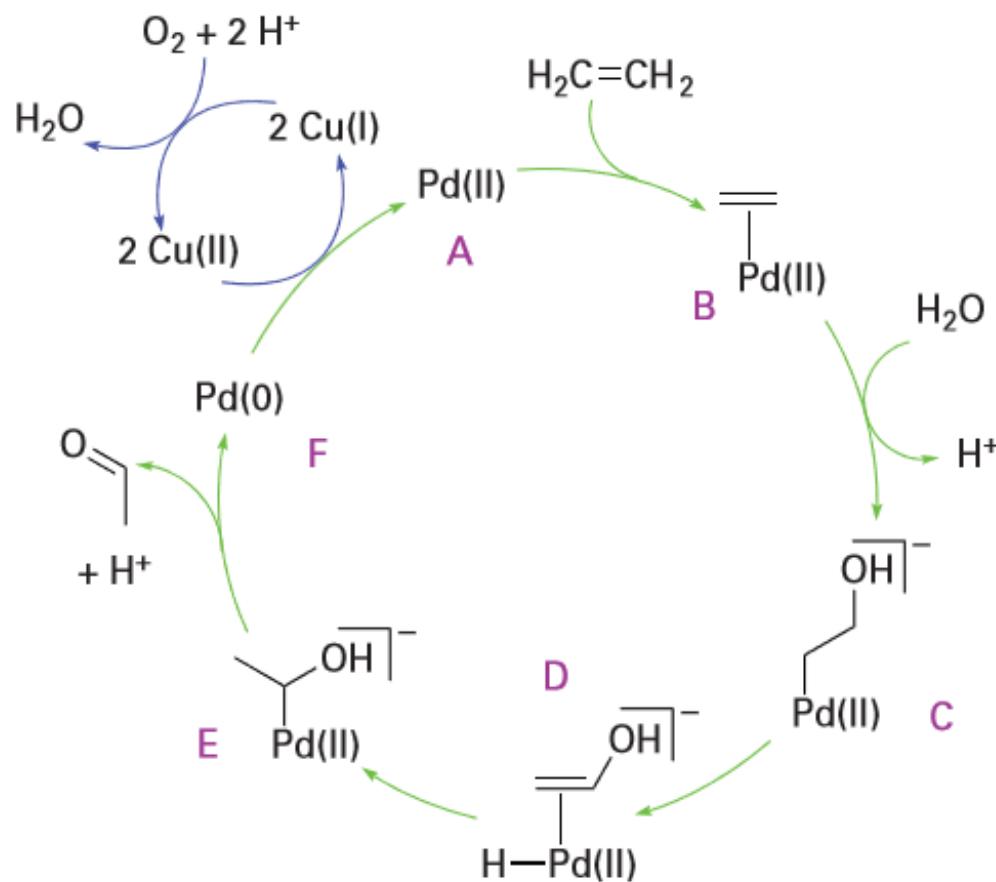


# Catalytic carbonylation of methanol

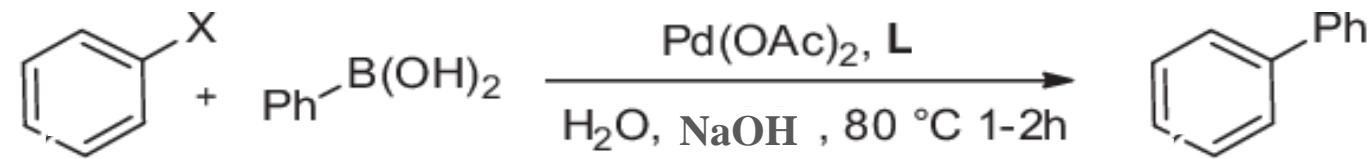


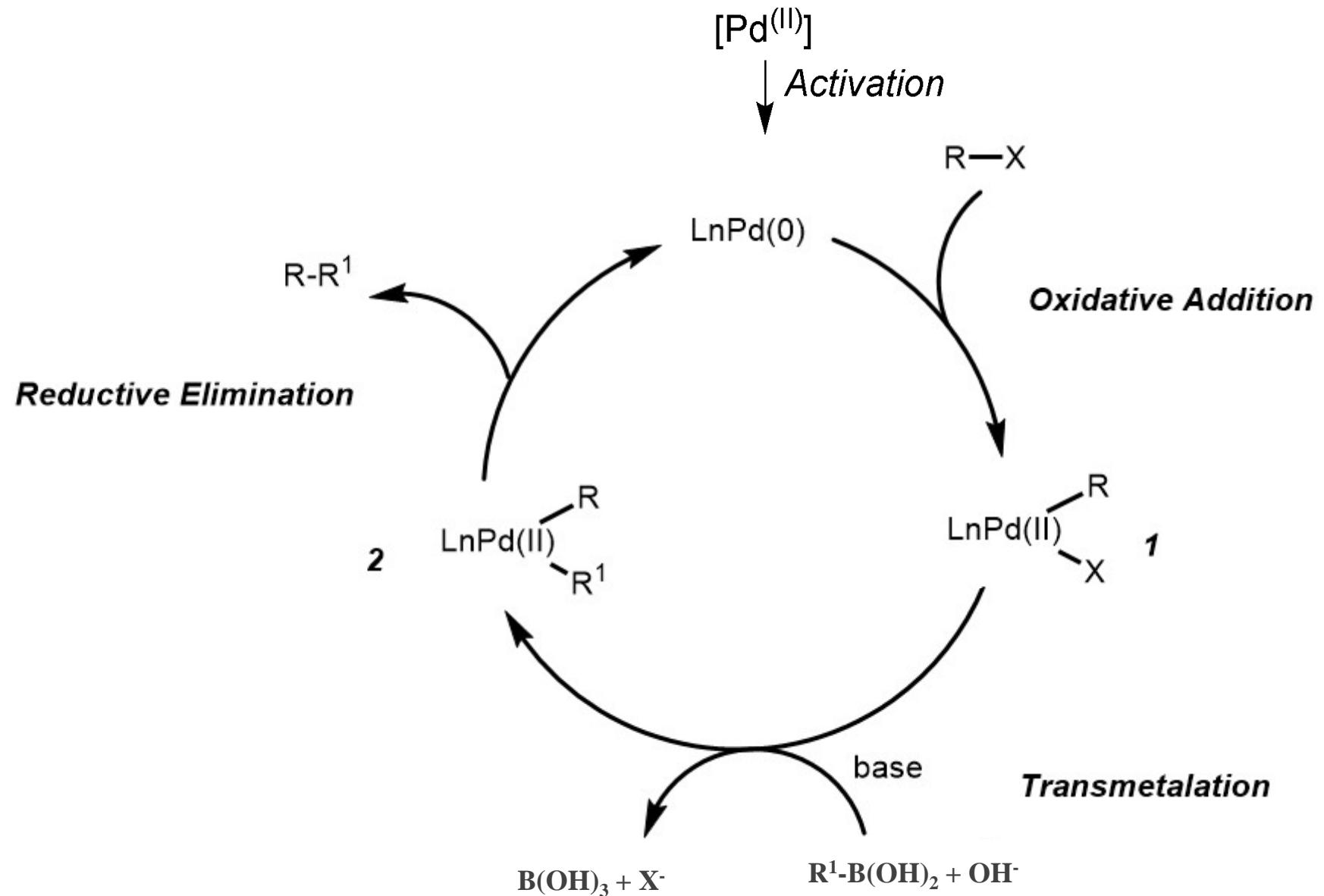
# Wacker Oxidation of alkenes

Wacker process is used to produce acetaldehyde from ethylene and oxygen using a palladium catalyst and  $\text{Cu}^{2+}$  as promoter



# Suzuki cross coupling reactions





Rank	Chemical	Catalytic process	Rank	Chemical	Catalytic process
1	Sulfuric acid	$\text{SO}_2$ , oxidation, heterogeneous	12	Ammonium nitrate	Precursors catalytic
2	Ethene	Hydrocarbon cracking, heterogeneous	13	Urea	$\text{NH}_3$ , precursor catalytic
3	Propene	Hydrocarbon cracking, heterogeneous	14	Ethylbenzene	Alkylation of benzene, homogeneous
3	Polyethene	Polymerization, heterogeneous	15	Styrene	Dehydrogenation of ethylbenzene, heterogeneous
5	Chlorine	Electrolysis, not catalytic	16	HCl	Precursors catalytic
6	Ammonia	$\text{N}_2 + \text{H}_2$ , heterogeneous	17	Cumene	Alkylation of benzene,
7	Phosphoric acid	Not catalytic	18	Ethylene oxide	heterogeneous
8	1,2-Dichloroethane	Ethene + $\text{Cl}_2$ , heterogeneous	19	Ammonium sulfate	Ethene + $\text{O}_2$ , heterogeneous
9	Polypropene	Polymerization, heterogeneous	20	Sodium carbonate	Precursors catalytic
10	Nitric acid	$\text{NH}_3 + \text{O}_2$ , heterogeneous			Not catalytic
11	Sodium hydroxide	Electrolysis, not catalytic			

Source: Facts & Figures for the Chemical Industry, *Chem. Eng. News*, 2009, 87, 33.

## Top 20 synthetic chemicals in the USA in 2008

## Catalytic efficiency and lifetime:

Turnover number (TON):

The turnover number is the **maximum number of cycles** for which **a catalyst survives**

High turnover number indicate catalyst is more stable for longer run and efficient. For industrial applications the TON is in the range  $10^6$ - $10^7$

What is turnover frequency (TOF)?

The turnover frequency is the **number of** molecular reactions or **catalytic cycles** carried out by **single catalyst center per unit time**

High turnover frequency indicates catalyst is very reactive

Q. The reaction between bromobenzene and phenylboronic acid required 10 mg palladium catalyst and 2 hrs time. If 0.25 moles of biphenyl was generate during the reaction and atomic mass of palladium is 106.42, then calculate the TON and TOF for the catalyst

Amount of product formed = **0.25 mole**

$$\text{Catalyst required} = \frac{10}{1000} \text{ g} = \frac{10}{1000 \times 106.42} \text{ mole} = 0.000093 \text{ mole}$$

$$\text{TON} = \frac{\text{moles of Product formed}}{\text{moles of catalyst used}} = \frac{0.25}{0.000093} = 2688.17$$

$$\text{TOF} = \frac{\text{TON}}{\text{Time(min)}} = \frac{2688.17}{120 \text{ min}} = 22.4 \text{ min}^{-1}$$

## What is the stability of a catalyst?

The chemical, thermal, and mechanical stability of a catalyst determines its lifetime in industrial reactors. Catalyst stability is influenced by numerous factors, including decomposition, coking, and poisoning. Catalyst deactivation can be followed by measuring activity or selectivity as a function of time. Catalysts that lose activity during a process can often be regenerated before they ultimately have to be replaced. The total catalyst lifetime is of crucial importance for the economics of a process.

## Selectivity of the catalyst:

A selective catalyst yields a high proportion of the desired product with minimum amounts of side products.



when metallic silver is used to catalyst for the oxidation of ethylene with oxygen to produce oxirane (ethylene oxide), the reaction is accompanied with the formation of undesirable  $CO_2$  and  $H_2O$ . This lack of selectivity increases the consumption of ethene, so chemists are constantly trying to devise a more selective catalyst for oxirane synthesis.

# **Types of Catalytic reaction**

## → **I. Homogeneous**

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Typically, all the reactants and catalysts either are in liquid or gas phase

## → **II. Heterogeneous**

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Reactions of liquid or gases in the presence of solid catalysts are the typical examples

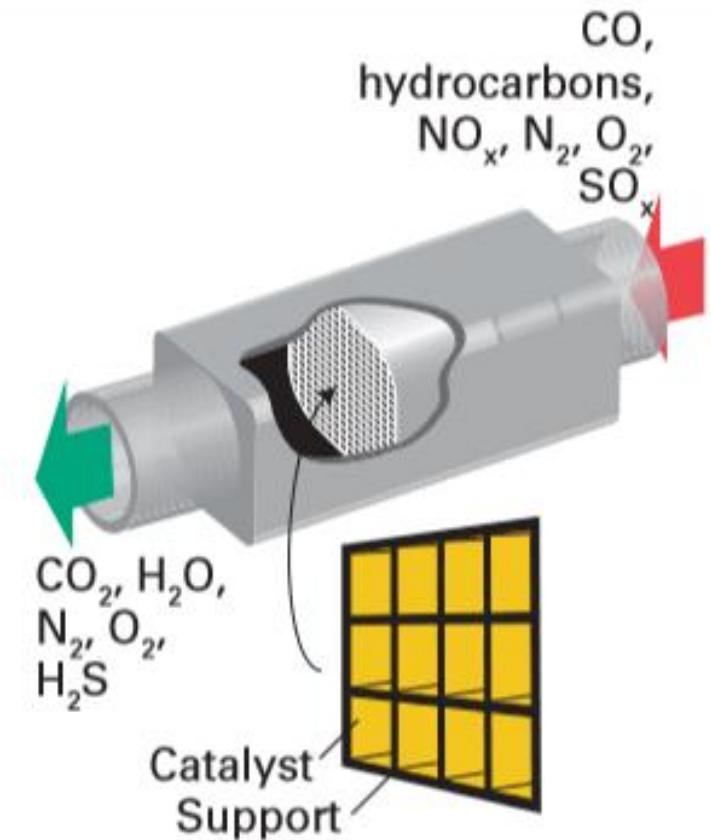
e.g. Hydrogenation of alkene/alkyne over Raney Ni catalyst

# Heterogeneous solid catalysis is strongly associated with adsorption phenomenon

- At least one of the reactant needs to be **adsorbed on the surface of the catalyst**
- Adsorption of a component ‘A’ on surface of material ‘B’: component ‘A’ is called **adsorbate** and surface ‘B’ is called **adsorbent**
- The surfaces include both **external surface and internal surface** due to the pores  
For porous materials: the internal surface area due to the pores is much higher than the external surface area.

**Heterogeneous catalysts** are used very **extensively** in **industry** and have a much **greater economic impact** than homogeneous catalysts. One attractive feature is that many of these **solid catalysts are robust at high temperatures** and therefore tolerate a wide range of operating conditions. Reactions are faster at high temperatures, so at high temperatures solid catalysts generally produce higher outputs for a given amount of catalyst and reaction time than homogeneous catalysts operating at lower temperatures in solutions. **Easy separation of the product from the catalyst**, resulting in efficient and more environmentally friendly processes.

The catalytic converter consists of a honeycomb stainless steel or ceramic structure on to which first silica and alumina are deposited followed by a mixture of platinum, rhodium, and palladium as nanoparticles, with diameters typically between 10 and 50 nm. A three-way catalytic converter, used with petrol (gasoline) engines undertakes the following three reactions.

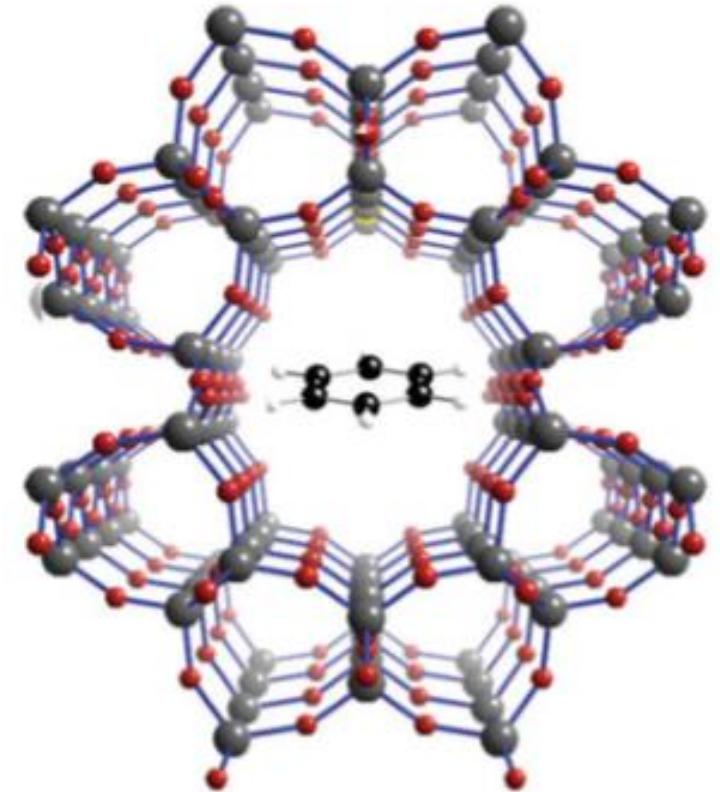


**Figure 26.4** A heterogeneous catalyst in action. The automobile catalytic converter oxidizes CO and hydrocarbons, and reduces nitrogen and sulfur oxides. The particles of a metal catalyst are supported on a robust, ceramic honeycomb.

# Zeolites

**Zeolites** are examples of uniform catalysts. They are prepared as very fine crystals that contain large **regular channels** and cages defined by the crystal structure.

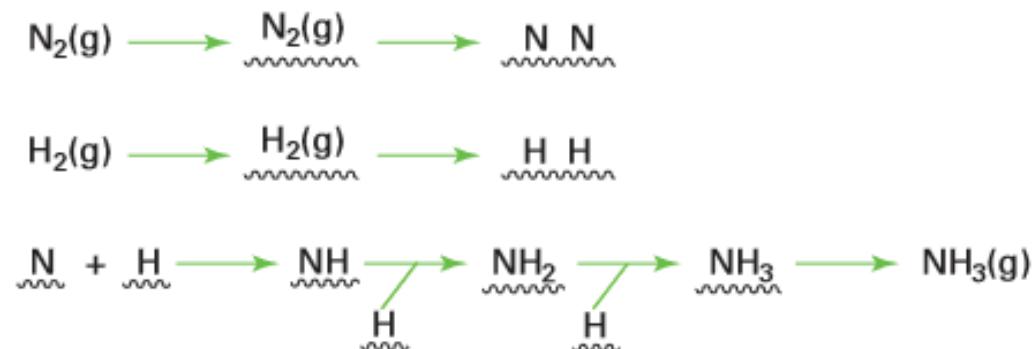
The **zeolites absorbs molecules small enough to enter the channels** and excludes larger molecules. This selectivity, in combination with catalytic sites inside the cages, provides a degree of **control over catalytic reactions**.



A view into the channels of zeolite theta-1 with an absorbed benzene molecule in the large central channel

## Ammonia synthesis:

Iron metal, together with small quantities of alumina and potassium salts and other promoters, is used as the catalyst for ammonia synthesis. **Rate-determining step** under normal operating conditions is the **dissociation of  $\text{N}_2$**  coordinated to the catalyst surface. The other reactant,  $\text{H}_2$ , undergoes much more facile dissociation on the metal surface and a series of insertion reactions between adsorbed species leads to the production of  $\text{NH}_3$ . Because of the slowness of the  $\text{N}_2$  dissociation, it is necessary to run the ammonia synthesis at high temperatures, typically **400°C**. High pressures in the order of **100 atm** are used to favour of the formation ammonia.

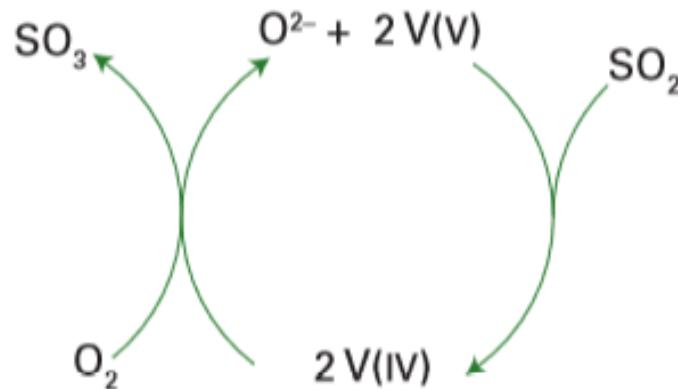


# Sulfurdioxide oxidation

The most widely used catalyst for the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  is **molten potassium vanadate** supported on a high-surface-area silica.

The oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  is a key step in the production of sulfuric acid.

In the first stage, the **combustion of sulfur** raises the temperature to about  $600^\circ\text{C}$  then **cooling and pressurize the gas mixture** before the catalytic stage to shift the equilibrium to the right.

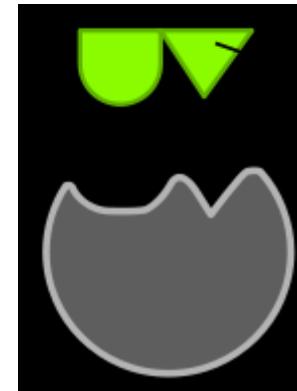


## Fischer-Tropsch synthesis

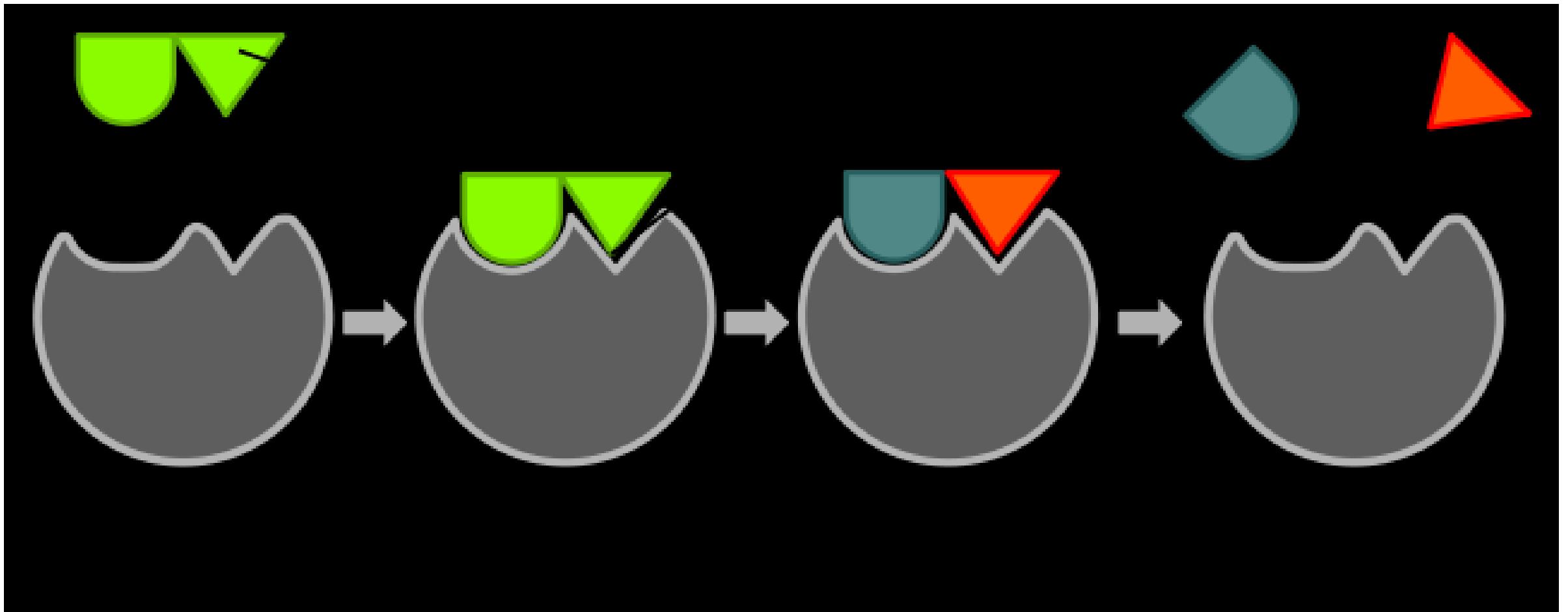
Hydrogen and carbon monoxide can be converted to hydrocarbons and water by reaction over iron or cobalt catalysts



# Enzyme Catalysis



- Homogeneous catalysis
- Reactions catalyzed by certain complex organic substance called as Enzyme
- Enzymes are proteins with high molecular mass  $\geq 10,000$ , derived from living organism
- Enzymes are selectively catalyzes the specific reaction



# Enzymes: Substrate selectivity



Diastase enzyme catalyze starch to maltose sugar.

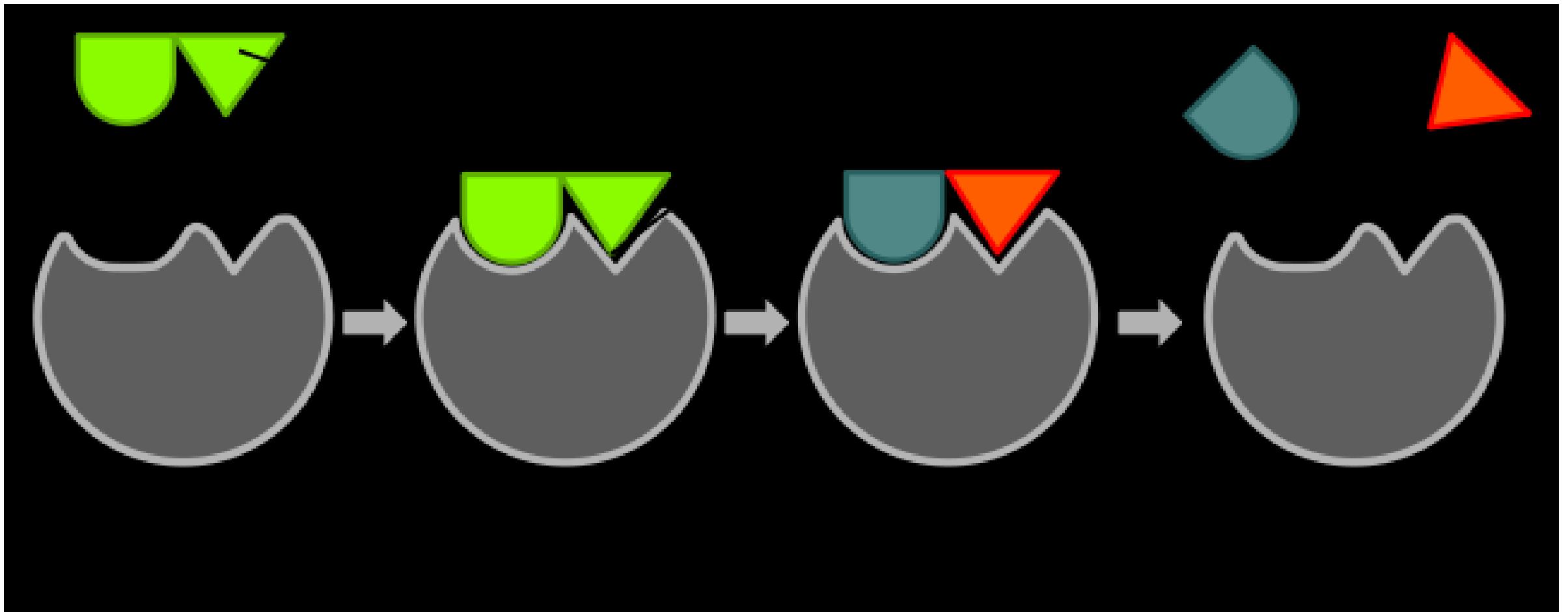


Invertase enzyme is converted cane sugar into glucose and fructose

# Cofactor

A **cofactor** is a non-protein chemical compound or metallic ion that is required for an enzyme's activity. Cofactors can be considered "helper molecules" that assist in biochemical transformation.

Cofactors can be inorganic ions or complex organic molecules called **coenzymes**, the latter of which is mostly derived from vitamins and other organic essential nutrients in small amounts.



## **Coenzyme**

A coenzyme is an organic non-protein compound that binds with an enzyme to catalyze a reaction. A coenzyme cannot function alone, but can be reused several times when paired with an enzyme.

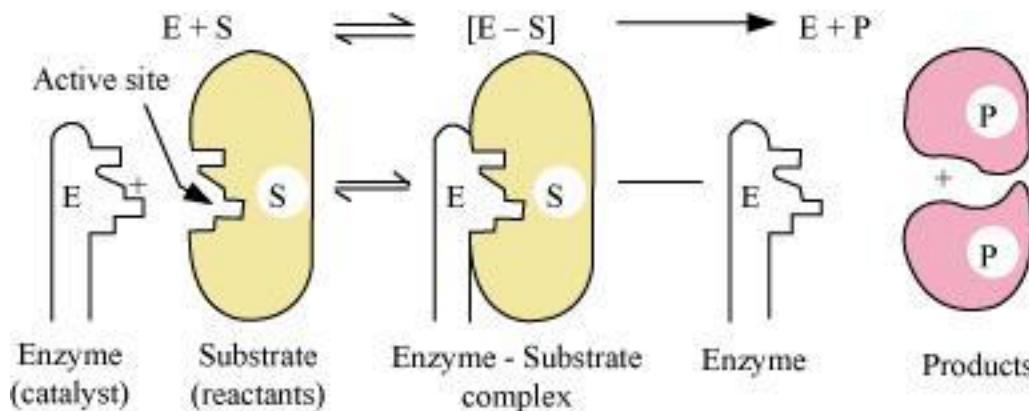
## **Functions of Coenzymes**

An enzyme without a coenzyme is called an *apoenzyme*.

Without coenzymes or cofactors, enzymes(apoenzyme) cannot catalyze reactions effectively, even may not function at all.

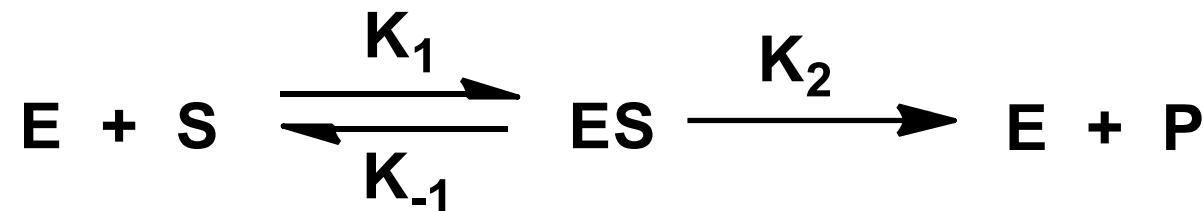
When an apoenzyme gains a coenzyme, it then becomes an active enzyme (*holoenzyme*). Active enzymes change substrates into the products

# Mechanism and Kinetics of Enzyme Catalysis



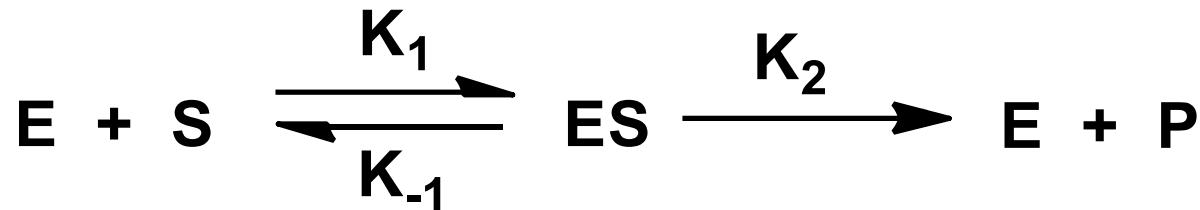
- Formation of **enzyme substrate complex** is a critical event in an enzyme-catalyzed reaction.
- Michaelis and Menten proposed that the **binding of the substrate and the enzyme is reversible** and derived a kinetic model for a simple single substrate enzymatic reaction.
- This is useful for understanding the various factors that influence rate of the reaction, viz. concentration, temperature and pH of the system.

Consider a simple single substrate reaction, where free enzyme E binds to the substrate S to form a complex ES, the forms product P and then dissociates.



The dissociation of ES complex into free enzyme and product is the slowest and hence it is the rate-limiting step in the reaction.

Throughout the reaction, the total concentration of the enzyme will be the concentration of enzyme at the beginning  $[E_0]$  minus concentration of total enzyme bound with substrate  $[ES]$ .



At pre-steady state, substrate concentration is more than that of the enzyme concentration

As reaction proceeds, the concentration of the enzyme substrate complex increases with time and reaches a steady state

After this stage, the concentration does not change further with time

## Assumptions in Michaelis and Menten Kinetics

- Once the system attains a steady state, the concentration of ES remains the same throughout the process.  $\frac{d[ES]}{dt} = 0$
- The free enzyme [E] at any point of time in the reaction will be equal to the concentration of the enzyme substrate complex [ES] subtracted from the total enzyme concentration [E<sub>0</sub>]

$$[E] = [E_0] - [ES]$$

Rate of formation of  $ES = K_1 [E][S] = K_1 ([E_0] - [ES])[S]$

Rate of breakdown of  $ES = K_{-1}[ES] + K_2[ES]$

**From the steady state assumption,  
rate of formation = rate of breakdown**

$$ES = K_1 [E][S] = K_1 ([E_0] - [ES])[S]$$

$$ES = K_{-1}[ES] + K_2[ES]$$

$$K_1([E_0] - [ES])[S] = K_{-1}[ES] + K_2[ES]$$

$$K_1 [E_0][S] - K_1 [ES][S] = (K_{-1} + K_2)[ES]$$

$$K_1 [E_0][S] = (K_{-1} + K_2)[ES] + K_1[ES][S]$$

$$K_1 [E_0][S] = \{(K_{-1} + K_2) + K_1 [S]\}[ES]$$

$$[ES] = \frac{K_1[E_0][S]}{(K_{-1} + K_2) + K_1[S]} = \frac{[E_0][S]}{\frac{(K_{-1} + K_2)}{K_1} + [S]}$$

$$[ES] = \frac{[E_0][S]}{K_m + [S]}$$

$$\frac{(K_{-1} + K_2)}{K_1} = K_m$$

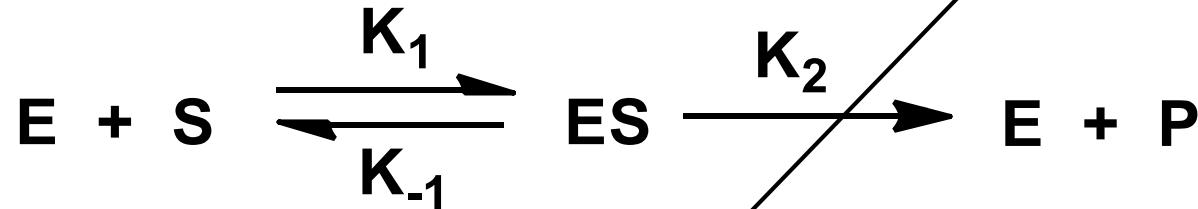
↑

**Michaelis-Menten rate constant**

## Michaelis and Menten

$$\text{Rate of formation of the products (V)} = K_2[ES] = \frac{K_2[E_0][S]}{K_m + [S]}$$
$$= \frac{V_{\max}[S]}{K_m + [S]}$$

When rate of formation of product is maximum



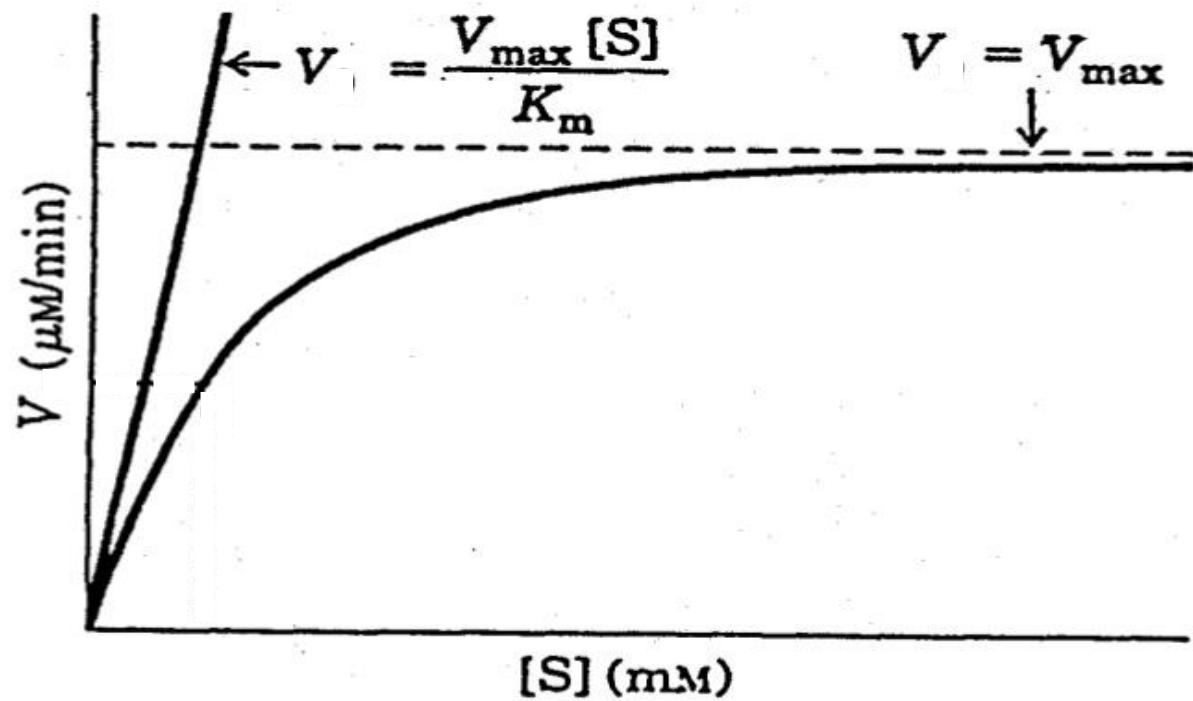
$$[ES] = [E_0]$$

$$\text{We know, } V = K_2[ES]$$

$$\text{Then, } V_{\max} = K_2[E_0]$$

$$\text{Rate of formation of the products (V)} = \frac{V_{\max}[S]}{K_m + [S]}$$

Michaelis-Menten Curve



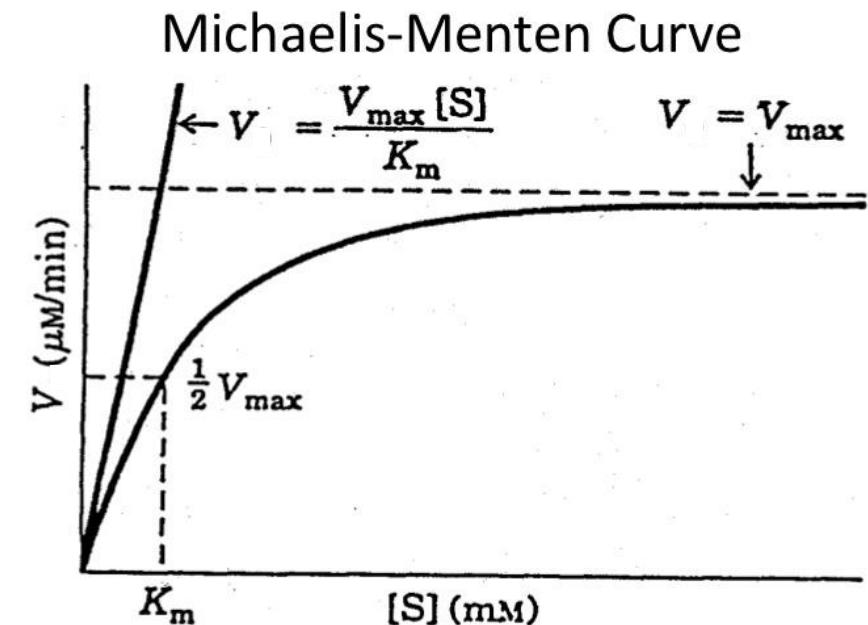
Rate of formation of the products,  $V = \frac{V_{\max}[S]}{K_m + [S]}$

**Key point:**

$$V = \frac{V_{\max}[S]}{[S] + [S]} = \frac{V_{\max}[S]}{2[S]} = \frac{V_{\max}}{2}$$

(a)  $K_m$  must have same unit as  $[S]$

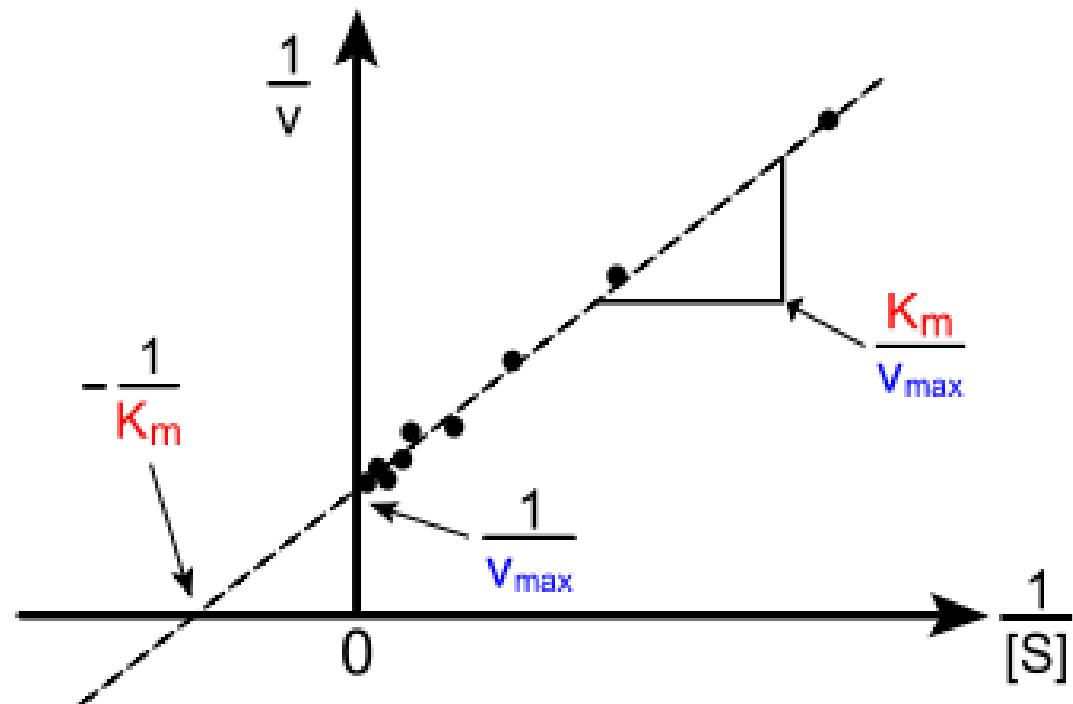
(b) At some point  $K_m$  must be equal to  $[S]$



## Lineweaver-Burk (double reciprocal plot)

From Michaelis and Menten eq<sup>n</sup>. we found  $V = \frac{V_{\max}[S]}{K_m + [S]}$

Lineweaver-Burk (double reciprocal plot)  $\frac{1}{V} = \frac{K_m}{V_{\max}[S]} + \frac{1}{V_{\max}}$



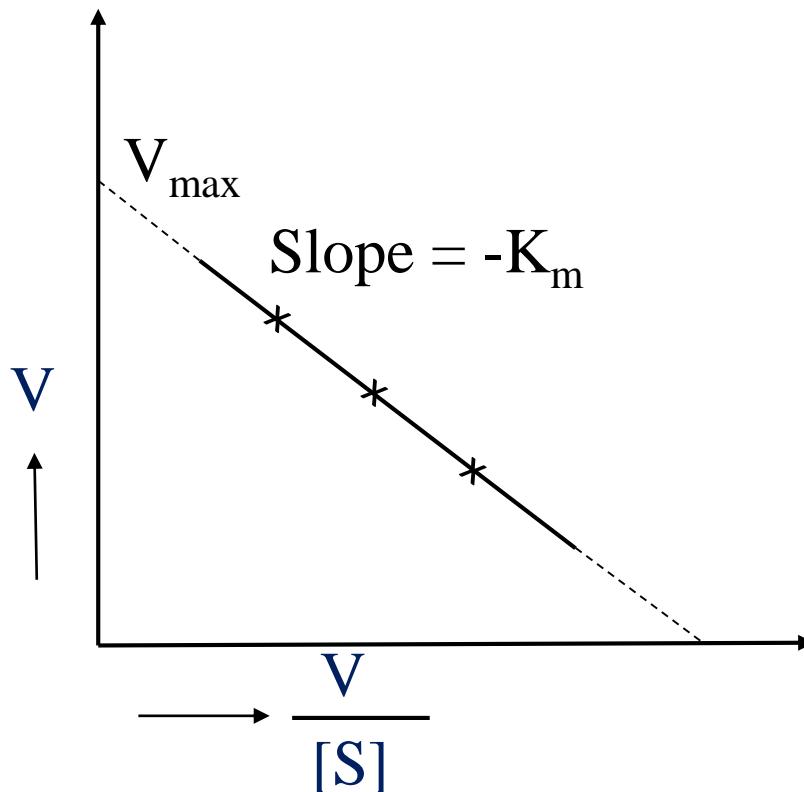
## Eadie-Hofstee diagram

Rate of formation of the products,  $V = \frac{V_{\max} [S]}{K_m + [S]}$

$$\left( \frac{1}{V} = \frac{K_m}{V_{\max}[S]} + \frac{1}{V_{\max}} \right) V V_{\max}$$

$$V_{\max} = K_m \frac{V}{[S]} + V$$

$$V = -K_m \frac{V}{[S]} + V_{\max}$$



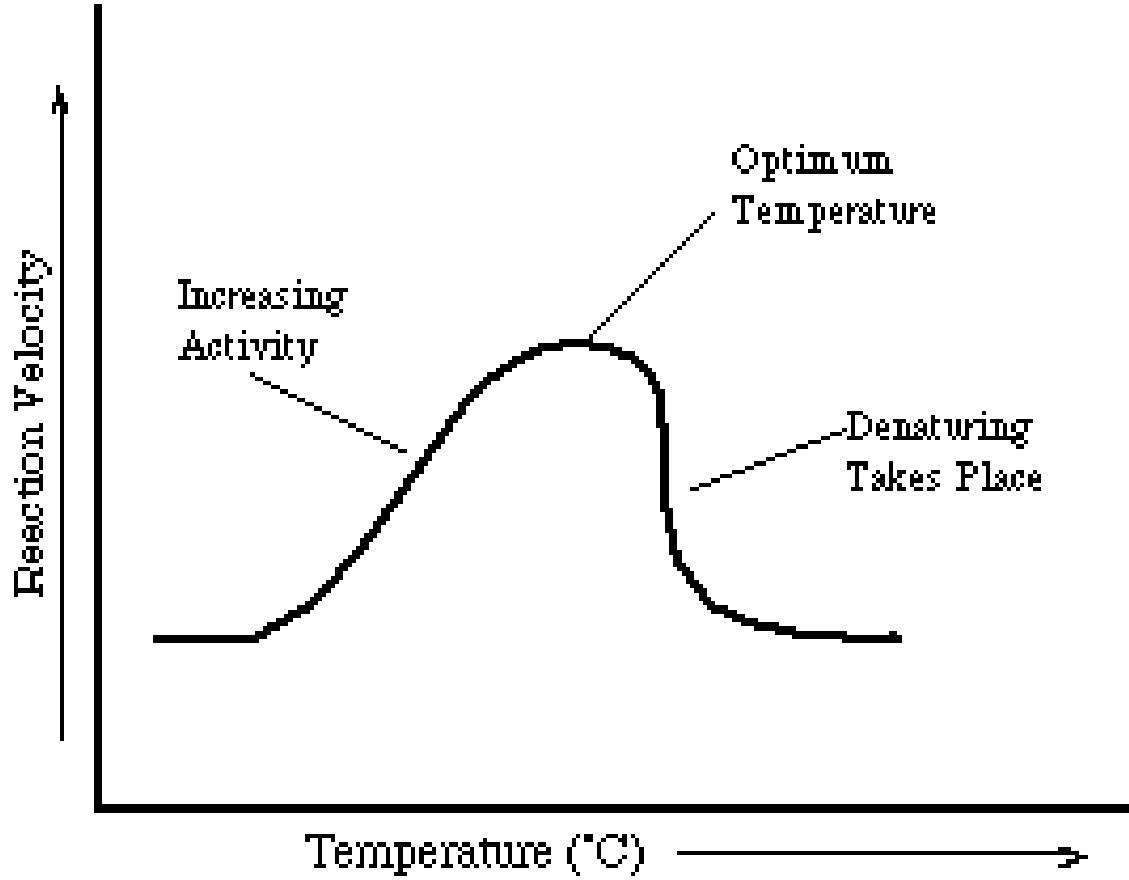
## Temperature effect

Rate of an enzyme-catalyzed reaction increases with the temperature upto a certain temperature

Enzymes are adversely affected by high temperatures and the reaction rate increases with temperature to a maximum level, then abruptly declines with further increase of temperature

Because most animal enzymes rapidly become denatured at temperatures above 40°C

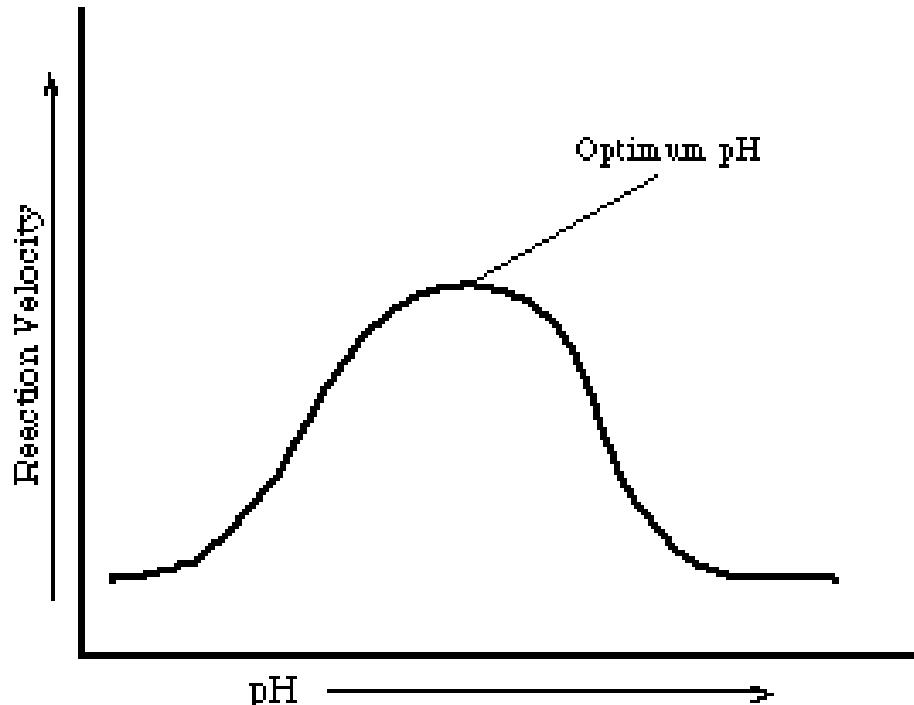
Enzymes can be deactivated at even moderate temperatures. Thus, enzymes stores at 5°C or below.



## Effects of pH

Enzymes are affected by changes in pH. The most favorable pH value ( at the point where the enzyme is most active) is known as the optimum pH

Extremely high or low pH values generally result in complete loss of activity for most enzymes



# **Electrochemical corrosion Mechanisms, control and prevention**

Ref: A Text book of Engineering Chemistry by Shashi Chawla

# Corrosion

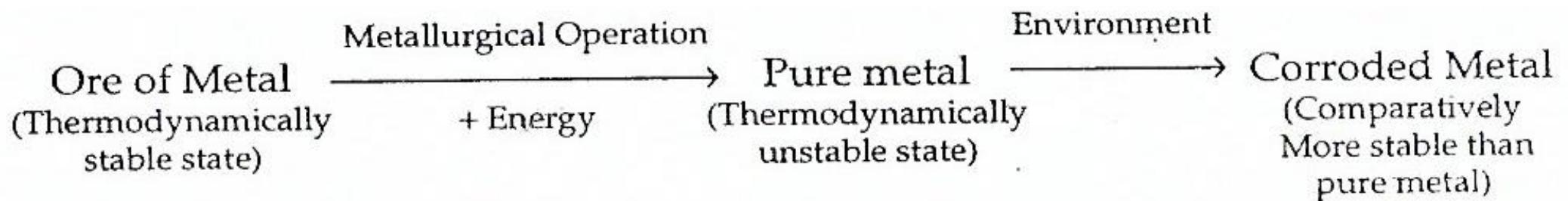
Corrosion is the process of gradual and irreversible damage or deterioration of a material due to the unwanted chemical or electro chemical interaction with its environment.



➤ Metals get oxidized

## □ Cause of corrosion

- Metal exist in nature as its ore
- During metallurgy energy is spent to get the pure metal from ore
- So the metal is thermodynamically unstable
- It has the tendency to go back to its original state



## □ Effect of corrosion

- (a) Loss of useful properties of metal and thus loss of efficiency,
- (b) Decrease in production rate, because efficiency is less and replacement of corroded equipment is time-consuming,
- (c) Increase in maintenance and production cost, and
- (d) Contamination of product.

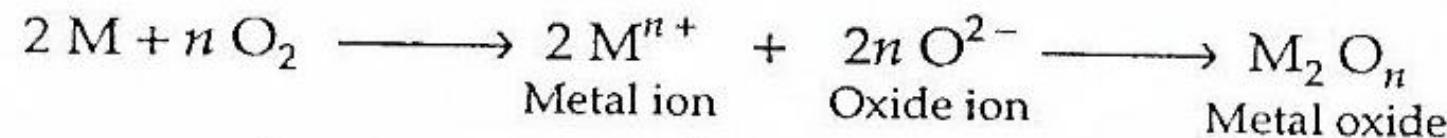
## □ Types of corrosion

- Chemical or Dry corrosion: under anhydrous condition
- Electro chemical or wet corrosion

## 1. Chemical or Dry corrosion

Direct interaction of metal surface with atmospheric gases or anhydrous liquid, leads to chemical corrosion

It generally takes place in absence of moisture via



**Alkali and alkaline earth metals get oxidized at low temperature other metals except Ag, Au and Pt gets oxidized at high temperature**

### Pilling-Bedworth rule:

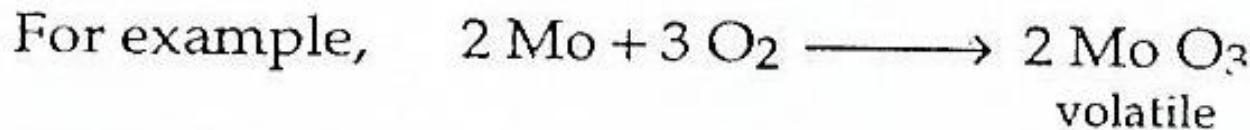
Smaller the specific volume ratio, between the metal oxide and metal, greater is the corrosion

$$\text{specific volume ratio} \left( = \frac{\text{volume of metal oxide}}{\text{volume of metal}} \right),$$

## Effect of chemical or dry corrosion

Thin layer of ***metal oxide*** formed at the surface of the metal

- >(i) stable, impervious and tightly-adhering, like the oxide films on Cu or Al, it acts as a protective coating and thus further corrosion is prevented.
- (ii) unstable and decomposes back to metal and oxygen. That's why Ag, Au and Pt do not undergo oxidation corrosion.
- (iii) Volatile, the moment it is formed it gets volatilized and metal surface again gets exposed for further attack leading to continuous and rapid corrosion.



Hence Mo undergoes excessive corrosion.

- (iv) Porous, hence further attack through cracks or pores continues and hence the corrosion continues till the entire metal is converted to metal oxide.

## Liquid metal corrosion

Liquid metal corrosion occurs when liquid metal is allowed to flow over solid metal at high temperature. It leads to weakening of the solid metal due to (i) its dissolution in liquid metal or (ii) penetration of liquid metal into solid metal. For example, coolant (Sodium metal) leads to corrosion of cadmium in nuclear reactor.

## 2. Electro chemical corrosion or wet corrosion :

Mostly takes place under wet or moist condition through the formation of a short circuit galvanic cells

Most common than dry corrosion

## Standard Reduction Potentials at 25 °C

	Reduction Half-Reaction	E° (V)	
<b>Stronger oxidizing agent</b> 	$\text{F}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(aq)$	2.87	<b>Weaker reducing agent</b> 
	$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(l)$	1.78	
	$\text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l)$	1.51	
	$\text{Cl}_2(g) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(aq)$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33	
	$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(l)$	1.23	
	$\text{Br}_2(aq) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(aq)$	1.09	
	$\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$	0.80	
	$\text{Fe}^{3+}(aq) + \text{e}^- \longrightarrow \text{Fe}^{2+}(aq)$	0.77	
	$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(aq)$	0.70	
	$\text{I}_2(s) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(aq)$	0.54	
	$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(aq)$	0.40	
	$\text{Cu}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Cu}(s)$	0.34	
	$\text{Sn}^{4+}(aq) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(aq)$	0.15	
	$2 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{H}_2(g)$	0	
<b>Weaker oxidizing agent</b> 	$\text{Pb}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Pb}(s)$	-0.13	<b>Stronger reducing agent</b> 
	$\text{Ni}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Ni}(s)$	-0.26	
	$\text{Cd}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Cd}(s)$	-0.40	
	$\text{Fe}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Fe}(s)$	-0.45	
	$\text{Zn}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Zn}(s)$	-0.76	
	$2 \text{H}_2\text{O}(l) + 2 \text{e}^- \longrightarrow \text{H}_2(g) + 2 \text{OH}^-(aq)$	-0.83	
	$\text{Al}^{3+}(aq) + 3 \text{e}^- \longrightarrow \text{Al}(s)$	-1.66	
	$\text{Mg}^{2+}(aq) + 2 \text{e}^- \longrightarrow \text{Mg}(s)$	-2.37	
	$\text{Na}^+(aq) + \text{e}^- \longrightarrow \text{Na}(s)$	-2.71	
	$\text{Li}^+(aq) + \text{e}^- \longrightarrow \text{Li}(s)$	-3.04	

## Electro chemical corrosion involves:

- (i) Separate 'anodic' and 'cathodic' parts/areas between which current flows through the conducting medium.
- (ii) Occurrence of oxidation (corrosion) at anodic areas which generates metallic ions,
- (iii) Non-metallic ions like  $\text{OH}^-$  or  $\text{O}^{2-}$  are formed at cathodic areas, and
- (iv) Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosion products somewhere between anodic and cathodic areas.

## Rusting of iron

In neutral aqueous medium in presence of oxygen

In acidic medium with the evolution of Hydrogen gas

$\text{Fe}^{2+}$  ions originates at anode and  $\text{OH}^-$  ions originate at cathode

$\text{Fe}^{2+}$  ions diffuses more rapidly as the size is small, so corrosion occurs at anode  
but rust deposited at cathode

# Cathodic reaction

## In presence of dissolved oxygen

- (a) in acidic medium :  $4 \text{ H}^+ + \text{O}_2 + 4 e^- \rightarrow 2 \text{ H}_2\text{O}$
- (b) in neutral or weakly alkaline medium :  $2 \text{ H}_2\text{O} + \text{O}_2 + 4 e^- \rightarrow 4 \text{ OH}^-$

## In absence of oxygen

- (a) in acidic medium  $2 \text{ H}^+ + 2 e^- \rightarrow \text{H}_2$
- (b) in neutral or alkaline medium :  $2 \text{ H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + 2 \text{ OH}^-$

# Comparison of Chemical Corrosion with Electrochemical Corrosion

S.No.	<i>Chemical Corrosion</i>	<i>Electrochemical Corrosion</i>
1.	It occurs in <u>dry condition</u> .	It occurs in <u>wet condition</u> (in the presence of electrolyte or moisture)
2.	It involves the <u>direct chemical attack</u> of the metal by environment.	It involves the setting up of a large number of <u>galvanic cells</u> .
3.	It is explained by <u>absorption mechanism</u> .	It is explained by <u>mechanism of electrochemical reactions</u> .
4.	It occurs on both <u>homogeneous</u> and <u>heterogeneous surfaces</u> .	It occurs only on <u>heterogeneous metal surface</u> .
5.	Corrosion is <u>uniform</u> .	Corrosion is <u>not uniform</u> , if the <u>anode area is small</u> , pitting is more frequent.
6.	It is a <u>slow process</u> .	It is a <u>fast process</u> .
7.	Corrosion products <u>accumulate at the same place where corrosion occurs</u> .	Corrosion occurs at the <u>anode</u> , but products accumulate near the <u>cathode</u> .

## **Passivation:-**

The phenomenon by which the a metal or alloy shows high corrosion resistance due to the formation of a highly protective very thin and quite invisible surface coating

Passivation takes place only in certain environment which tend to maintain the protective film

eg: stainless steel alloy of Fe (Ti, Cr, Al, and Cr)

Exhibit outstanding corrosion resistance in the presence of Oxygen (Formed Oxide film automatically repairs in oxidizing environment but corrode easily in reductive environment)

Conc.  $\text{HNO}_3$  have no effect, presence of Cr maintain a protective oxide and shows high corrosion resistance in  $\text{HNO}_3$  solution.

## Galvanic series (Electrode potential series):-

The galvanic series plays a vital role in determining and preventing corrosion

Essentially, galvanic corrosion occurs when two different metals immersed in an electrolyte are joined together.

### *Galvanic series :*

Mg, Mg alloys, Zn, Al, Cd, Mild steel, Cast iron, Solder, Pb, Sn,

Anodic

(Easily corroded)

Brass,  
Cu,  
Ni,

Cathodic (Protected)

Pt, Au, Ti, Ag, Cr, Stainless steel

Passivation makes effective electrode potentials of some metals more positive so they act as cathodic and exhibit noble behavior

# **Difference between Electro chemical series and Galvanic series**

<b>Electrochemical series</b>	<b>Galvanic series</b>
Predicts the relative displacement tendencies of metals and nonmetals	Predicts the corrosion tendencies of both metals and non metals in actual environment
Depends on centration of salt in the electrolyte (Particularly the same metal)	It does not
Reference electrode is SHE	Reference electrode is calomel electrode
Position of the alloy is not listed	Position of the metal alloy is deferent from metal
Effect of environment is not predicted	Predicted

# **Types of Electrochemical corrosion**

- 1. Galvanic corrosion**
- 2. Pitting corrosion**
- 3. Crevice corrosion**
- 4. Concentration cell corrosion**
- 5. Waterline corrosion**

# 1. Galvanic corrosion or differential metal corrosion(DMC)

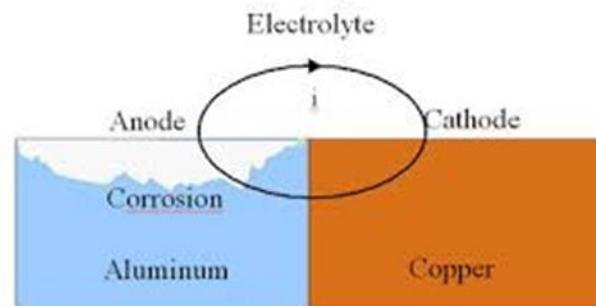
Galvanic Corrosion can occur when dissimilar metals are in contact in the presence of an electrolyte.



Metal which is higher up in the electrochemical series can act as anode (High electrode potential) and undergo corrosion

Eg, Zn (corroded) and Cu (protected)

- Zn and Ag
- Fe and Cu



**It can be minimized**  
Avoiding galvanic couple  
Providing insulating material

$$E^{\circ}_{(Zn+2/Zn)} = -0.76 \text{ V}; E^{\circ}_{(Ag+/Ag)} = +0.80$$

## 2. Pitting corrosion

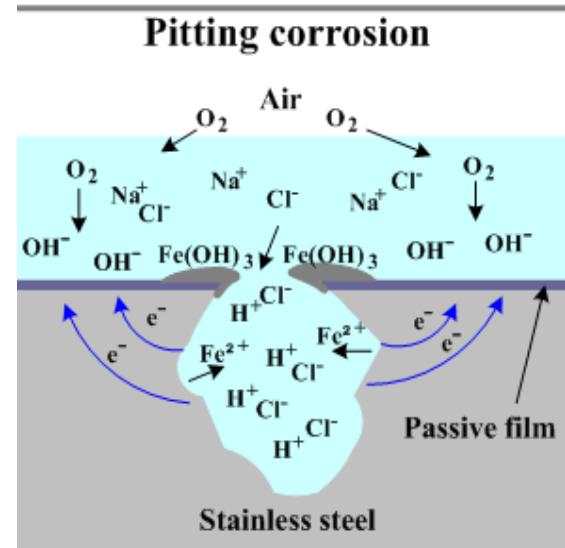
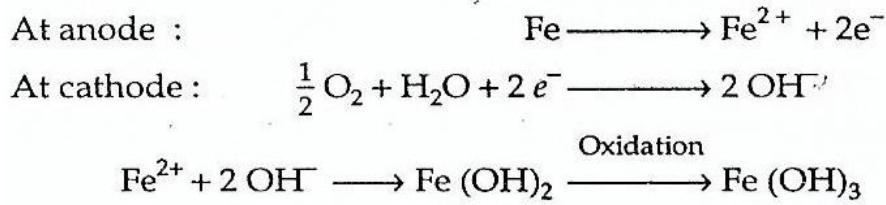
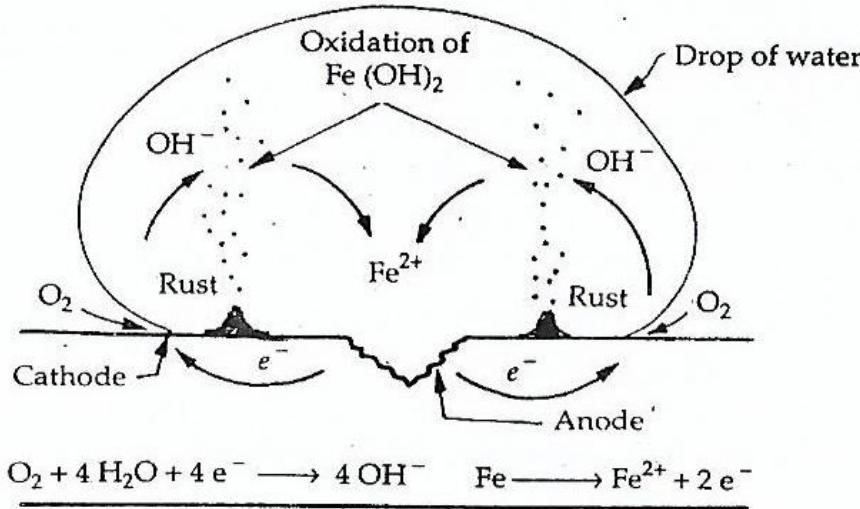
Localized corrosion of a metal surface confined to a point or small area, that takes the form of cavities

This is usually found on passive metals and alloys such aluminum alloys, stainless steels and stainless alloys

When the ultra-thin oxide film is chemically or mechanically damaged and does not immediately repassivate



# Pitting corrosion



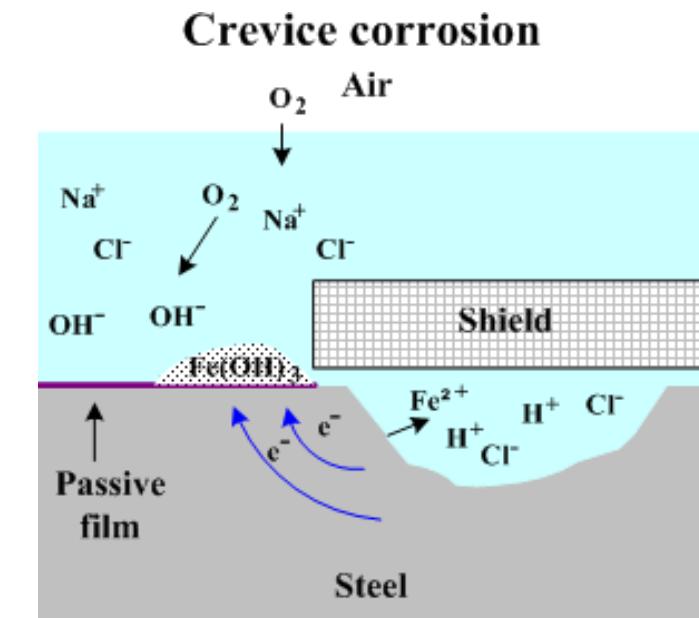
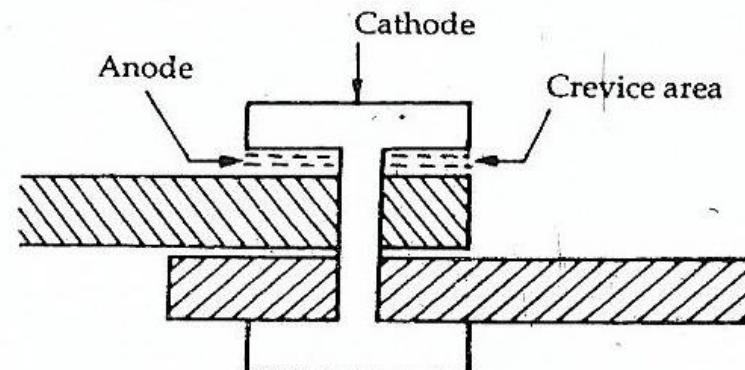
- Non uniform
- Results in the formation of pits or cavities
- Resulting from a localized accelerated attack
- Once a small pit is formed, the rate of corrosion is high

### 3. Crevice corrosion

Electrochemical oxidation-reduction (redox) process



Occurs within localized volumes of stagnant solution trapped in pockets, corners or beneath a shield (seal, deposit of sand, gasket, fastener, etc.).

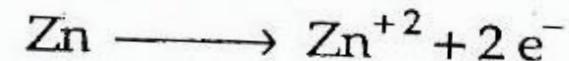


## 4. Concentration cell corrosion

When metallic surface is partially immersed in an electrolyte and partially exposed to air

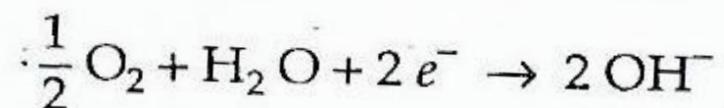


Poorly oxygenated metallic part becomes anodic and undergoes oxidation.



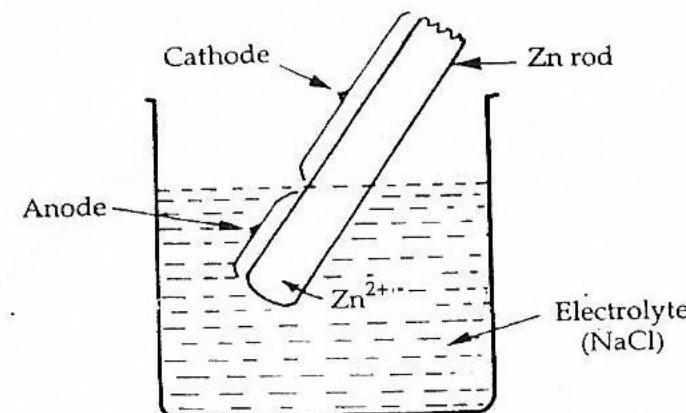
Well oxygenated part becomes cathodic.

At the cathode,  $\text{O}_2$  takes up electrons to form  $\text{OH}^-$  ions.



The  $\text{Zn}^{+2}$  and  $\text{OH}^-$  ions interact to give  $\text{Zn(OH)}_2$

Thus, corrosion occurs at anode.



## 5. Water-line corrosion

When water is stored in a metallic tank, it is observed that the metal below the waterline gets corroded

It is because the metal below the waterline is poorly oxygenated and acts as an anode

The metal above the waterline is highly oxygenated and acts as a cathode

Hence corrosion of metal below the waterline takes place

Marine plants cause waterline corrosion to ocean going ships

# Factors influencing corrosion

S. No.	<i>Nature of the metal</i>	<i>Nature of the environment</i>
1. 2. 3. 4. 5. 6. 7.	Purity of metal, Physical state of the metal, Nature of the oxide film, Position in the Galvanic series, Relative areas of the anode and cathode Solubilities of the product of corrosion, Volatility of corrosion products,	Temperature, Humidity, Effect of pH, Nature of electrolyte, Conductance of the corroding medium, Formation of oxygen concentration cell, Presence of suspended particles in atmosphere, Presence of impurities in atmosphere

# **Protective measures against Corrosion**

## **Modification of the environment:**

Either by removal of corrosion stimulant or by the use of corrosion inhibitors

## **Modification of the properties of metal:**

e.g. alloying, refining, annealing etc

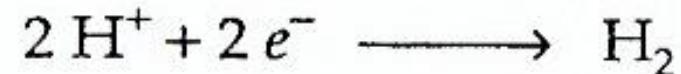
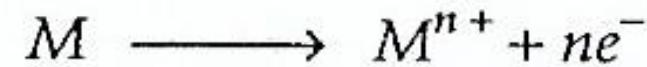
## **Use of protective coating (metallic, organic or inorganic) :**

Cathodic protection, Electroplating etc

## Cathodic protection

In acidic environment,

Metal undergo oxidation (act as anode)  
Accompanied by a reduction reaction



Cathodic protection prevents corrosion by

converting all of the anodic (active) sites on the metal surface to cathodic (passive) sites

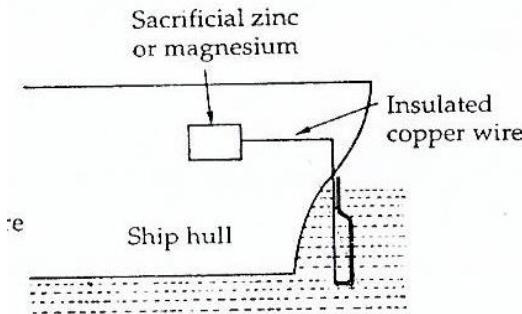
Two types cathodic protection:

1. Sacrificial anodic protection
2. Impressed current cathodic protection

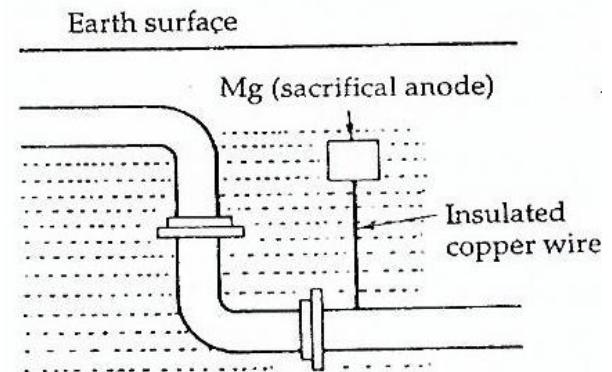
# 1. Sacrificial anodic protection

- Metal is connected with a wire to a more active metal called sacrificial anode
- The corrosion is concentrated at the more active metal eg, Zn, Al, Mg and their alloys
- Zn is used when there is good electrolyte like sea water
- Mg is used in case of high resistivity electrolytes such as soil

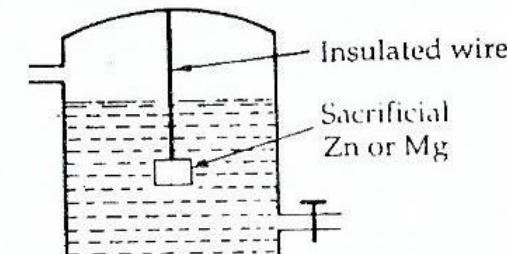
**Application** (a) Protection of underground cable and pipelines from soil corrosion



(b) Protection ships and boats hull from marine corrosion, Zn and Mg sheets are hung around the ship which act as an anode



(c) In domestic water boilers or tanks, Mg is used to prevent the formation of rusty water



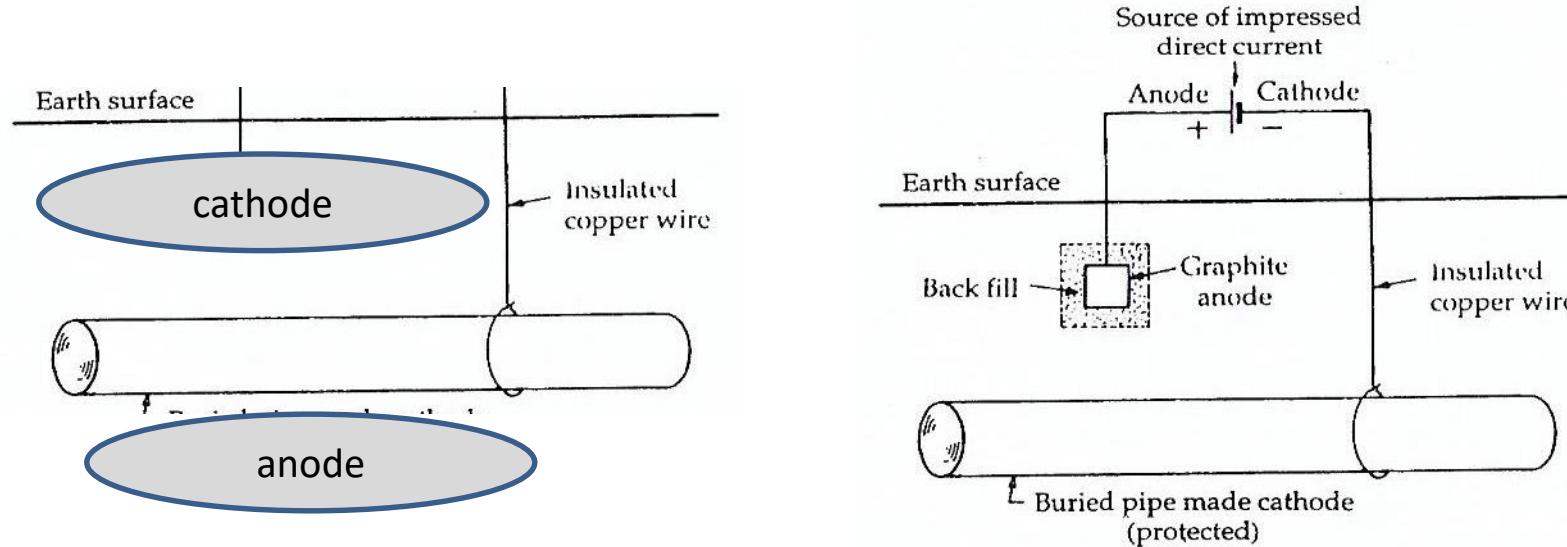
## **2. Impressed current cathodic protection**

Current from an external source is applied in opposite direction to nullify the corrosion current

This converts the corroding anode to cathode and prevent corrosion

The anode may be an inert material such as graphite, carbon, stainless steel, scrap iron

# Impressed current cathodic protection



*Applications.* This protection method is useful when electrolyte resistivity and current requirements are high. It is well-suited for large structures and long-term applications. Maintenance and operating costs can be reduced by employing automatic impressed current cathodic protection.

This protection technique is employed in the case of buried structures such as pipe-lines, tanks, marine piers, transmission line towers, laid-up ships etc.

## **Electro plating**

The process of plating one metal onto a base metal by passing current through an electrolyte containing soluble salt of the coating metal to prevent corrosion of the base metal

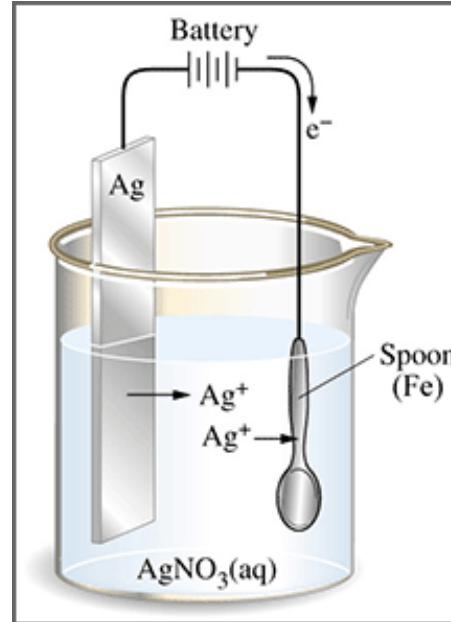
There are also specific types of electroplating such as copper plating, silver plating, and chromium plating.

Electroplating enhances the resistance to corrosion, physical appearance, hardness and surface properties

Clean metal is acting as a cathode and inert material such as carbon or graphite act as anode

Metal electrolytes are deposited on cathode

# Electro plating



When direct current is passed, coating metal ions migrate to the cathode and get deposited there in the form of thin-layer

# **Electrochemistry**

# **Electrochemistry:**

The study of production of electricity from energy released during spontaneous chemical reactions

The use of electrical energy to bring about non-spontaneous chemical transformations.

The branch of physical chemistry that studies the relationship between chemical reactions and electricity

## **Importance :**

A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods.

Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices.

The reactions carried out electrochemically can be energy efficient and less polluting.

Electrochemistry is useful for creating ecofriendly technologies.

# Batteries



Chemicals inside the battery reacts and create electricity

# Fuel cell

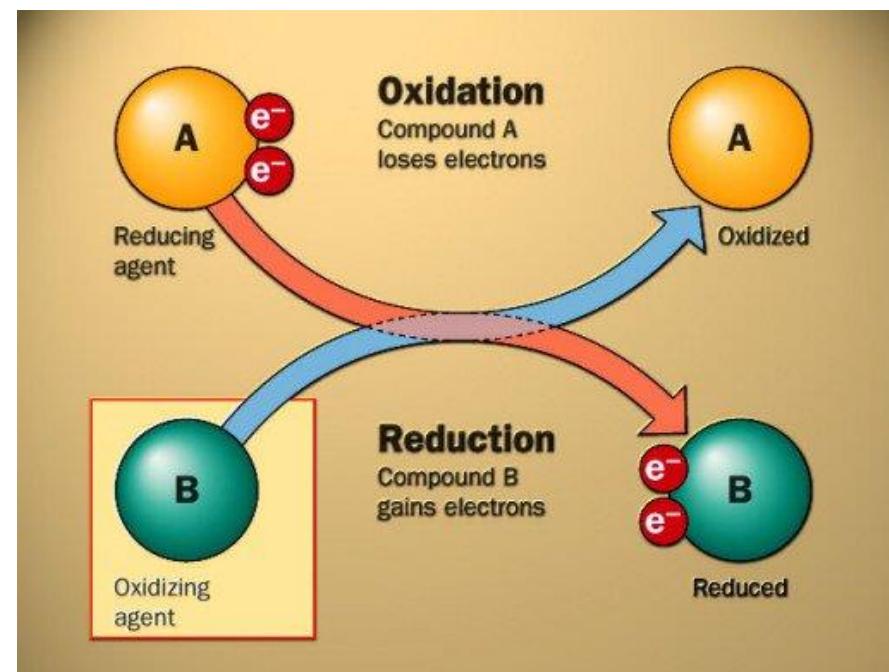


**Fuel cells** in vehicles generate electricity to power the motor, generally using oxygen from the air and compressed hydrogen.

# Redox reaction

Transfer of electrons between chemical species

Most often with one species undergoing oxidation while another species undergoes reduction



## **Electrochemical cell:**

A device capable of either generating electrical energy from chemical reactions or using electrical energy to cause chemical reactions.

**Thus electrochemical cells may be used for two purposes**

**Types :**

Galvanic Cells -

I. To convert chemical energy into electrical energy

Electrolytic Cells -

II. To convert electrical energy into chemical energy

# Electrochemical cell

## Galvanic cell

Produces electricity as a result of spontaneous reaction occurring in the cell

**Dry cells, mercury cells, Ni-Cd cells**

## Electrolytic cell

A non-spontaneous reaction is driven by an external source of current

# Electrochemical cell

**An electrochemical cell typically consists of:**

- -Two electronic conductors (also called electrodes)
- -An ionic conductor (called an electrolyte)

**Modes of charge transport**

- Charge transport in the electrodes occurs via the motion of electrons (or holes)
- Charge transport in the electrolyte occurs via the motion of ions (positive and negative)

## Galvanic cell / Voltaic Cell:

A device in which electrical current generates by a spontaneous redox reaction

- Cell energy is extracted from the overall redox reaction is the sum of these two half-reactions. It is converted to electric current.

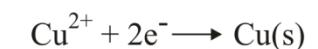
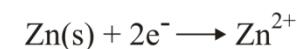
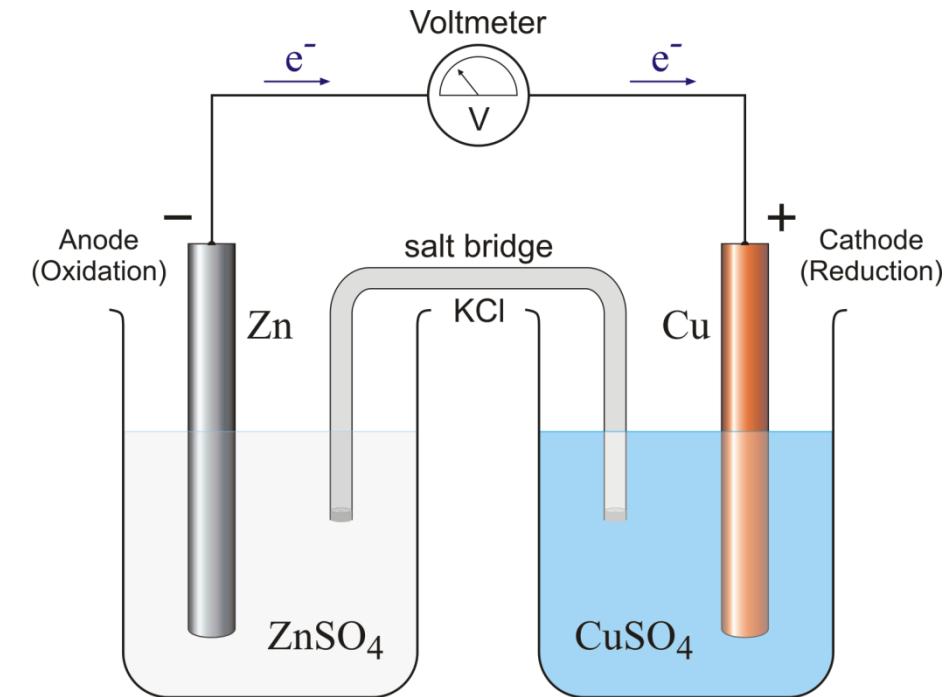
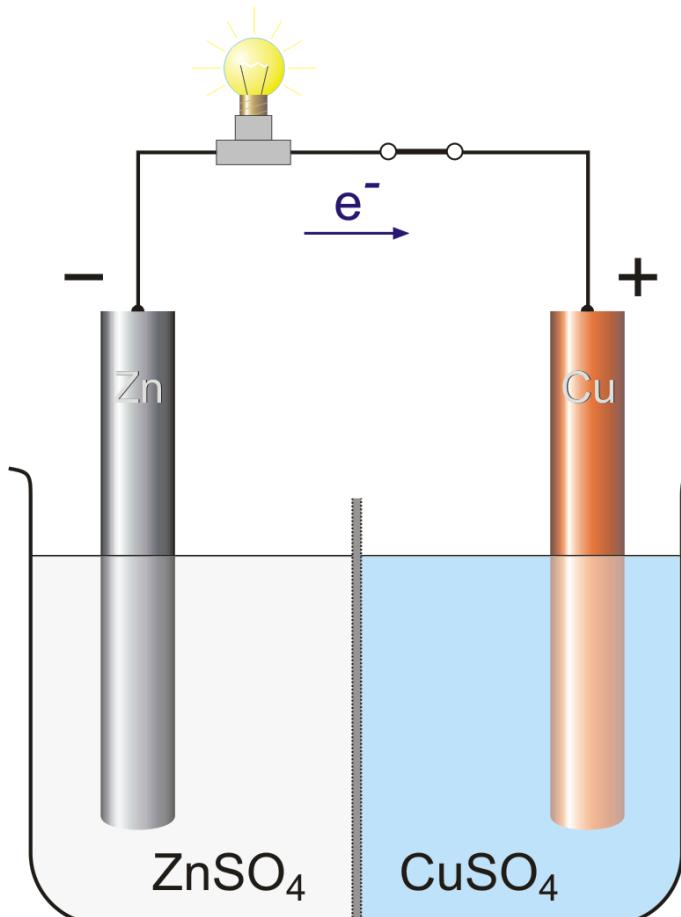
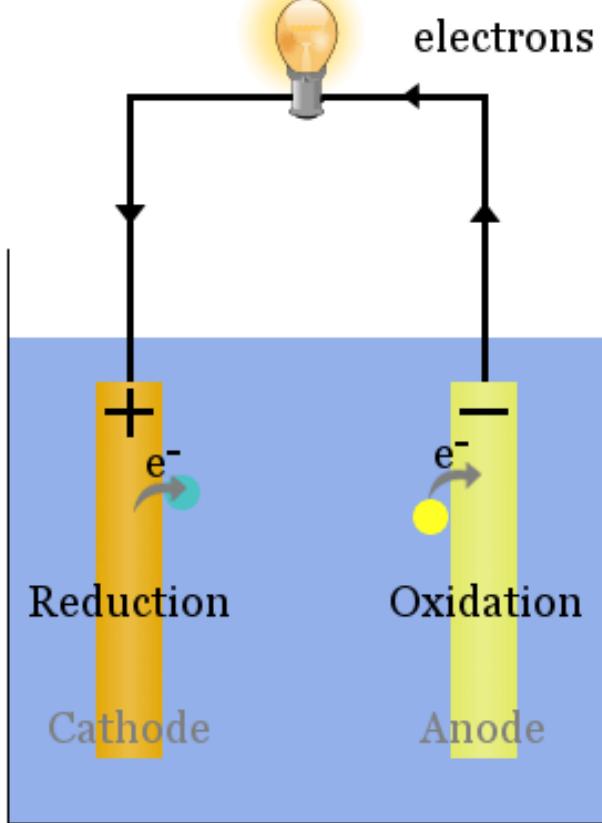


Daniell Cell is a Galvanic Cell in which Zinc and Copper are used for the redox reaction to take place.

The overall redox reaction is the sum of these two:



# Voltaic cell



Zinc metal gets oxidized: goes into solution:  $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}$

Copper ions in solution reduced: copper metal deposited on the copper electrode



Electrons for reduction obtained from the zinc electrode external wire

If the electrolytes are different the compartments are joined through a salt bridge. Containing a concentrated solution of electrolyte [KCl in agar jelly and this complete the electrical circuit.

Chloride ions migrate through the membrane, react with the zinc ions

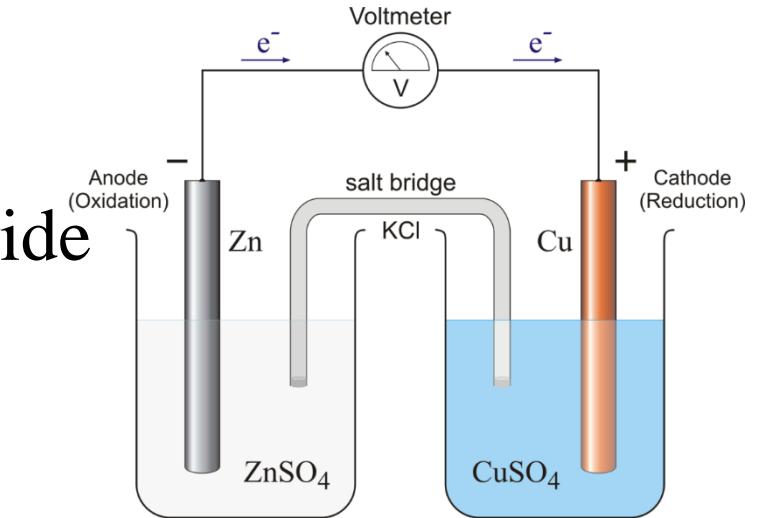
Daniel cell has a porous membrane instead of a salt bridge.

# Salt bridge

Isolate two halves of electrochemical cell while allowing migration of ions and current flow.

Usually consists of a tube filled with potassium chloride

Separate species to prevent direct chemical reactions



Allows flow of ions from one half cell to the other

Keeps the solutions in the half cell electrically neutral

Minimizes liquid junction potential

## Preparation:

Prepared by adding agar-agar or gelatine to the aqueous solution of a strong electrolyte like NaCl or KCl etc. The electrolyte should be chemically inert.

Due to oxidation of zinc, zinc ions accumulate around Zn electrode. An equal number of  $\text{Cl}^-$  ions move from salt bridge to towards Zn electrode and  $\text{Na}^+$  towards cu electrode to keep the half cells are electrically neutral.

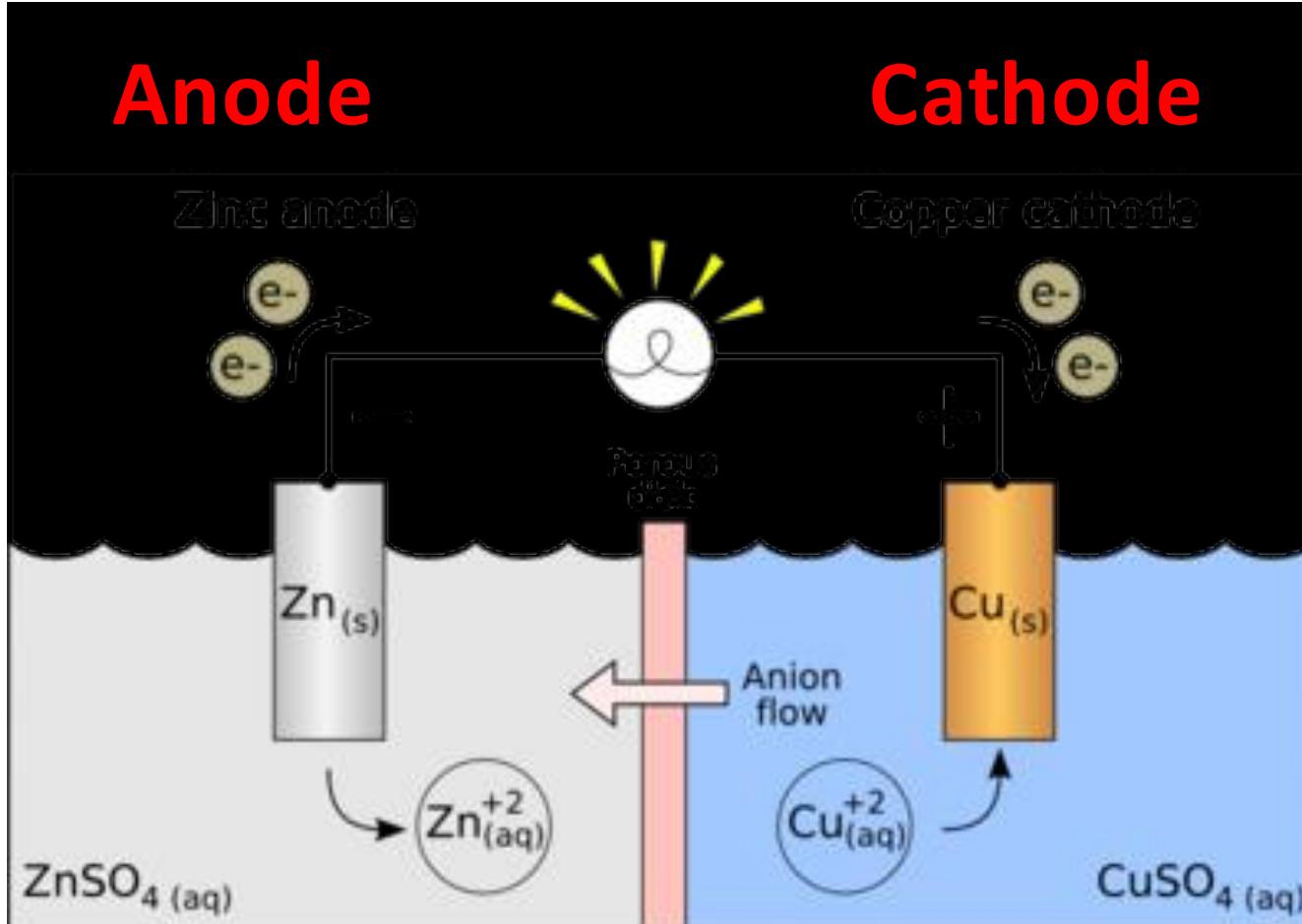
## Liquid junction potential

The unequal rates of migration of the cations and anions across a liquid-liquid junction give rise to a potential difference across the junction. This potential difference across the liquid-liquid junction is called liquid junction potential.

A salt bridge eliminates a direct contact between the two solutions, and thus minimizes the liquid junction potential. Liquid junction potential affects the overall cell potential.

## Daniel Cell:

If the salt bridge is replaced by a porous pot is known as Daniell cell.



## Half-Cell reactions and Electrodes:

A redox reaction is a reaction in which there is a transfer of electrons from one substance to another.

Any redox reaction may be expressed as the sum of the two half reactions. One of the half reactions shown a loss of electrons and the other shows a gain of electrons.

The reaction occurring in the Galvanic cell



In this reaction **Cu<sup>+2</sup>/Cu and Zn<sup>+2</sup>/Zn are called as redox couple**

**Anode:** where the oxidation half reaction take place

**Cathode:** The electrode where the reduction half reaction take place

When the electrons flow from the anode to cathode, the electrical energy is produced

Thus an electrochemical cell converts the chemical energy into electrical energy.

## Representation of a Cell or Cell diagram:

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. For this purpose consider that a cell consists of two half-cells.

Each half cell is again made of a metal electrode in contact with metal ions in solution.

In 1953, IUPAC recommended the following conventions for writing cell diagram.



A single vertical line represents a **phase boundary between** a metal electrode and an ion solution (electrolyte)

A metal electrode in the anode half-cell is on the left, while in the cathode half-cell it is on the right

Double vertical line represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing

The symbol for the inert electrode like the platinum electrode is often enclosed in a bracket.



The value of the EMF (Electromotive Force) of a cell is written on the right on the cell diagram.



## **Electrode Potential (Reduction Potential):**

The magnitude of the potential difference is a measure of the **tendency of the electrode to undergo oxidation or reduction or the tendency to lose or gain electrons.**

- If the reduction takes place at the electrode, it is termed as reduction potential.
- If the oxidation takes place at the electrode, it is called as oxidation potential.

$$\Delta G = -nFE$$

**n** is the number of electrons transferred in the cell reaction or half-reaction

**F** is the Faraday constant, the number of coulombs per mole of electrons:

$$F = 9.64853399(24) \times 10^4 \text{ C mol}^{-1}$$

# NERST EQUATION

$$E = E^0 - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

$$E_{cell} = E_{cell}^0 - \frac{2.303RT}{nF} \log \frac{[Red]}{[Ox]}$$

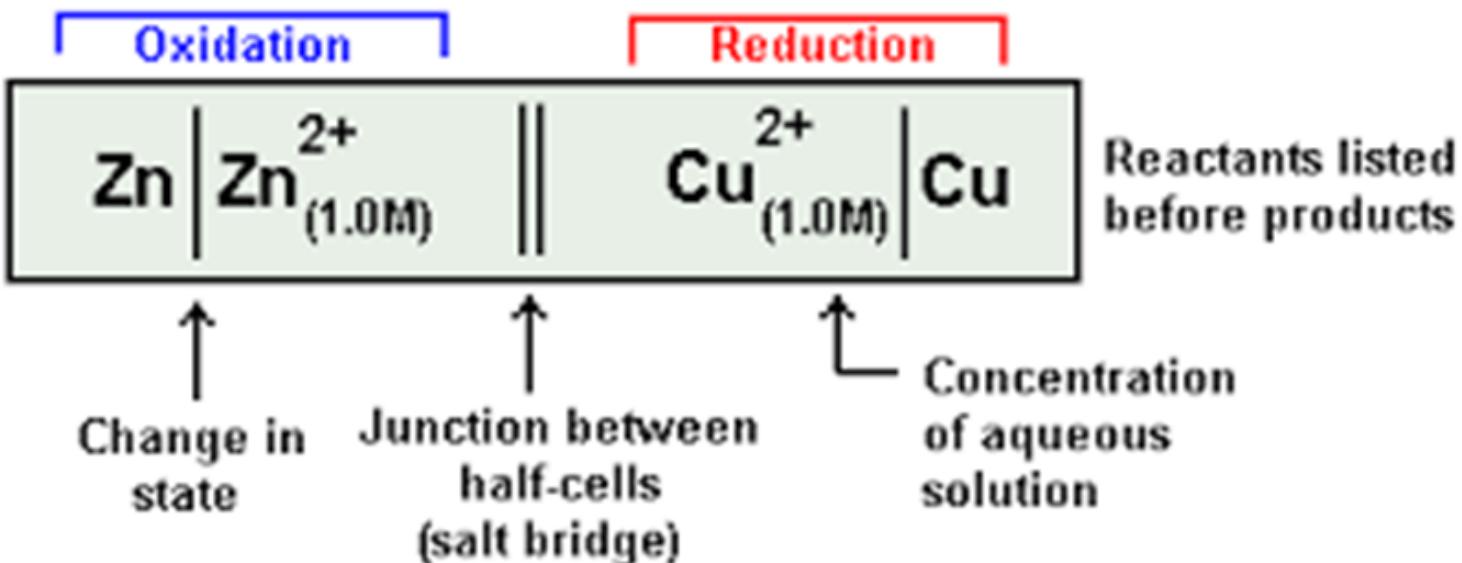
where,  $n$  = total number of electron lost or gained

$$F = 96500 \text{ C mol}^{-1}, T = 298\text{K}$$

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

$$Q = \text{reaction coefficient of overall reaction} = \frac{[Red]}{[Ox]}$$

Oxidation written before Reduction



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \left[ \frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right]$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.0591}{2} \log \left[ \frac{\text{Cu}^{2+}}{\text{Zn}^{2+}} \right]$$

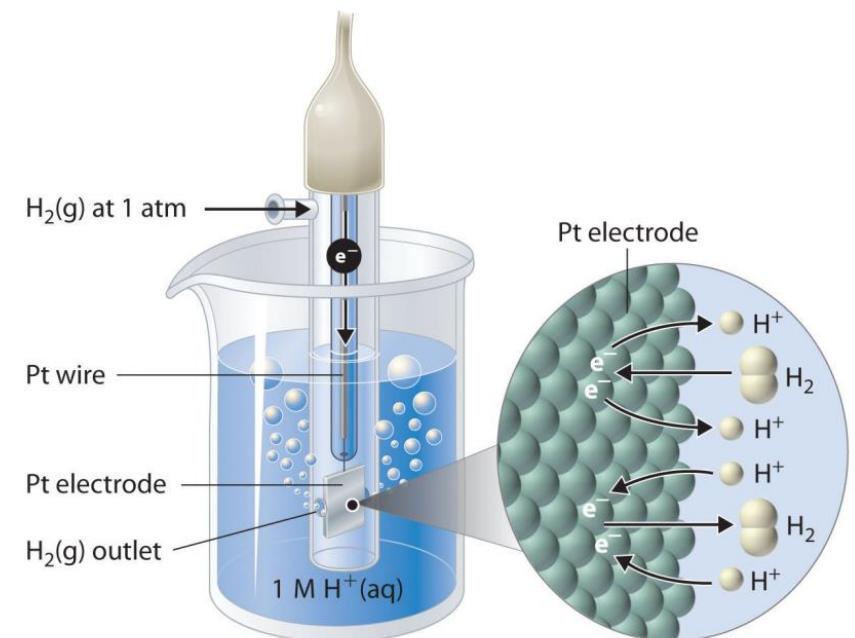
- According to the IUPAC, the reduction potential has been adopted for the designation of electrode potential.
- **Standard Electrode Potential ( $E_0$ ):** If the half-cell reaction is carried out at 298 K and the electrode is suspended in a solution of 1 molar concentration.
- There are no methods available to which we can measure the absolute electrode potential.

$$E_{cell} = E_R - E_L$$

- The electrode potential can be measured with respect to a standard hydrogen electrode.
- The electrode potential of an electrode is depends upon the concentration of ions in solution in contact with metal.
- Reduction potential of an electrode is directly proportional to the concentration of ions, whereas oxidation potential is inversely proportional to the concentration of ions.

## Measurement of Electrode Potential:

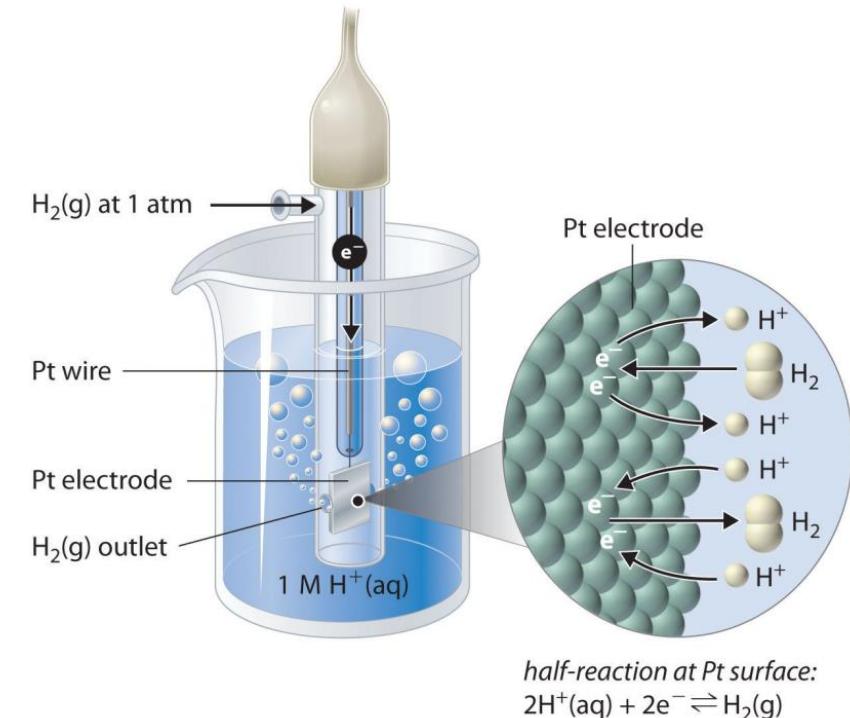
- Although it is not possible to determine the absolute value of the electrode potential of a single electrode, it can be determined with respect to a reference electrode.
- The reference electrode used is the standard hydrogen electrode (SHE) which is assigned the value zero.



half-reaction at Pt surface:  
 $2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons \text{H}_2(\text{g})$

# Standard Hydrogen Electrode (SHE):

- SHE contains hydrogen gas in contact with  $\text{H}^+$  ions of 1 M concentration at 298 K and at 1 atm pressure.
- The inert metal (**Pt**) act as a source or sink of electrons. This can be denoted as

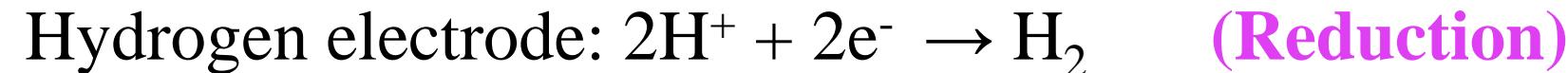
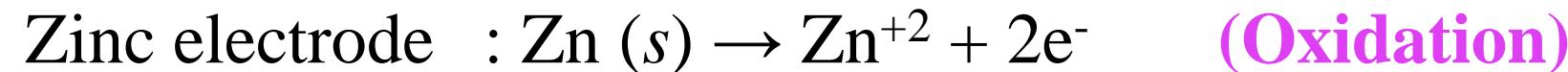


- Hydrogen electrode can act as either a cathode or anode depending on the other electrode in the cell
- When the electrode is acting as a cathode, the reaction is:  
$$2\text{H}^+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g})$$
- When the electrode is acting as an anode, the reaction is:  
$$\text{H}_2 (\text{g}) \rightarrow 2\text{H}^+ (\text{aq}) + 2 \text{e}^-$$
- Based on the electrode potential obtained with reference to hydrogen, electrochemical series is obtained.
- To determine the electrode potential of the given electrode, the electrode is coupled with SHE.
- The EMF of the cell (electrode potential) is then determined with the help of a potentiometer. The electrode potential of SHE is arbitrarily taken as zero<sup>442</sup>

If the Zn electrode (Zn rod is dipped in an electrolyte) is coupled with SHE

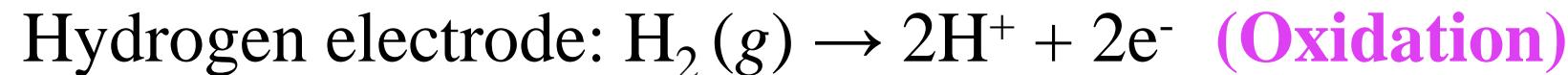
Oxidation takes place at the Zn electrode

- The two half-cell reactions are:



EMF of the cell is + 0.76 V. Therefore the oxidation potential of the Zn electrode is taken as + 0.76 V and the reduction potential is taken as – 0.76 V.

Similarly, when a Cu electrode (Cu rod is dipped in an electrolyte) is coupled with SHE. **Reduction takes place at the Cu electrode.**

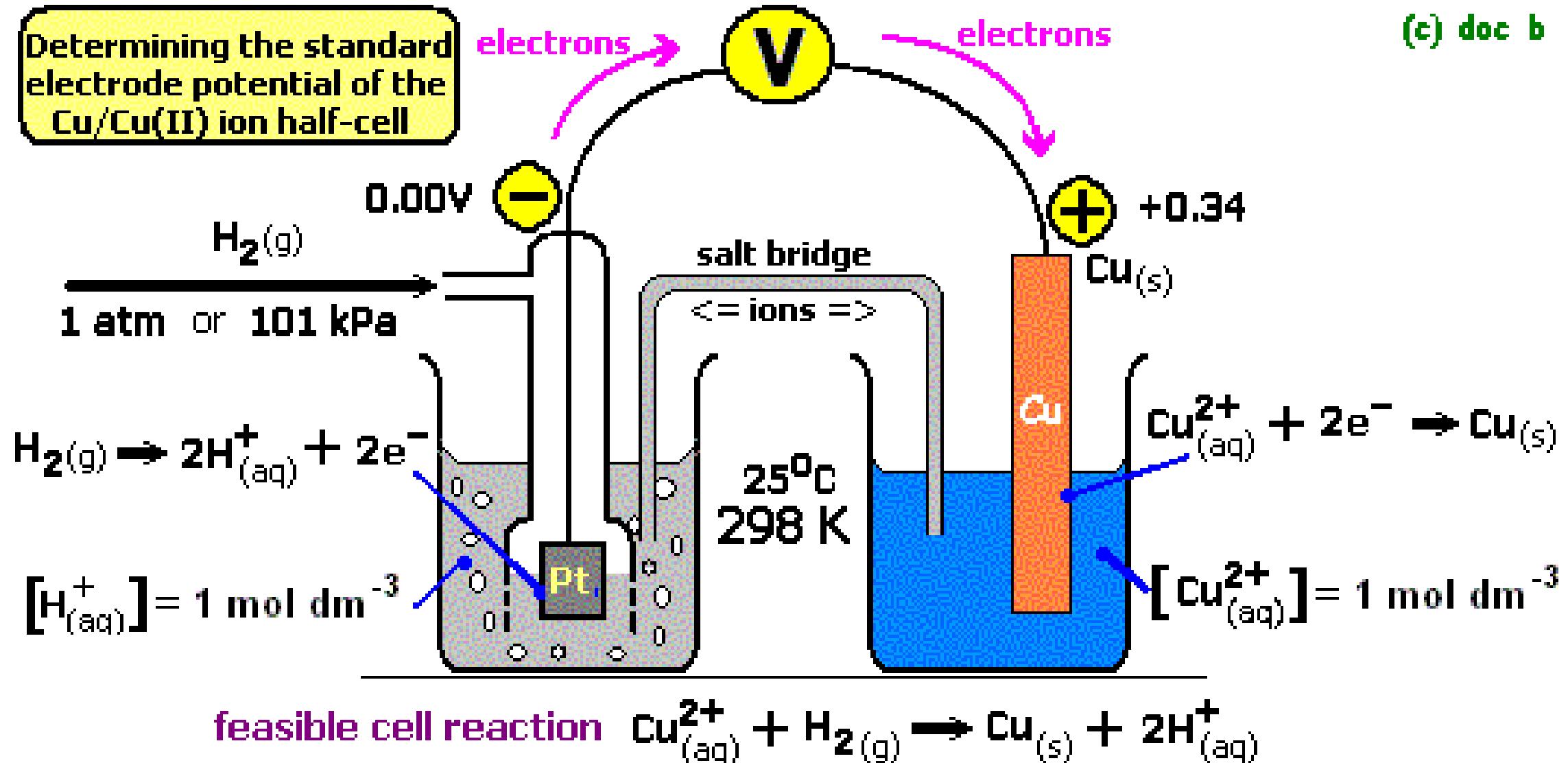


EMF of the cell is + 0.34 V.

Thus the reduction potential of the Cu electrode is taken as + 0.34 V

(c) doc b

Determining the standard electrode potential of the Cu/Cu(II) ion half-cell



## **Electrochemical series/Activity series:**

- According to the IUPAC, the reduction potential has been adopted for the designation of electrode potential.
- The standard potential of an electrode can be measured with reference to a standard hydrogen electrode, which has been assigned the value zero.
- The arrangement of various electrodes in the increasing order of their standard electrode potential (reduction potential) values is called as electrochemical series.

### Electrochemical Series

### Thermodynamics measurement

STANDARD Reduction potential -  $H_2$  as std

**WEAK  
Oxidizing Agent**

**TOP left**  
 • Low ↓ tendency gain e  
 •  $Li^+ + e \rightarrow Li$   
 •  $E^\circ Li = -3.04V$   
 • WEAK oxidizing Agent  
 • Red NOT favourable ( $E^\circ = -ve$ )

**STRONG  
Reducing Agent**

**TOP right**  
 • High ↑ tendency lose e  
 •  $Li \rightarrow Li^+ + e$   
 •  $E^\circ Li = +3.04V$   
 • STRONG reducing Agent  
 • Oxi favourable ( $E^\circ = +ve$ )

**Strong  
Oxidizing Agent**

**WEAK  
Reducing Agent**

Oxidized sp	↔	Reduced sp	$E^\circ/V$
$Li^+ + e^-$	↔	$Li$	-3.04
$K^+ + e^-$	↔	$K$	-2.93
$Ca^{2+} + 2e^-$	↔	$Ca$	-2.87
$Na^+ + e^-$	↔	$Na$	-2.71
$Mg^{2+} + 2e^-$	↔	$Mg$	-2.37
$Al^{3+} + 3e^-$	↔	$Al$	-1.66
$Mn^{2+} + 2e^-$	↔	$Mn$	-1.19
$H_2O + e^-$	↔	$H_2 + OH^-$	-0.83
$Zn^{2+} + 2e^-$	↔	$Zn$	-0.76
$Fe^{2+} + 2e^-$	↔	$Fe$	-0.45
$Ni^{2+} + 2e^-$	↔	$Ni$	-0.26
$Sn^{2+} + 2e^-$	↔	$Sn$	-0.14
$Pb^{2+} + 2e^-$	↔	$Pb$	Compared to H <sub>2</sub> as std -0.13
$H^+ + e^-$	↔	$1/2H_2$	0.00
$Cu^{2+} + e^-$	↔	$Cu^+$	+0.15
$SO_4^{2-} + 4H^+ + 2e^- \leftrightarrow H_2SO_3 + H_2O$			+0.17
$Cu^{2+} + 2e^-$	↔	$Cu$	+0.34
$1/2O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$			+0.40
$Cu^+ + e^-$	↔	$Cu$	+0.52
$1/2I_2 + e^-$	↔	$I$	+0.54
$Fe^{3+} + e^-$	↔	$Fe^{2+}$	+0.77
$Ag^+ + e^-$	↔	$Ag$	+0.80
$1/2Br_2 + e^-$	↔	$Br$	+1.07
$1/2O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$			+1.23
$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$			+1.33
$1/2Cl_2 + e^-$	↔	$Cl^-$	+1.36
$MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$			+1.51
$1/2F_2 + e^-$	↔	$F$	+2.87

$E^\circ_{cell}/Cell$  Potential - EMF in volt

EMF when half cell connect to SHE std condition  
Std potential written as std reduction potential

## **Important features of electrochemical series:**

1. Metals near the top of the series are strongly electropositive, they lose e<sup>-</sup> readily to give cations.
2. The lower the position of metal in the series, the greater is its tendency to be reduced.
3. Metals having higher position in the series are strong reducing agents
4. Metals near the bottom of the series are stable, and their ions are easily reduced to be metals.

## **Important features of electrochemical series:**

5. metals in the upper part in electro chemical series can displace metals below them from their salts. E.g. Fe displaces Cu from  $\text{Cu}^{2+}$  solution.

$\text{Li}^+/\text{Li}$  has the lowest reduction potential, that means all ions below it can be reduced by Li.

6. Metals above hydrogen displace hydrogen from dilute acids.

7. Similarly, an oxidizing agent with a higher reduction potential will oxidize any reducing agent with a lower reduction potential.

# **Importance of electrochemical series**

## **1. Calculation of standard EMF of cell:**

Standard EMF of cell = [standard reduction potential of the reduction half-reaction - standard reduction potential of the oxidation half-reaction]

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

## **2. Predicting whether a metal can liberate hydrogen from acid solutions or not:**

Metal having less reduction potential than SHE: liberates hydrogen from acids  
e.g., Zn, Fe, Mg.

# Importance of electrochemical series

## 3. Predicting feasibility of redox reaction:

1. The species with higher reduction potential undergoes reduction and the one with lower reduction potential undergoes oxidation

2.  $E_{cell}$  value is positive

$$E_{cell} = E_{cathode} - E_{anode}$$

$$\Delta G = - nFE$$

## 4. Predicting anode and cathode

Electrode with lower reduction potential: Anode

Electrode with higher reduction potential: Cathode

# Importance of electrochemical series

## 5. Predicting oxidizing and reducing ability:



$$E_0 = +0.34 \text{ V}$$



$$E_0 = 0.00 \text{ V}$$



$$E_0 = -0.25 \text{ V}$$



$$E_0 = -0.76 \text{ V}$$

Cu<sup>2+</sup> can oxidize H<sub>2</sub>, Ni, and Zn

H<sub>2</sub> can reduce Cu<sup>2+</sup>

H<sup>+</sup> Can oxidize Ni and Zn

Ni can reduce H<sup>+</sup> and Cu<sup>2+</sup>

Ni<sup>2+</sup> can oxidize Zn

Zn can reduce Ni<sup>2+</sup>, H<sup>+</sup>, Cu<sup>2+</sup>



Increasing strength as reducing agent

Q1. A cell is prepared by dipping a copper rod in 1M CuSO<sub>4</sub> solution and a Zn rod in 1M ZnSO<sub>4</sub> solution. The standard reduction potentials of Cu and Zn are 0.34 and -0.76 respectively.

- (i) Which electrode will be positive? (iii) What is the cell reaction?
- (ii) How will the cell be represented? (iv) What will be the EMF of the cell?

Ans: (i) Cathode is the positive electrode and has greater reduction potential than the second electrode of the cell. Therefore, the positive electrode is the copper electrode.

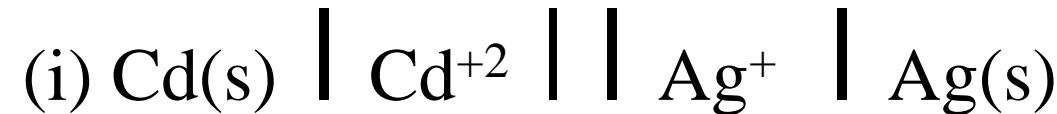


(iii) Cell reaction is the sum of oxidation half-cell reaction plus reduction half-cell reaction.



(iv) (E<sup>o</sup><sub>cell</sub>) = (E<sup>o</sup><sub>right</sub>) – (E<sup>o</sup><sub>left</sub>); E<sup>o</sup><sub>cell</sub> = 0.34 – (-0.76), E<sup>o</sup><sub>cell</sub> = 1.1 V

Q2. For the cells shown below, write cell reactions and Calculate standard cell potentials



$$E^{\circ}_{(Zn+2/Zn)} = -0.76 \text{ V}; E^{\circ}_{(Cd+2/Cd)} = -0.40 \text{ V}; E^{\circ}_{(Au+3/Au)} = +1.42 \text{ V}; E^{\circ}_{(Ag+/Ag)} = +0.80$$

Ans. (i)  $E^{\circ}_{\text{cell}} = 1.2 \text{ V}$

(ii)  $E^{\circ}_{\text{cell}} = 1.16 \text{ V}$

(iii)  $E^{\circ}_{\text{cell}} = 1.86 \text{ V}$

Q3. Calculate the standard reduction electrode potential of  $\text{Zn}^{+2}/\text{Zn}$  electrode when the cell potential ( $E^\circ$ ) for the cell is 1.10V



Ans

$$(E^\circ_{\text{cell}}) = (E^\circ_{\text{cathode}}) - (E^\circ_{\text{anode}})$$

$$1.10 = 0.34 - (E^\circ_{\text{anode}})$$

$$(E^\circ_{\text{anode}}) = -0.76 \text{ V}$$

$$E^\circ_{(\text{Zn}^{+2}/\text{Zn})} = -0.76 \text{ V}$$

**Q4.** Predict the reaction of  $\text{H}_2\text{SO}_4$ , 1 (M) with the following metals.

- (i) Zn(ii) Fe(iii) Cu (iv) Cd

$$E^\circ_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}; E^\circ_{\text{Fe}^{+2}/\text{Fe}} = -0.44 \text{ V}; E^\circ_{\text{Cu}^{+2}/\text{Cu}} = +0.34 \text{ V}; E^\circ_{\text{Cd}^{+2}/\text{Cd}} = -0.40 \text{ V};$$

**Ans.**

(i) The reduction potential of Zn is lower than reduction potential of  $\text{H}^+$  ions. Therefore, Zn will be oxidized and  $\text{H}^+$  will undergo reduction. Hence, the reaction will be spontaneous and  $\text{H}_2$  gas will be released.

(ii)  $\text{H}_2$  gas will be released.

(iii) The reduction potential of Cu is greater than the reduction potential of  $\text{H}^+$  ions; Thus Cu should undergo reduction. Therefore, no reaction occurs between copper and  $\text{H}_2\text{SO}_4$ .

(iv)  $\text{H}_2$  gas will be released.

## 6. Predicting feasibility of a redox reaction.

A redox reaction is feasible (or occurs) spontaneously when it fulfills the following conditions.

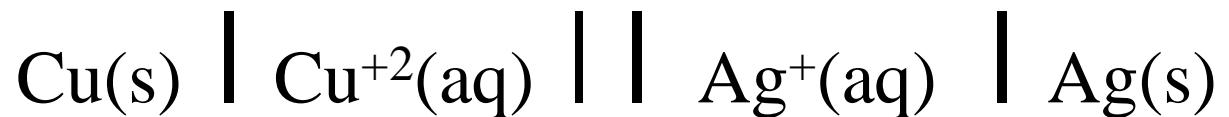
- (i) The species which has higher reduction potential undergoes reduction and the one with lower reduction potential is oxidized.
- (ii) If the value of  $E^{\circ}_{\text{cell}}$  is positive, the reaction is spontaneous.

Q5. Predict the feasibility of the reaction between  $\text{Ag}^{+}(\text{aq})$  and  $\text{Cu}(\text{s})$ .

Given,  $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$ ;  $E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} = +0.34 \text{ V}$

Ans.

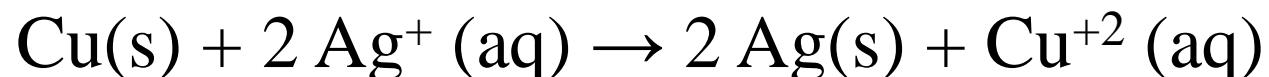
In this cell, the copper electrode will function as an anode and silver electrode as a cathode. Thus the cell will be



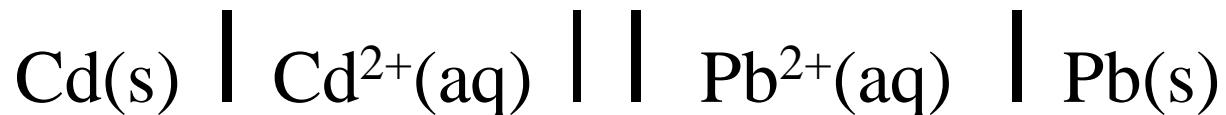
And the EMF of the cell is  $E^{\circ}_{\text{cell}} = 0.80 - 0.34$

$$E^{\circ}_{\text{cell}} = 0.46 \text{ V}$$

Since,  $E^{\circ}_{\text{cell}}$  is positive, the reaction occurs between the reacting species. The cell reaction is



Q6. Standard oxidation potential of Cd/Cd<sup>+2</sup> and Pb/Pb<sup>+2</sup> electrodes is 0.40 and 0.13 respectively, state whether the following cell is feasible.



Ans.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E^{\circ}_{\text{cell}} = -0.13 - (-0.40) = 0.27 \text{ V}$$

Since, calculated value of  $E^{\circ}_{\text{cell}}$  is positive, the cell is feasible.

**Q7.** Can we use a copper vessel to store 1 M AgNO<sub>3</sub> solution? Given

$$E^{\circ}_{(\text{Cu}^{2+}/\text{Cu})} = 0.34 \text{ V}; \quad E^{\circ}_{(\text{Ag}^{2+}/\text{Ag})} = 0.80 \text{ V};$$

**Ans.**

According to the standard reduction potential values, copper will function as an anode (i.e. Cu metal will be oxidized to Cu<sup>+2</sup> and silver ions will be reduced to silver metal at the cathode). Therefore, the copper vessel will dissolve in AgNO<sub>3</sub> if kept in it. Hence we cannot store AgNO<sub>3</sub> in a copper vessel.

Q8. A copper wire is dipped in  $\text{AgNO}_3$  solution kept in a beaker A, and a silver wire is dipped in a solution of  $\text{CuSO}_4$  kept in a beaker B. Predict in which beaker the ions present will get reduced. Given



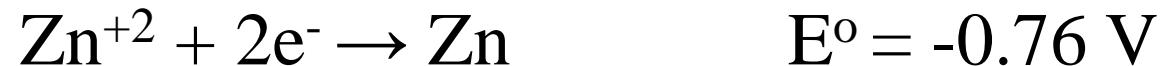
Ans. Silver ions will get reduced in beaker A, while no reaction will occur in beaker B

## Predicting the anode or cathode.

The values of the electrode potential of the electrodes in a cell helps in predicting the anode and cathode.

- An electrode with lower reduction potential (lying in the lower part of the series) can easily lose the electrons and will act as an anode.
- The electrode with higher electrode potential will act as cathode.

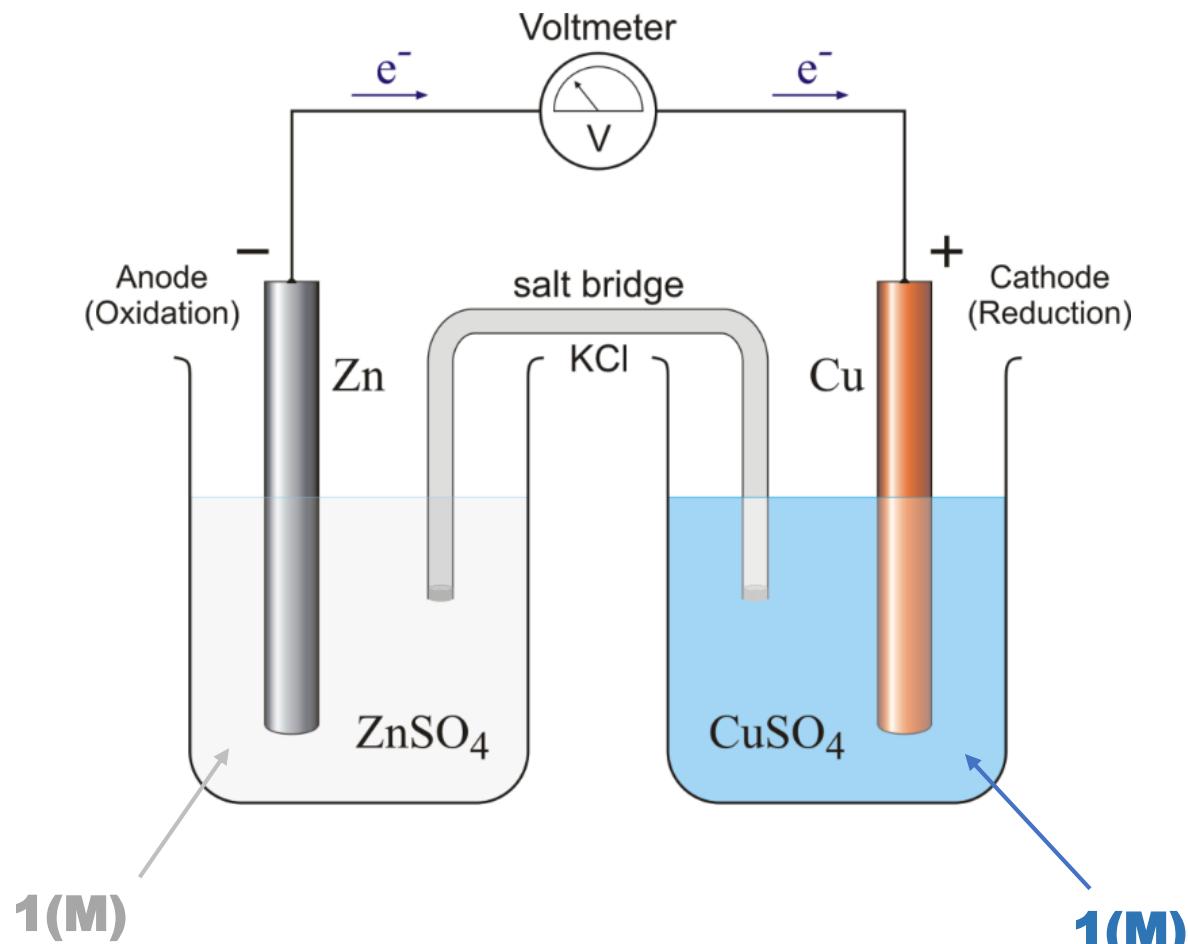
Q9. Consider a Zn-Cu cell



Which of these will act as anode and which as cathode.

Ans. Standard reduction potential of Cu is more than the standard reduction potential of Zn. Thus, Zn will act as anode and Cu will act as cathode.

# Potentiometry



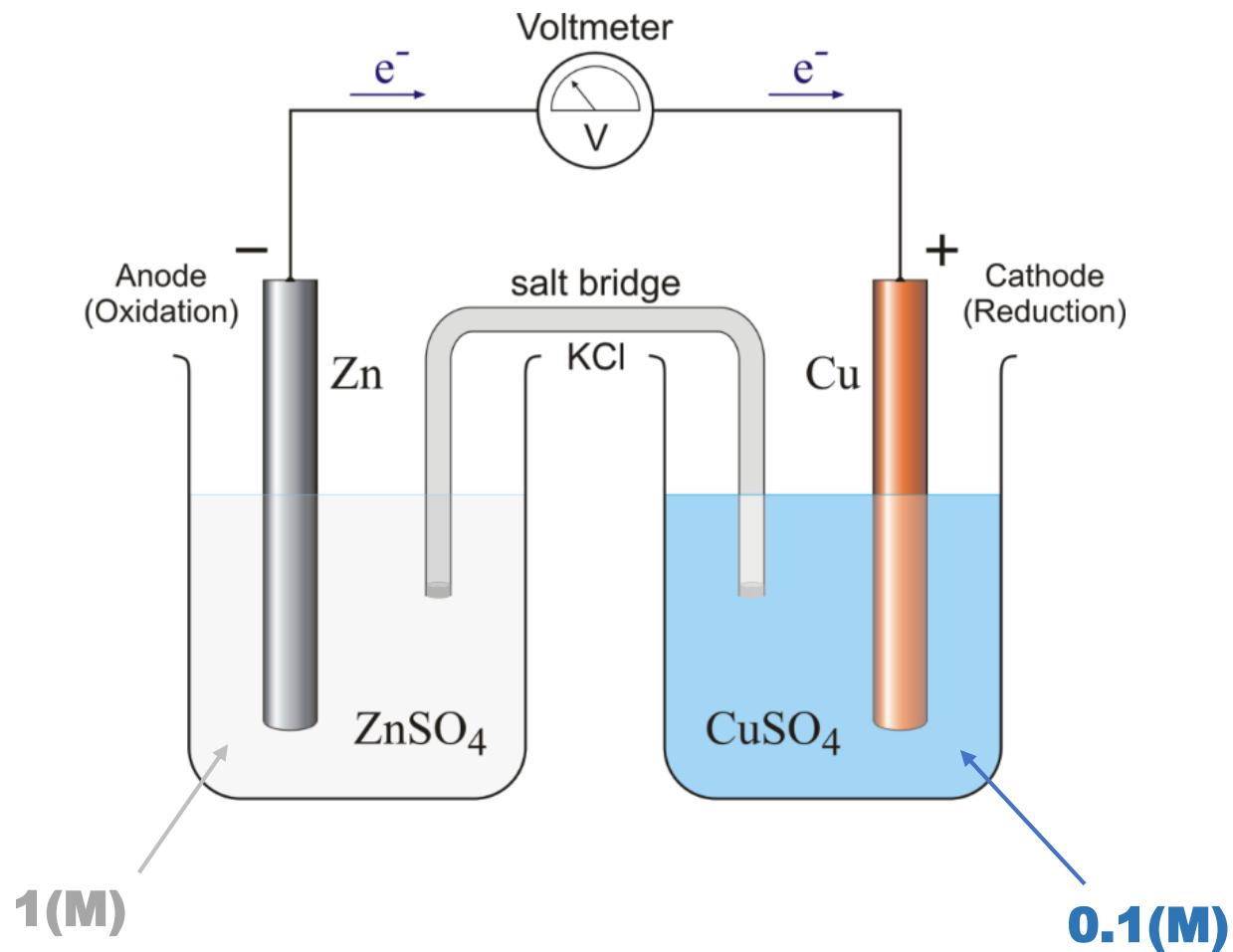
$$E_{cell} = E_R - E_L$$

$$E_{cell} = 0.34 - (-0.76)$$

$$E_{cell} = 1.1 \text{ V}$$

$$E^{\circ}_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}$$

$$E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} = +0.34 \text{ V}$$



$$E^{\circ}_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}$$

$$E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} = +0.34 \text{ V}$$

~~$$E_{cell} = E_R - E_L$$

$$E_{cell} = 0.34 - (-0.76)$$

$$E_{cell} = 1.1 \text{ V}$$~~

## Nerst Equation

$$E = E^0 - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E_{cell}^0 - \frac{2.303RT}{nF} \log Q$$

$$E_{cell} = E_{cell}^0 - \frac{0.059}{n} \log Q$$

*where, n = total number of electron lost or gained*

*F = 96500 C mol<sup>-1</sup>, T = 298K, R = 8.314 JK<sup>-1</sup>mol<sup>-1</sup>*

*Q = reaction coefficient of overall reaction*

Q1 For the cells given below, calculate the standard cell potentials when 1(M) ZnSO<sub>4</sub> and 0.1(M) CuSO<sub>4</sub> solutions are used



$$E^{\circ}_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}$$

$$E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} = +0.34 \text{ V}$$



$$E_{cell} = E_{cell}^{\circ} - \frac{0.059}{n} \log Q$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.059}{2} \log 10$$

$$E_{cell} = 1.1 - 0.0295 = 1.075 \text{ V}$$

$$Q = \frac{[\text{Zn}^{2+}] [\text{Cu(s)}]}{[\text{Cu}^{2+}] [\text{Zn(s)}]}$$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1(\text{M})}{0.1(\text{M})} = 10$$

# Potentiometry

When the pair of electrodes is placed in the solution it shows the potential difference with the change in the concentration of the ions.

*Here the measurement of potential of an electrochemical cell without drawing appreciable current*

Combining two half-cells (two half-redox reactions) and measuring the potential difference between them that gives  $E_{cell}$

If the potential of one half-cell (one- half reaction) is held constant then the potential of the other half (half cell or half reaction) will be known and consequently the concentration of the species on this side can be measured.

## Requirement:

1. Reference Electrode
2. Indicator Electrode
3. Potential Measuring Device

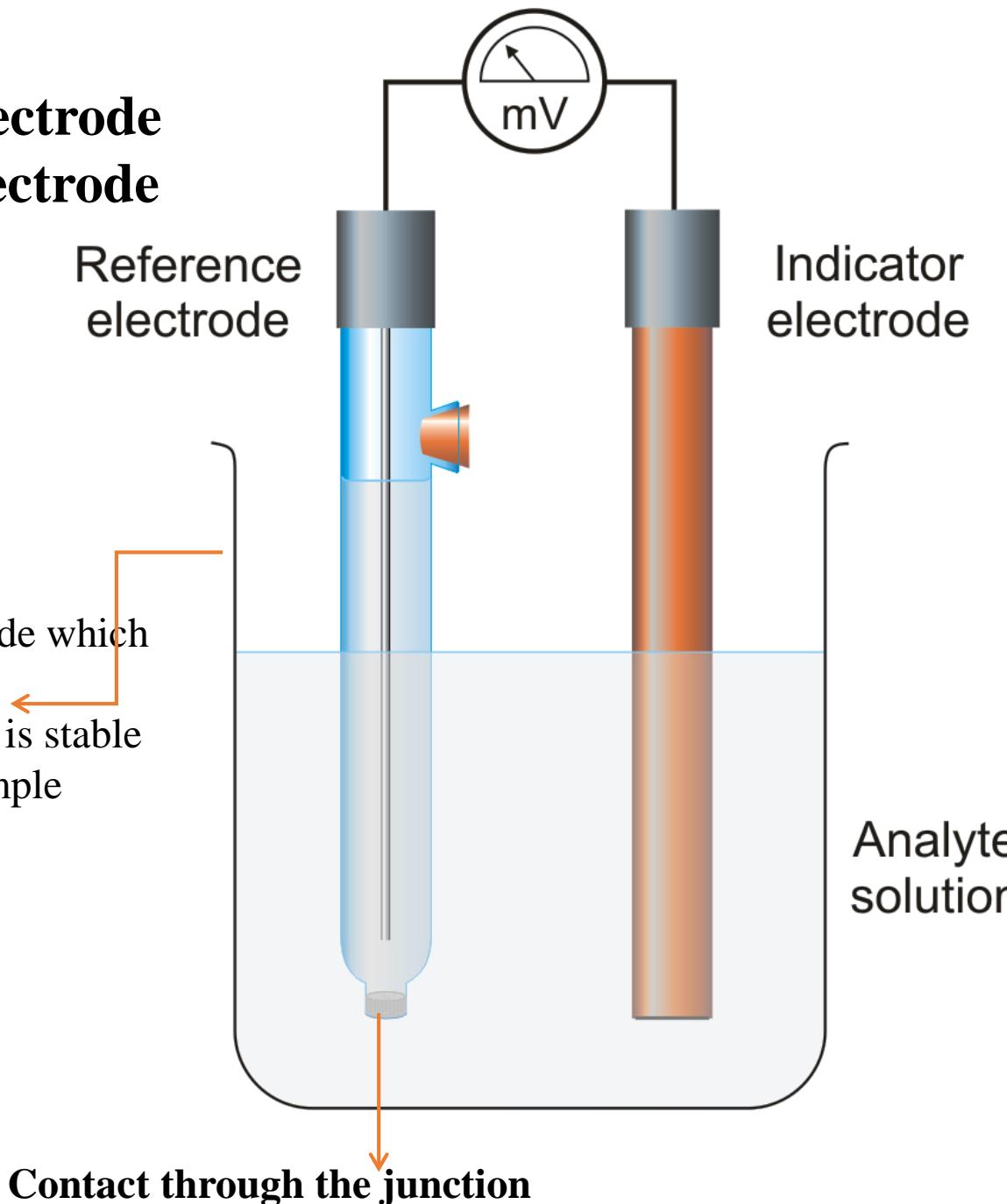
**Reference electrode | Salt bridge | analyte solution | Indicator electrode**



$$E_{cell} = E_{ind} - E_{ref} + E_j$$

$$E_{cell} \equiv E_{ind} - E_{ref}$$

1. SHE
2. Calomel Electrode
3. Ag/AgCl electrode



- **Metallic electrode**
  1. Electrode of First kind
  2. Electrode of 2<sup>nd</sup> kind
  3. Inert redox electrode

- **Membrane electrode**
  1. Glass membrane
  2. Liquid membrane
  3. Crystalline membrane

# **Reference Electrodes**

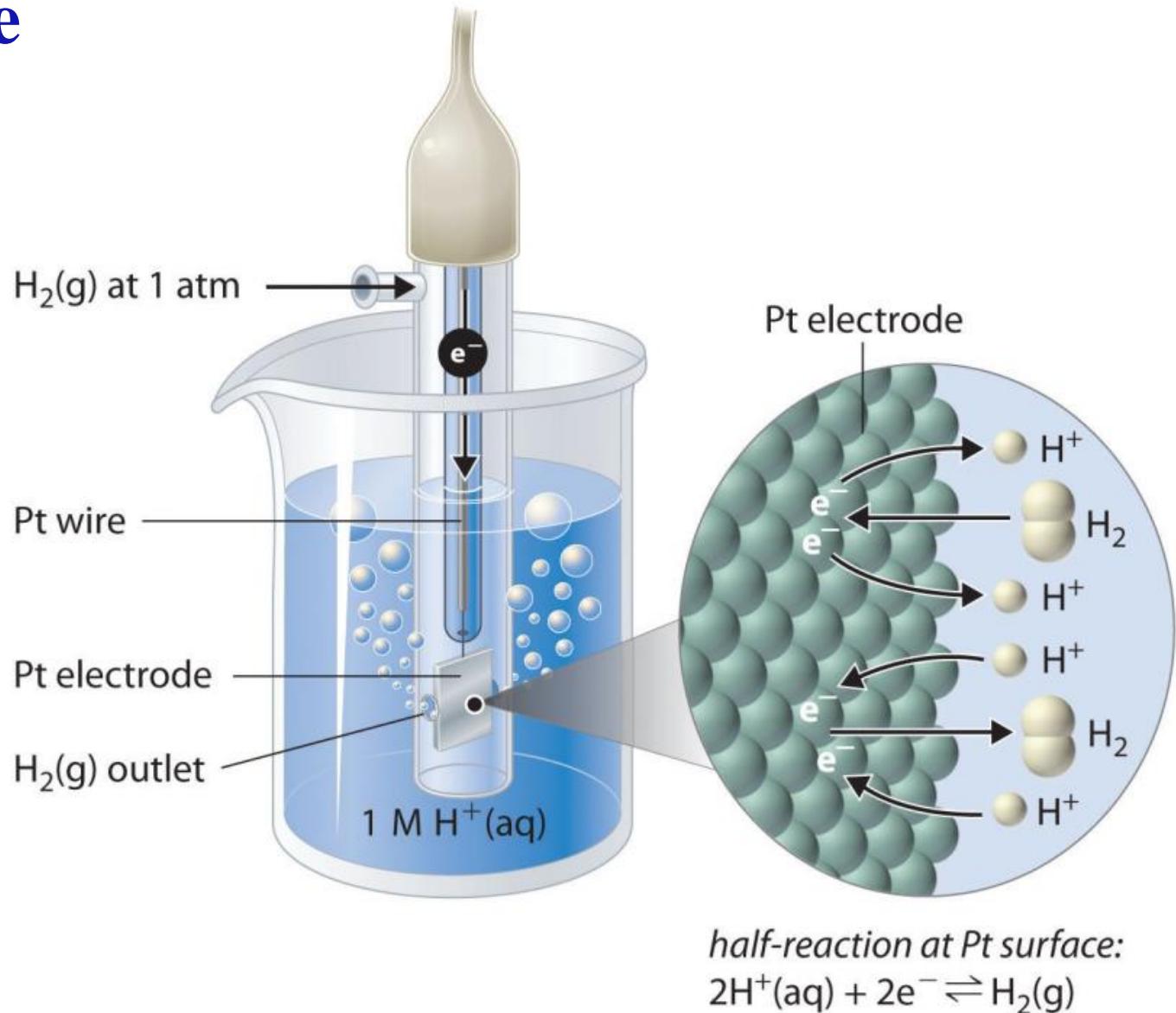
Whose potential value is accurately known. It is independent of the concentration of the analyte or any other ions in the solution under study.

- 1. Standard Hydrogen Electrode (SHE)**
- 2. Calomel Electrode**
- 3. Ag/AgCl electrode**

# 1. Standard Hydrogen Electrode (SHE)

Pt; H<sub>2(g)</sub>(1atm)/ H<sup>+</sup><sub>(aq)</sub> (1M)

## Gas electrode



## 2. Calomel Electrode

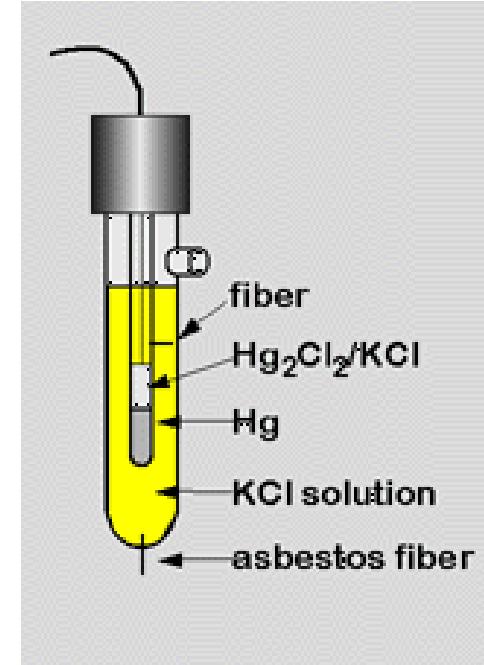
Hg in contact with saturated solution of  $\text{Hg}^+$  ion ( $\text{Hg}_2\text{Cl}_2$ -calomel)

Also contain a known concentration of saturated KCl



Hg is liquid and  $\text{Hg}_2\text{Cl}_2$ -is a solid

Electrode potential depends on the chloride ion concentration



$[\text{Cl}^-]$  in KCl; saturated:-  $E = 0.244 \text{ V}$

Saturated Calomel electrode is widely used (SCE)

## Reference Electrodes

If the electrode undergoes reduction,



If the electrode undergoes oxidation,

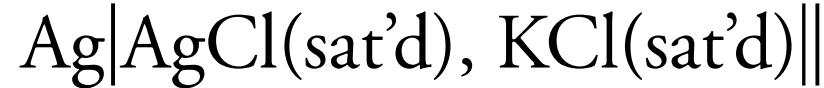


*Electrode reaction of SCE ,       $Hg_2Cl_2(s) \rightleftharpoons 2 Hg(l) + 2Cl^-$*

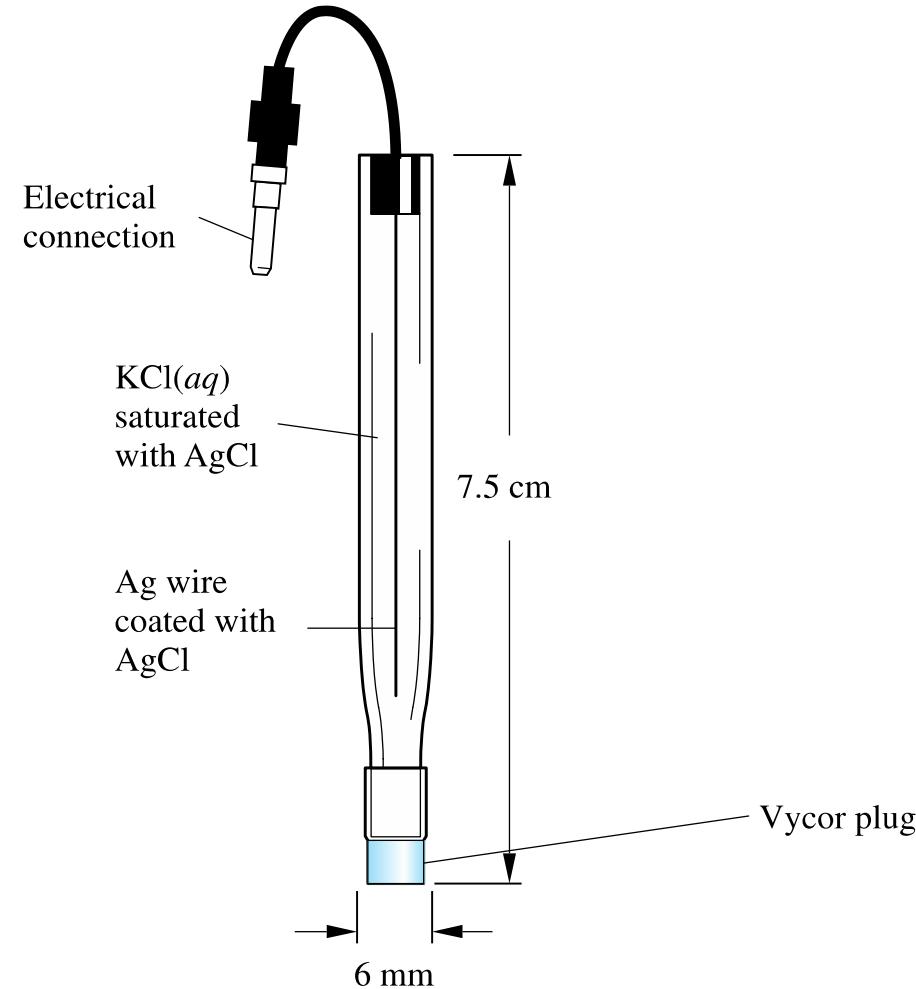
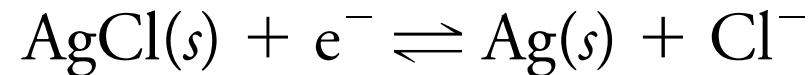
**Electrode is reversible with respect to  $Cl^-$  ions**

### 3. Ag/AgCl Electrode

Half-cell representation:



Half-cell reaction:



**Ag/AgCl Electrode** Can be used when temperature grater than 60 °C but Calomel electrode cannot used at temperature grater than 35 °C.

# **Indicator Electrodes**

An ideal indicator electrode responds rapidly and reproducibly to the changes in the activity of ions

<b>Metallic Indicator Electrodes</b>	<b>Membrane Indicator Electrode (ion selective electrodes)</b>
Electrode of First kind	Glass membrane
Electrode of Second kind	Liquid membrane
Inert Redox Electrodes	Crystalline membrane

# Metallic Indicator Electrodes

1. **Electrode of first kind :** Pure metal electrode is in equilibrium with its cation in the solution. A single reaction is involved.

**Copper - Indicator electrode,**

**Saturated calomel electrode - Reference electrode**



2. **Electrode of second kind:**

Metals not only serve as indicator electrodes for their own cations but also **respond** to the activities of **anions** that form sparingly soluble precipitates or stable complexes with such cations.

e.g. Ag in saturated AgCl solution. Ag can serve as indicator electrode for chloride ion.

**3. Inert redox electrodes:** Pt, Pd, Au and Graphite electrodes (carbon) can be used to monitor redox systems.

e.g. Pt electrode is a convenient indicator electrode for titrations involving standard cerium(IV) solution.

## **Membrane Indicator Electrode (Ion Selective Electrodes)**

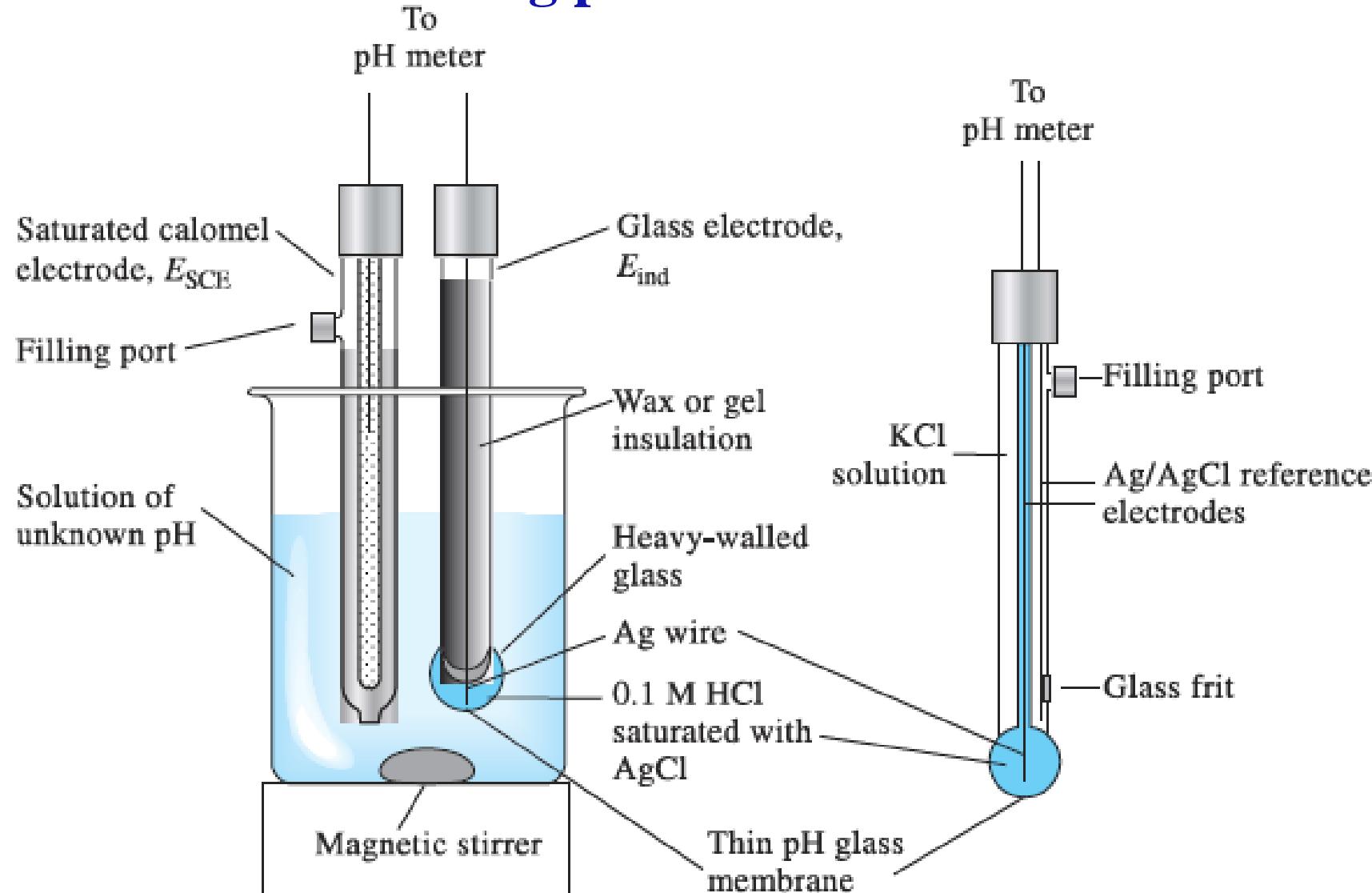
The most convenient method for determining pH has

Measurement of the potential that appears across a thin glass membrane that separates two solutions with different hydrogen ion concentrations.

Selectivity and sensitivity of glass membranes towards hydrogen ions are reasonably well understood.

# Membrane Indicator Electrode (Ion Selective Electrodes)

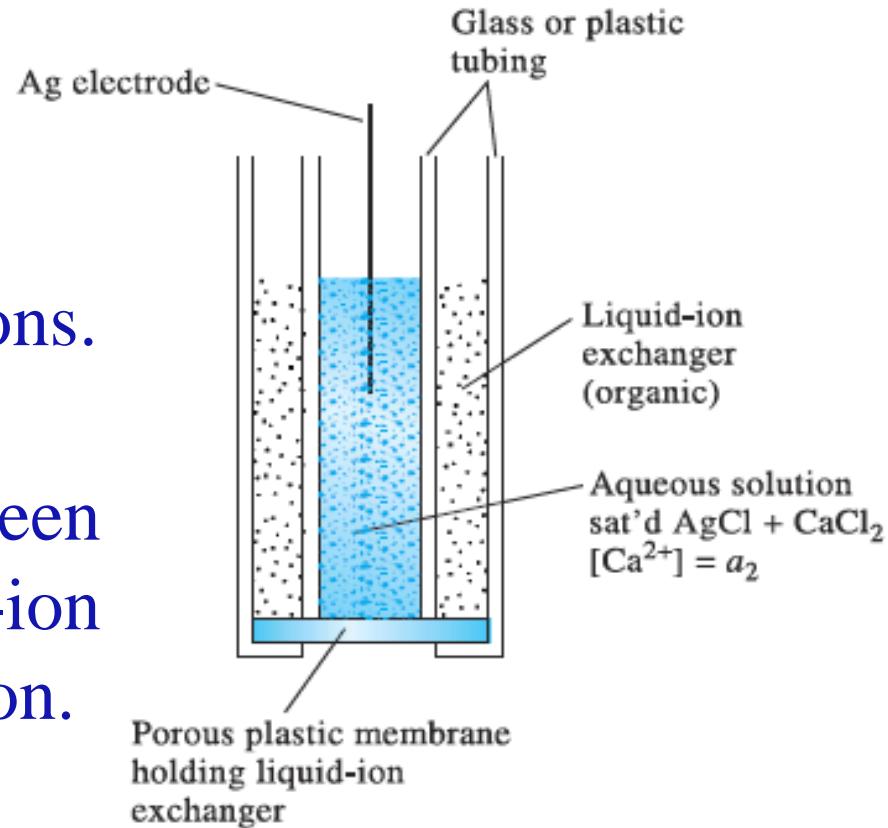
## 1. Glass Electrodes for measuring pH



## 2. Liquid-Membrane Electrodes

Useful for numerous polyvalent cations and anions.

The potential develops across the interface between the solution containing the analyte and a liquid-ion exchanger that selectively bonds with the analyte ion.



**Figure 21-12** Diagram of a liquid-membrane electrode for  $\text{Ca}^{2+}$ .

It consists of a conducting membrane that selectively binds calcium ions, an internal solution containing a fixed concentration of calcium chloride, and a silver electrode that is coated with silver chloride to form an internal reference electrode.

The active membrane ingredient is an ion exchanger that consists of a calcium dialkyl phosphate that is nearly insoluble in water

The ion exchanger is dissolved in an immiscible organic liquid that is forced by gravity into the pores of a hydrophobic porous disk. This disk then serves as the membrane

## Crystalline-Membrane Electrodes

Membranes prepared from silver halide pellets have been used successfully in electrodes for the selective determination of chloride, bromide, and iodide ions.

- Similarly, polycrystalline  $\text{Ag}_2\text{S}$  membrane has been used for the determination of sulfide ion.
- Silver ions are sufficiently mobile to conduct electricity through the solid medium.

Mixtures of PbS, CdS, and CuS with Ag<sub>2</sub>S provide membranes that are selective for Pb<sup>+2</sup>, Cd<sup>+2</sup>, and Cu<sup>+2</sup> respectively. Silver ion must be present in these membranes to conduct electricity because divalent ions are immobile in crystals (charge dislocation).

- Membrane made up of crystal of lanthanum fluoride doped with europium(II) fluoride has been used for the determination of fluoride ion.
- The potential that develops across the crystalline solid-state electrodes is described by

# **Types of Potentiometry**

## **Classifications of Potentiometry**

1. Acid- Base titrations (Strong acid *vs.* Strong base)
2. Redox titrations
3. Precipitation titrations (the one performed in the laboratory)

# Applications of Potentiometry

## 1. Acid- Base titrations (Strong acid vs. Strong base)

e.g. HCl vs. NaOH

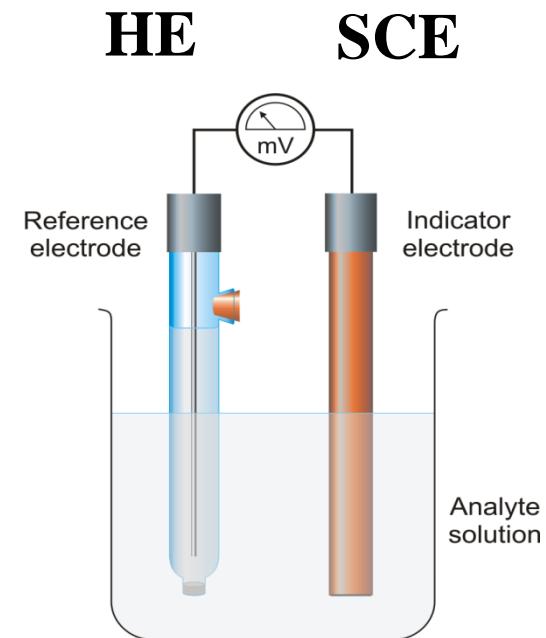
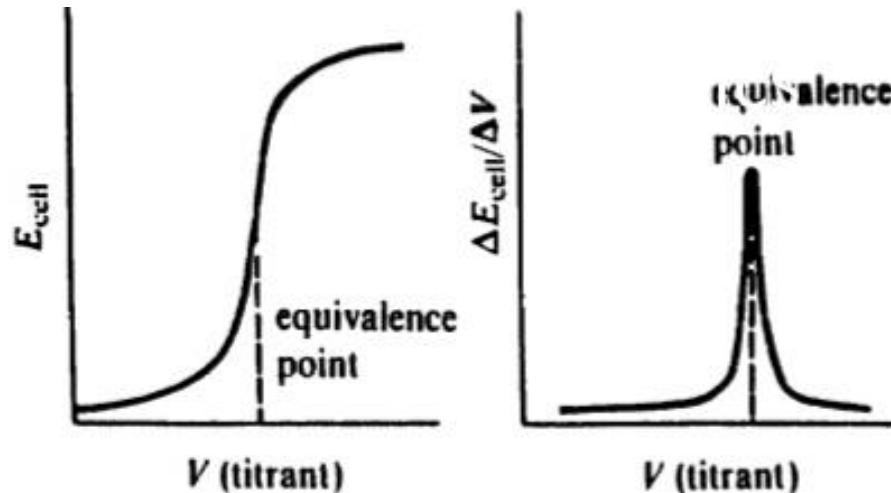
Pt,  $H_2$  (1 atm),  $H^+$  ( $c = \text{unknown}$ ) || KCl sat. soln;  $Hg_2Cl_2(s)$ , Hg

$$E = E_R - E_L = E_{\text{calomel}} - E_{\text{hydrogen}}$$

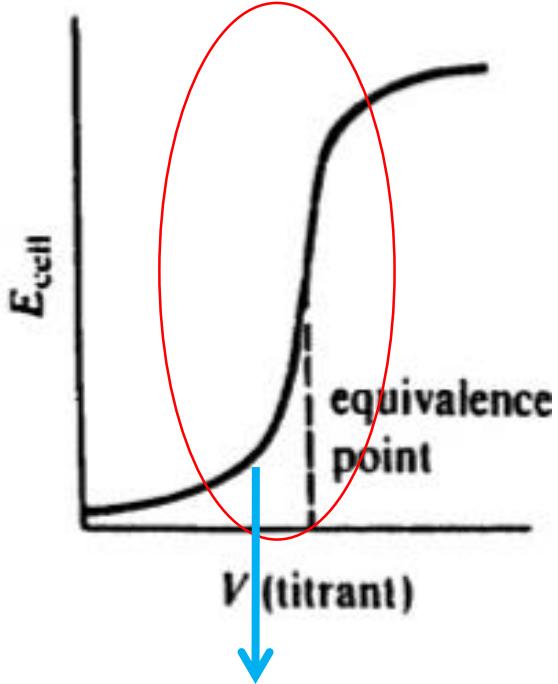
$$E = 0.2422 - 0.0591 \log H^+$$

$$E = 0.2422 + 0.0591 \text{ pH}$$

Titration curves..



$$E = 0.2422 - 0.0591 \log H^+$$



**10 fold decrease** in  $H^+$  ion concentration/ 1 unit increase in pH  
= **0.0591 V increase in potential**

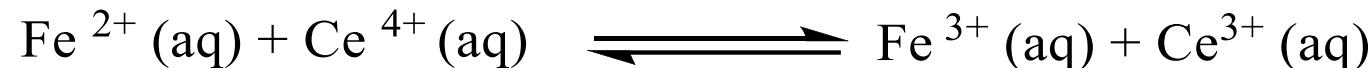
**After the end point:**

- Addition of NaOH does not change the  $[H^+]$
- No change in the EMF of the cell

**Why this sharp increase??**

## 2. Redox titrations :

Consider a redox titration of Fe (II) with a standard solution of cerium (IV)



**Initially the electrode potential is controlled by the ratio of  $[\text{Fe}^{3+}(\text{aq})]/[\text{Fe}^{2+}(\text{aq})]$**

$$E_{el} = E^0 el - 0.0591 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad \text{at } 25^\circ\text{C}$$

$$E_{el} = E^0 el + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

If the ratio of  $[\text{Fe}^{3+}(\text{aq})]/[\text{Fe}^{2+}(\text{aq})]$  is 0.01

$$E_{el} = E^0 el + 0.0591 \log (0.01)$$

$$E_{el} = E^0 el - 0.1182$$

With every 10 fold change in ratio : 0.0591 V decrease

**At equivalence point:**

$$\text{Fe}^{2+}(\text{aq}) = \text{Ce}^{4+}(\text{aq}) \text{ and } \text{Fe}^{3+}(\text{aq}) = \text{Ce}^{3+}(\text{aq})$$

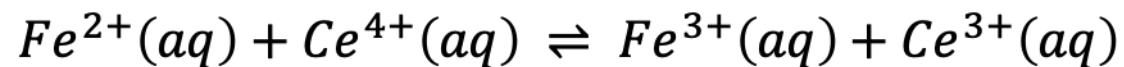
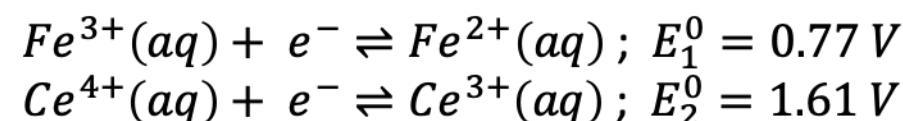
$$E_{el} = E_1^0 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} , E_{el} = E_2^0 + 0.0591 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$

## Adding and simplifying,

$$2E_{eq} = E_1^0 + E_2^0 + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]}$$

$$2E_{eq} = E_1^0 + E_2^0 + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} + 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{eq} = \frac{(E_1^0 + E_2^0)}{2}$$



Beyond equivalence point:  $[Fe^{2+}] = 0$ ; potential is governed by  $[Ce^{3+}(aq)]/[Ce^{4+}(aq)]$

$$E_{el} = E^0 - 0.0591 \log \frac{[Ce^{3+}]}{[Ce^{4+}]} \text{ at } 25^\circ C$$

## Galvanic cell,



Before equivalence point,

$$E_{cell} = E_R - E_L = E^0_{el} + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} - E_{Calomel}$$

$$E_{cell} = 0.77 V + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} - 0.2422 V$$

$$E_{cell} = 0.5278 V + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

At equivalence point,

$$E_{cell} = \frac{(E_1^0 + E_2^0)}{2} - 0.2422 V$$

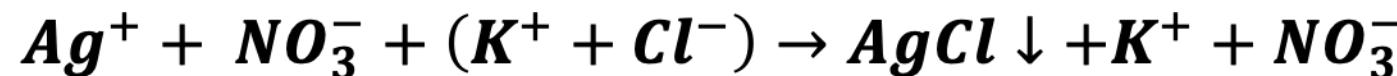
After equivalence point,

$$E_{cell} = 1.61V + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]} - 0.2422 V$$

$$E_{cell} = 1.3678 V + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]}$$

### 3. Precipitation titrations :

## Applications of Potentiometry



$$E_{el} = E^0_{el} + 0.0591 \log [Ag^+]$$

Potentiometric Titration Data for 2.433 mmol of Chloride with 0.1000 M Silver Nitrate

Volume AgNO <sub>3</sub> , mL	E vs. SCE, V	ΔE/ΔV, V/mL	Δ <sup>2</sup> E/ΔV <sup>2</sup> , V <sup>2</sup> /mL <sup>2</sup>
5.00	0.062		
15.00	0.085	0.002	
20.00	0.107	0.004	
22.00	0.123	0.008	
23.00	0.138	0.015	
23.50	0.146	0.016	
23.80	0.161	0.050	
24.00	0.174	0.065	
24.10	0.183	0.09	
24.20	0.194	0.11	2.8
24.30	0.233	0.39	4.4
24.40	0.316	0.83	-5.9
24.50	0.340	0.24	-1.3
24.60	0.351	0.11	-0.4
24.70	0.358	0.07	
25.00	0.373	0.050	
25.50	0.385	0.024	
26.00	0.396	0.022	
28.00	0.426	0.015	

# **Applications of Potentiometry**

## **Clinical Chemistry:**

- Ion-selective electrodes are important sensors for clinical samples because of their selectivity for analytes in complex matrices.
- The most common analytes are electrolytes, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{H}^+$  and  $\text{Cl}^-$  and dissolved gases such as  $\text{CO}_2$

## **Environmental Chemistry**

- For the analysis of  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_3$  in water and wastewater.
- One potential advantage of an ion-selective electrode is the ability to incorporate it into a flow cell for the continuous monitoring of wastewater streams

# Applications of Potentiometry

## Potentiometric Titrations

- Use of pH electrode to monitor the change in pH during the titration
- For determining the equivalence point of an acid-base titration.
- Possible for acid-base, complexation, redox, and precipitation titrations as well as for titrations in aqueous and non-aqueous solvents

Q1. At 298 K, for the cell represented as Pt , H<sub>2</sub> (1 atm) | H<sup>+</sup> || KCl (sat), Hg<sub>2</sub>Cl<sub>2</sub> (s) | Hg, Pt ; determine (i) emf when pH = 5.0 and (ii) concentration of H<sup>+</sup> when  $E_{\text{cell}} = 0.36$  V. Given  $E_0(\text{Hg}_2\text{Cl}_2|\text{Hg}) = 0.2415$  V.

Ans:

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.2415 - 0.0592 \log [\text{H}^+]$$

$$\begin{aligned}(i) \quad E_{\text{cell}} &= 0.2415 - 0.0592 \log [\text{H}^+] = 0.2415 + 0.0592 \text{pH} \\ &= 0.2415 + 0.0592 * 5 = \mathbf{0.5375 \text{ V}}\end{aligned}$$

$$(ii) \quad E_{\text{cell}} = 0.36 \text{ V}$$

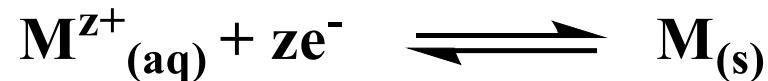
$$E_{\text{cell}} = 0.2415 + 0.0592 \text{pH}$$

$$\text{pH} = (E_{\text{cell}} - 0.2415) / 0.0592 = (0.36 - 0.2415) / 0.0592 = 2$$

$$[\text{H}^+] = \text{Antilog } (-2) = \mathbf{0.01 \text{ M}}$$

# Common Types of Reversible Electrodes

## 1. Metal-Metal Ion Electrodes



Z is valency of the metal

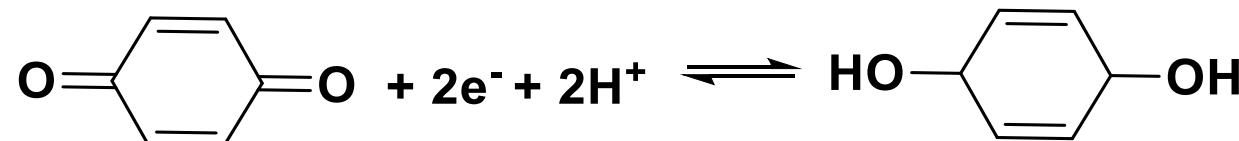
## 2. Gas Electrodes



## 3. Metal-Insoluble Metal Salt Electrodes



## 4. Oxidation-Reduction Electrodes



# Voltammetry

# **Electro Analytical Methods**

Electroanalytical methods are a class of techniques in analytical chemistry which **study an analyte by measuring the potential (volts) and/or current (amperes)** in an electrochemical cell containing the analyte.

**Potentiometry:** Potentiometric system measure voltage (i.e. potential) of a galvanic cell (produces electricity spontaneously) when current flow is zero.

**Voltammetry:** Voltammetric system usually measures current in an electrolytic cell (consumes power to cause an electrochemical reaction to occur).

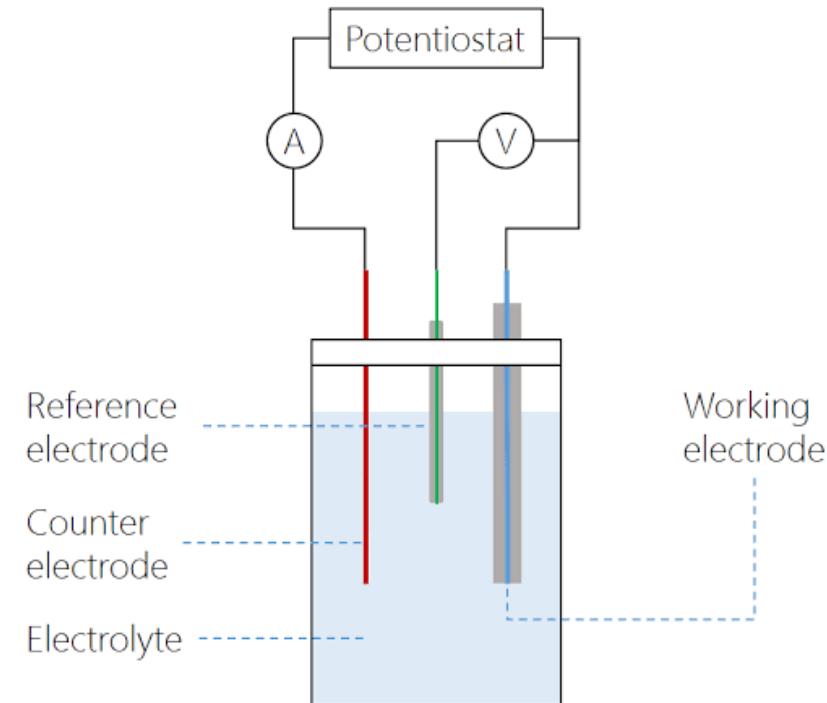
<b>Potentiometry</b>	<b>Voltammetry</b>
Two electrode system (Reference electrode and Indicator electrode)	Three electrode system (Reference electrode, Indicator electrode and counter electrode)
Fallows the Nernst equation	Deviated form the Nernst equation; depends upon concentration polarization
No use of current	Current measured with applied potential

# Electrode System

**Working electrode (WE):** Pt, Au, Glassy carbon

**Counter electrode (CE):** Pt wire,

**Reference electrode (RE):** Ag/Ag<sup>+</sup>, Ag/AgCl, SCE



The potential (V) is applied between the working and reference electrodes, while the current (A) is measured between the working and counter electrodes

# Reference and Counter Electrodes

**Reference electrode(RE):** Ag/Ag<sup>+</sup>, Ag/AgCl, SCE etc.

Electrode's potential is **known** and **constant**. The potential that is cycled is the **potential difference between the working electrode and the reference electrode**.

**Counter Electrode or Auxiliary Electrode (CE):** Pt wire

The purpose is to conduct electricity & maintaining the correct current.



## Working Electrode

The most important electrode in CV is the working electrode.

It can be made from a variety of materials including: Platinum, gold, silver, glassy carbon, nickel and palladium.

Redox reaction of the analyte takes place in **working electrodes**

# Voltammetry

Types

Linear Sweep Voltammetry (LSV)

**Cyclic Voltammetry (CV)**

Differential Pulse Voltammetry (DPV)

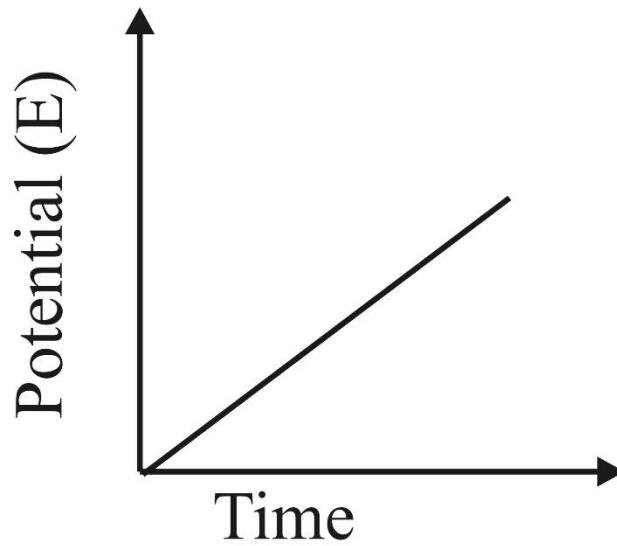
Square Wave voltammetry (SWV)

Stripping Voltammetry (SV)

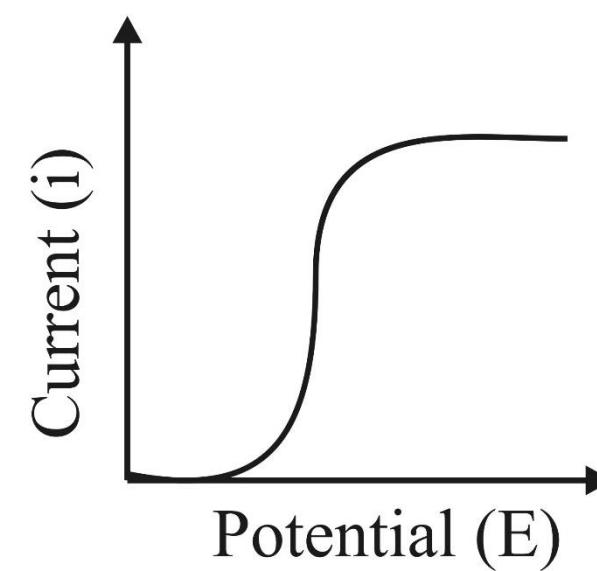
# Linear Sweep Voltammetry (LSV)

The potential is varied linearly from an initial potential (**Initial E**) to a final potential (**Final E**) at a constant rate (**Scan Rate**), and the current is monitored as a function of the **applied potential**.

**Apply Linear Potential with Time**



**Observed Current Changes with Applied Potential**



Linear scan voltammogram have a sigmoidal curve called **voltammetric wave**

Constant current beyond the steep rise - **limiting current  $i_l$**

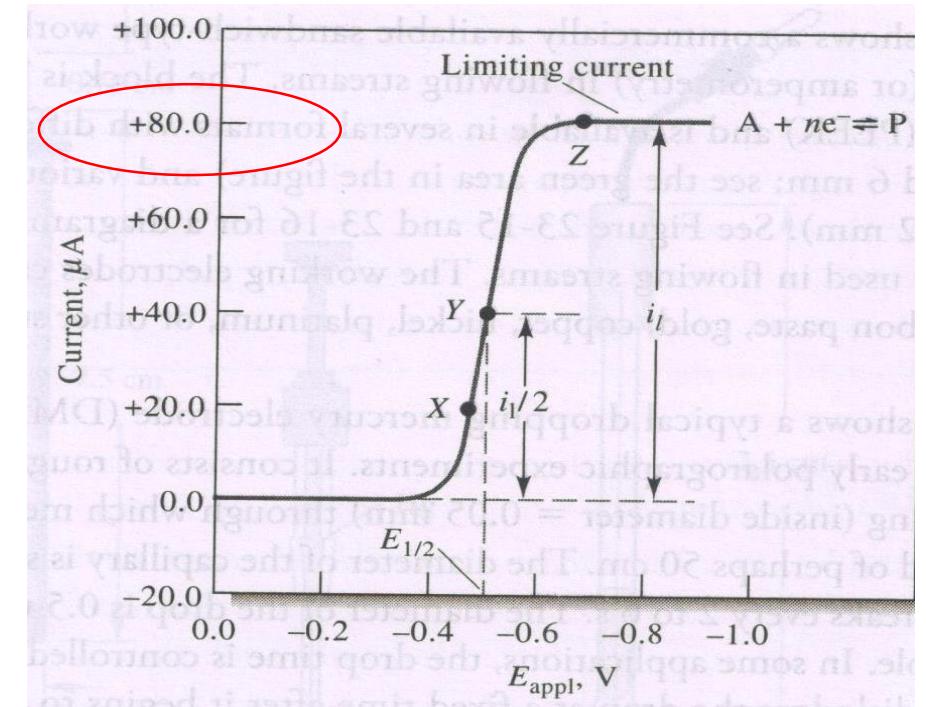
The reactants are brought to the surface of the electrode is by **a mass transfer process**

The rate of this process limits the current

**Half wave potentials ( $E_{1/2}$ )**- potential at which the **current is half of the limiting current**

$E_{1/2}$  is closely related to the standard reduction potentials ( $E^\circ$ ) for the half-reaction but not identical to that constant

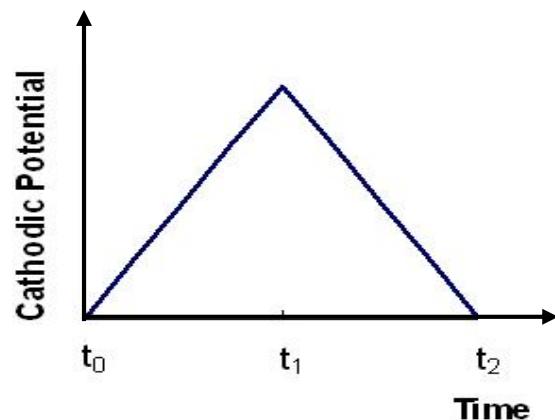
Used to identify the components of a solution



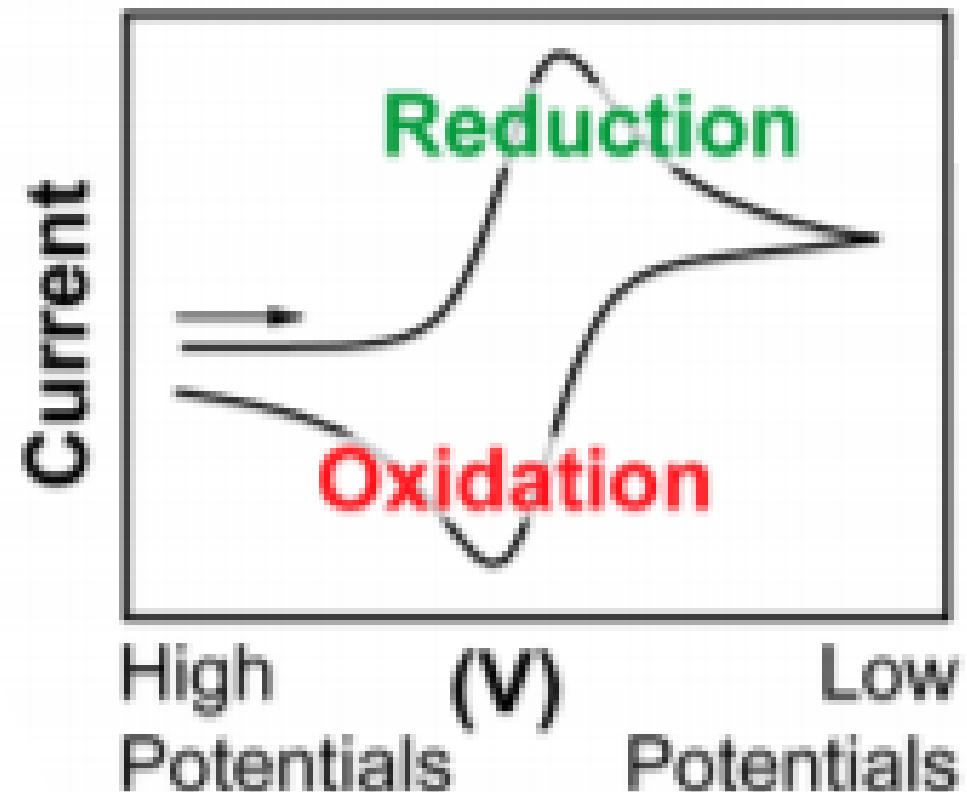
# Cyclic Voltammetry-Introduction

CV : A technique of potentiodynamic electrochemical measurement, would provide fundamental electron-transfer properties of the chemical compounds in solution.

After the set potential is reached in a CV experiment, the potential of working electrode is ramped in the opposite direction to return to the initial potential.

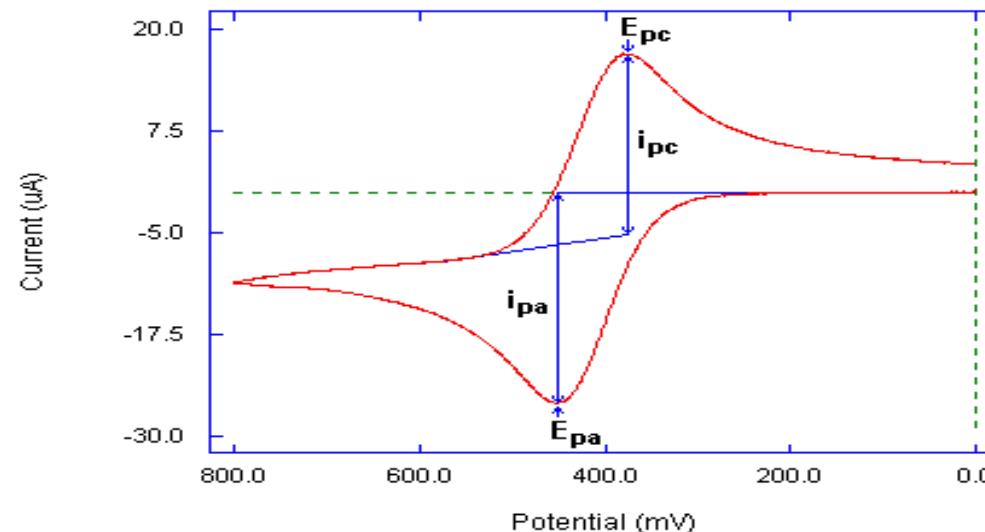


## US Convention



The current is plotted against the applied voltage to obtain the cyclic voltammogram. The rate of voltage change over time during each of these phases is known as the **scan rate (V/s)**.

The potential (V) is applied between the WE and RE, while the current (A) is measured between the WE and CE, indicating that the value of peak potential is depending on the reference electrode used.



## Cyclic Voltammetry Experimental Setup

Electrolyte is usually added to the test solution to ensure sufficient conductivity

The combination of the solvent, electrolyte, working electrode material determines the range of the potential

Electrodes are static and sit in unstirred solutions during CV measurement

Since cyclic voltammetry usually alters the charge of the analyte it is common for reduced or oxidized analyte to precipitate out onto the electrode

This layering of analyte can insulate the electrode surface, display its own redox activity in subsequent scans, or at the very least alter the electrode surface. For this and other reasons it is often necessary to clean electrodes between scans.

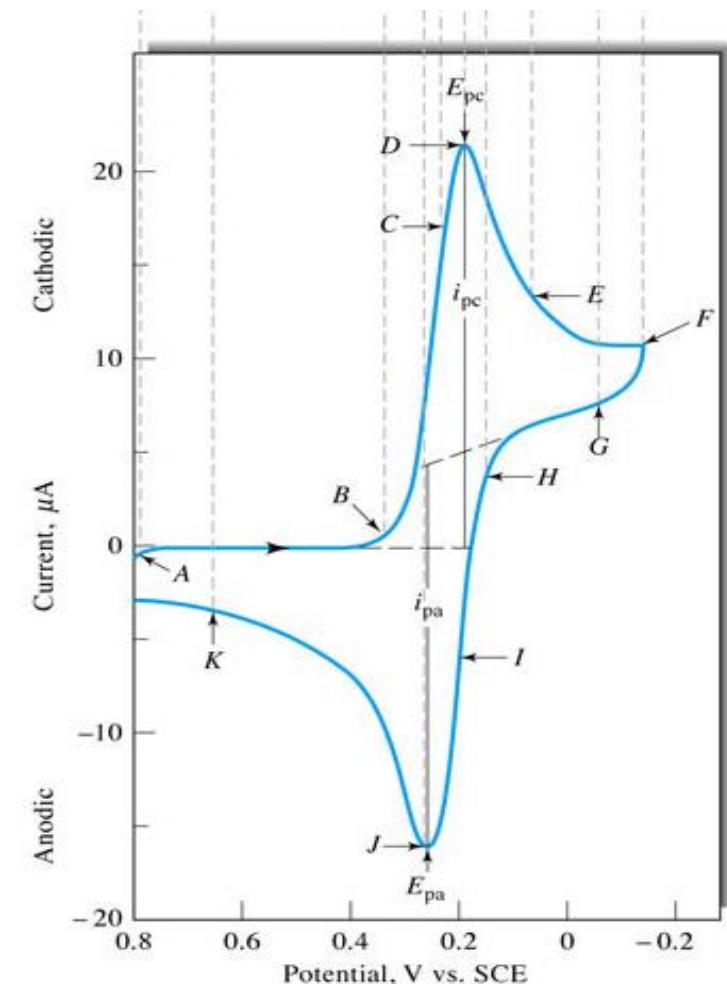
## Eg: Current response in $\text{K}_3\text{Fe}(\text{CN})_6$

$\text{Fe}(\text{CN})_6^{3-}$  to  $\text{Fe}(\text{CN})_6^{4-}$  in 1M  $\text{KNO}_3$ , cathodic reaction

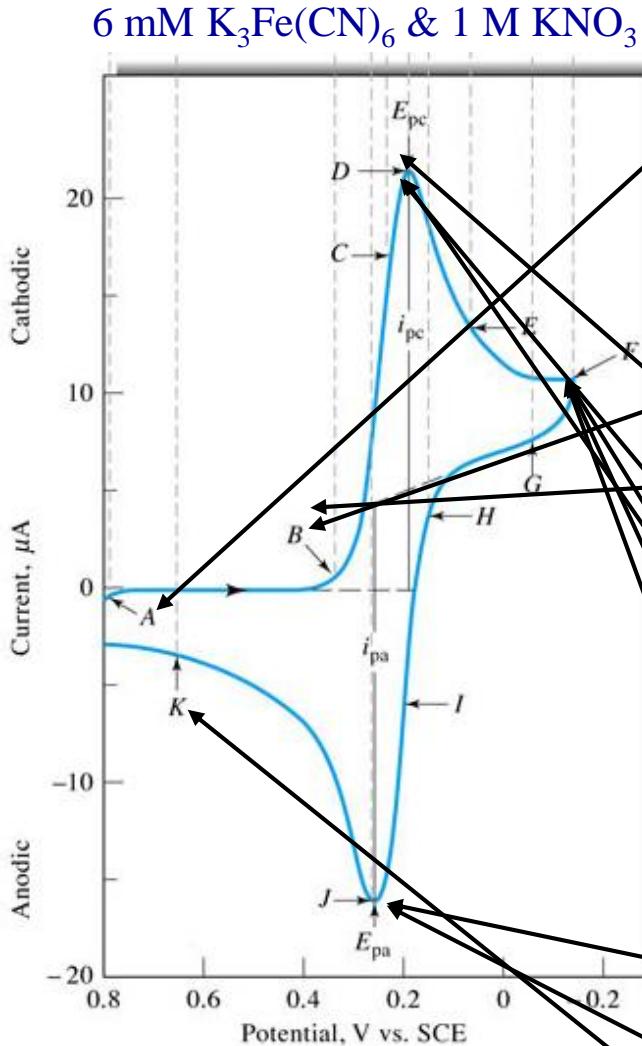
- ✓ No current between the potential of +0.7 and +0.4 V  
(Since no reducible or oxidizable species in this potential range )
- ✓ At approximately +0.4 V, a cathodic current begins to develop (at point B)
- ✓ Reduction of ferricyanide ion to ferrocyanide ion
- ✓ Cathodic reaction:



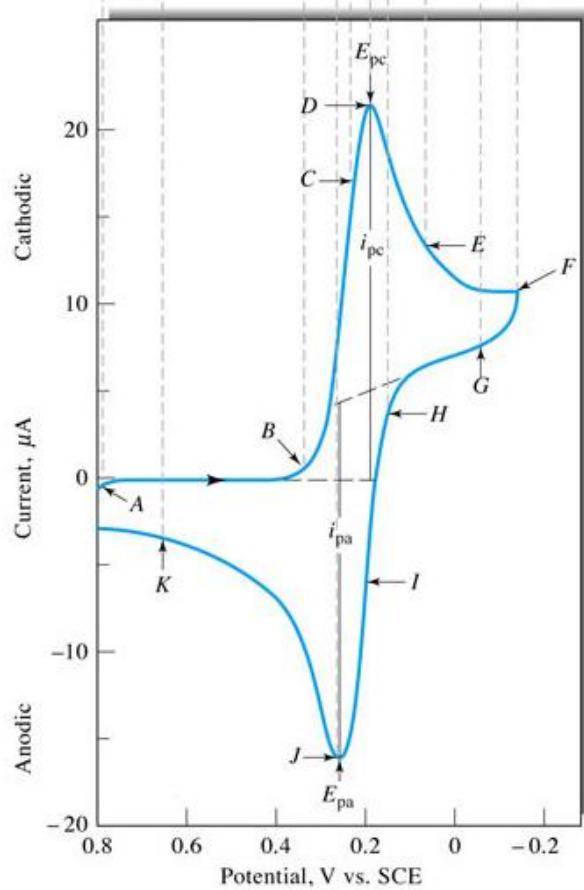
Cyclic voltammogram



## Working Electrode is Pt & Reference electrode is SCE



- A. Initial negative current due to oxidation of  $\text{H}_2\text{O}$  to give  $\text{O}_2$
- No current between A & B (+0.7 to +0.4V) no reducible or oxidizable species present in this potential range
- B. At 0.4V, current begins because of the following reduction at the cathode:  $\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$
- B.-D. Rapid increase in current as the surface concentration of  $\text{Fe}(\text{CN})_6^{3-}$  decreases
- D. Cathodic peak potential ( $E_{pc}$ ) and peak current ( $i_{pc}$ )
- D.-F. Current decays rapidly as the diffusion layer is extended further from electrode surface
- F. Scan direction switched (-0.15V), potential still negative enough to cause reduction of  $\text{Fe}(\text{CN})_6^{3-}$
- F.-J. Eventually reduction of  $\text{Fe}(\text{CN})_6^{3-}$  no longer occurs and anodic current results from the reoxidation of  $\text{Fe}(\text{CN})_6^{4-}$
- J. Anodic peak potential ( $E_{pa}$ ) and peak current ( $i_{pa}$ )
- K. Anodic current decreases as the accumulated  $\text{Fe}(\text{CN})_6^{4-}$  is used up at the anodic reaction



$$\Delta E_p = (E_{pa} - E_{pc}) = 0.0592/n$$

Where n = number of electrons involved in the half reaction

$$E^0 = \text{midpoint of } E_{pa} \rightarrow E_{pc}$$

Quantitative information can be obtained from the [Randles-Sevcik](#) equation

$$i_p = 2.686 \times 10^5 n^{3/2} A c D^{1/2} v^{1/2}$$

**$i_p$ : Peak current (Amperes)**

**A: Electrode area ( $\text{cm}^2$ )**

**c: Concentration ( $\text{mol}/\text{cm}^3$ )**

**v: Scan rate (V/s)**

**D: Diffusion coefficient ( $\text{cm}^2/\text{s}$ )**

Thus,

- can calculate standard potential for half-reaction
- number of electrons involved in half-reaction
- diffusion coefficients

Q. Calculate the cathodic peak current for the following redox process



in a cyclic voltammetric analysis with a scan rate of 20mV/s at an electrode of area  $0.12 \text{ cm}^2$ . 0.1 M analyte species is having a diffusion coefficient of  $4.05 \times 10^{-5} \text{ cm}^2/\text{s}$  in solution in 0.1M  $\text{H}_2\text{SO}_4$  solution.

Randles-Sevcik equation,  $i_p = 2.686 \times 10^5 \cdot n^{3/2} \cdot A \cdot c \cdot D^{1/2} \cdot v^{1/2}$

- $i_p$ : Peak current (Amperes)
- $A$ : Electrode area ( $0.12 \text{ cm}^2$ )
- $c$ : Concentration (0.1 M)
- $v$ : Scan rate (20 mV/s)
- $D$ : Diffusion coefficient ( $4.05 \times 10^{-5} \text{ cm}^2/\text{s}$ )

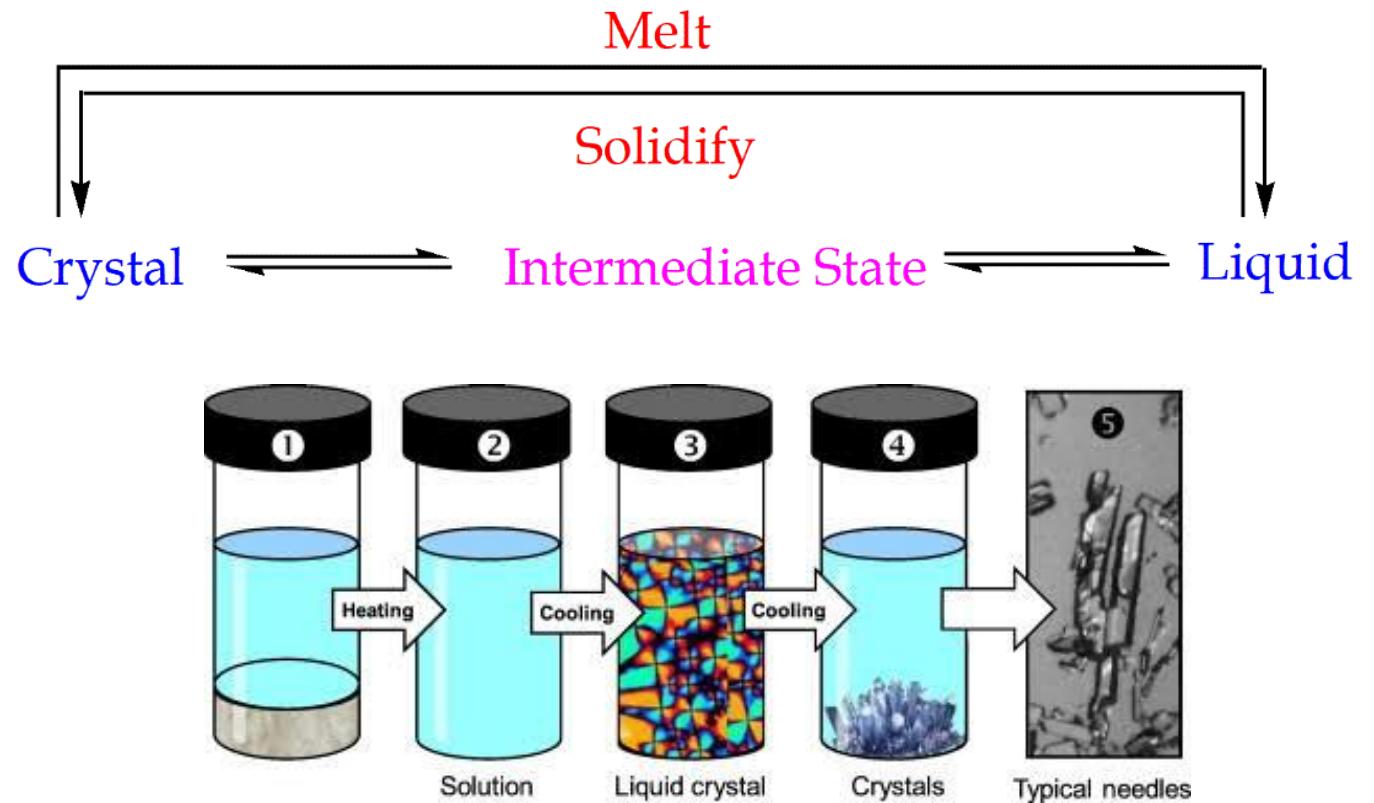
$$i_p = 2.686 \times 10^5 \cdot (1)^{3/2} \cdot (0.12 \text{ cm}^2) \cdot (0.1M) \cdot (4.5 \times 10^{-5} \text{ cm}^2\text{s}^{-1})^{1/2} \cdot (20 \text{ mV})^{1/2}$$



**LIQUID CRYSTAL**

# Introduction

A liquid crystal is an intermediate state between the crystalline solid and the ordinary liquid phase



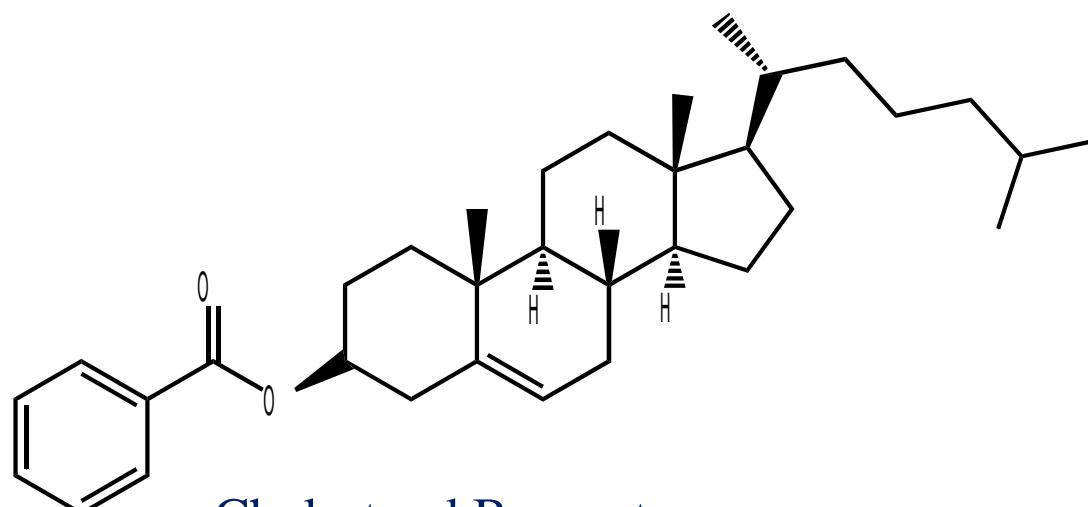
Condense fluid phases with spontaneous anisotropy

\***Anisotropy: Change in Physical Properties with direction; One of the property of Crystal Lattice**

# Discovery of Liquid Crystal

Discovered by Frederick Reinitzer in 1888

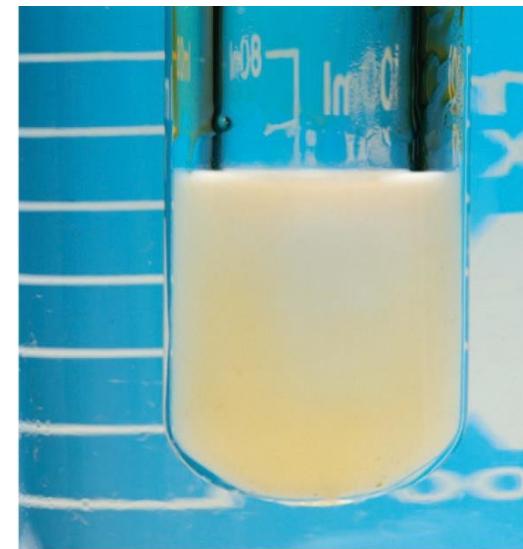
- Cholesteryl Benzoate shows two melting point
- One at  $145^{\circ}\text{C}$  into a cloudy fluid
- Another at  $179^{\circ}\text{C}$  to form clear liquid



Cholesteryl Benzoate

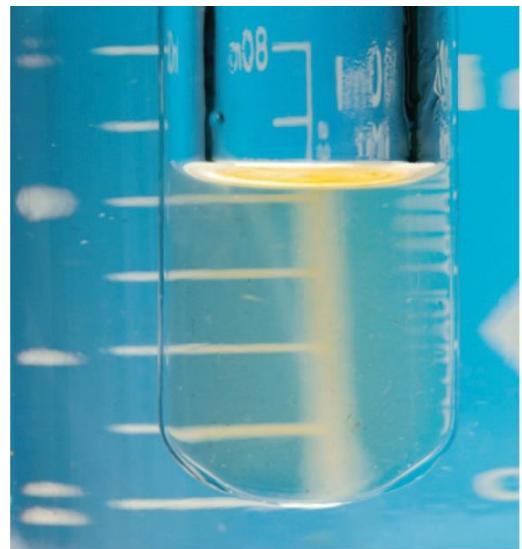
Solid  $T < 145^{\circ}\text{C}$

Viscous Milky Liquid



$145^{\circ}\text{C} < T < 179^{\circ}\text{C}$

Clear Liquid



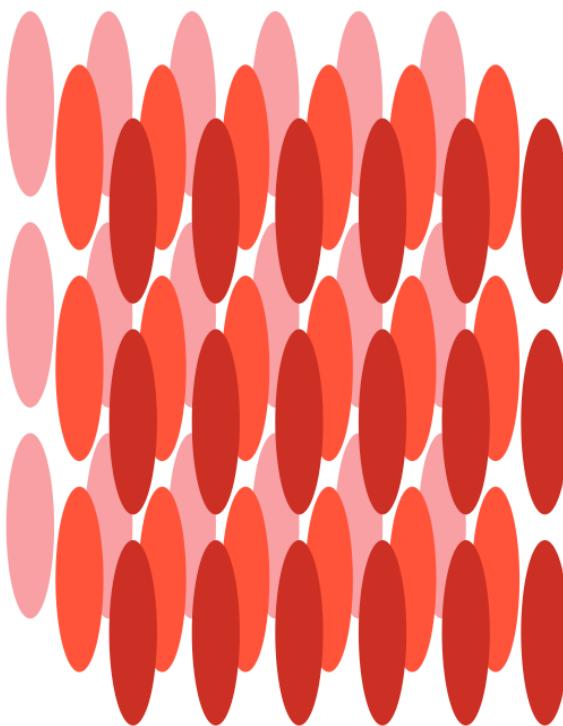
Above  $179^{\circ}\text{C}$

\*Viscous liquid form of Cholesteryl Benzoate is its liquid crystal form

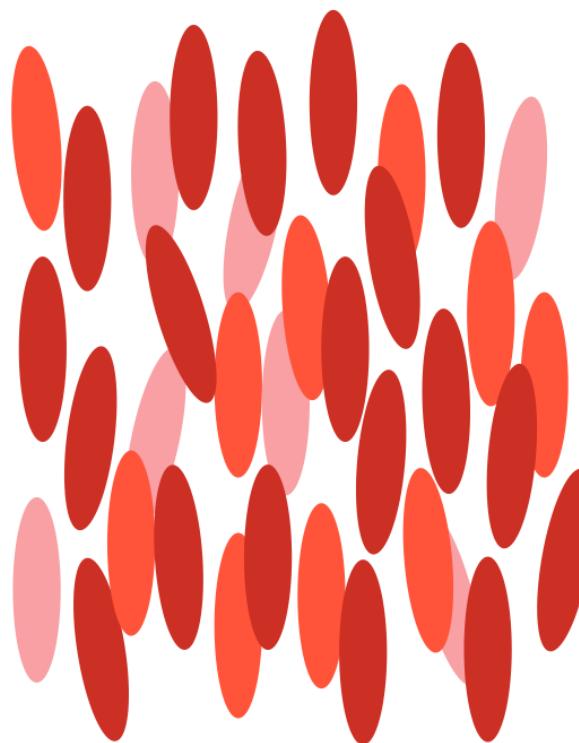
**Like crystalline solids, liquid crystals are anisotropic in nature**

Orientation of the molecules changes with temperature

Crystalline Solid

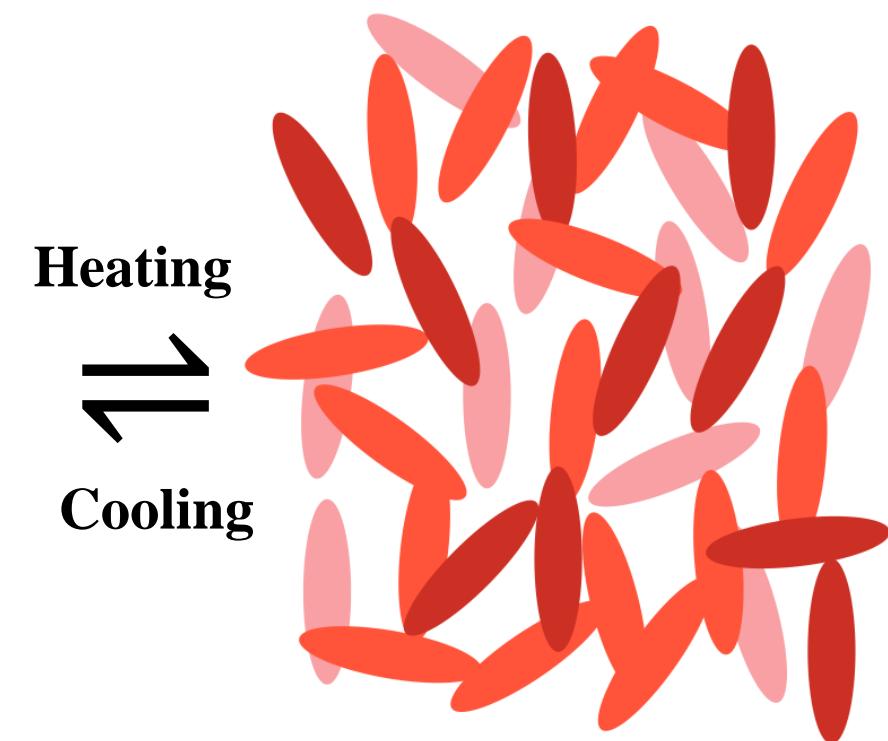


Liquid Crystal



Heating  
 $\rightleftharpoons$   
Cooling

Isotropic Liquid



Anisotropic

Isotropic

# Degree of Orders in Liquid Crystals

1. Positional order
2. Orientational Order
3. Bond orientational order

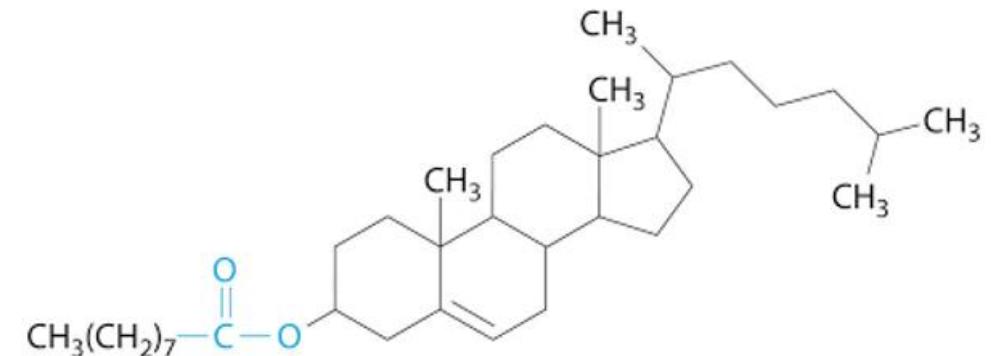
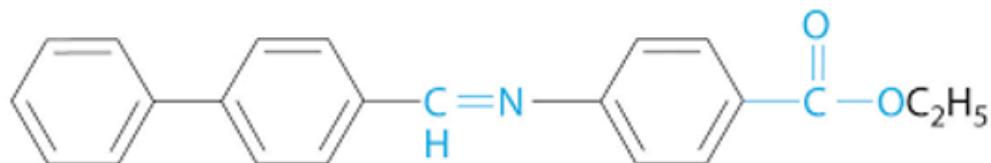
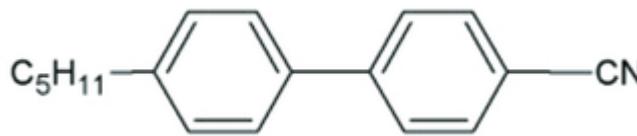


**Director:** It is the average direction of all molecules present in the LC

Substances that exhibit the properties of LC consist of long, rigid rod- or disk-shaped molecules that are easily polarizable

Molecules with polar group that exhibit dipole-dipole interaction or dipole induced interactions, hydrogen binding are capable of forming LC

## Examples



# Types of Liquid Crystals

## 1. Thermotropic Liquid Crystal

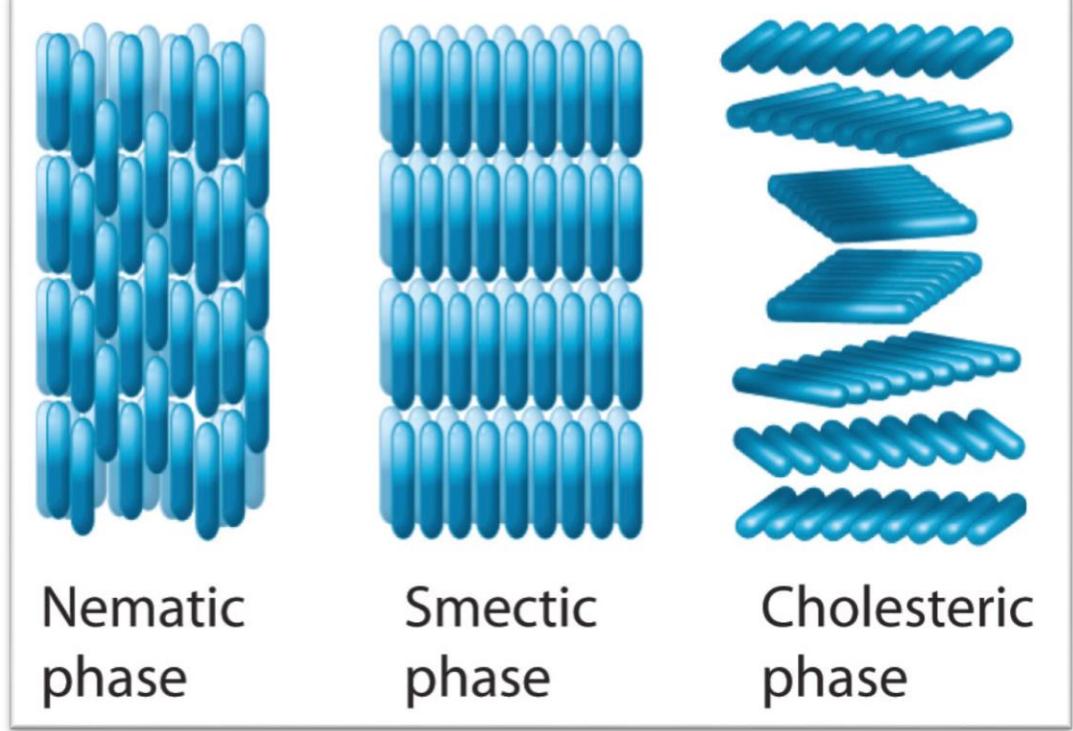
Phase forms as a function of temperature

## 2. Lyotropic Liquid Crystal

Phase forms as a function of concentration in a concentration

# 1. Thermotropic Liquid Crystal

- Most extensively used liquid crystal
- The phase changes with temperature



Based on the degree of alignment, thermotropic liquid crystal can be the following categories:

1. Smectic phase
2. Nematic phase
3. Cholesteric phase

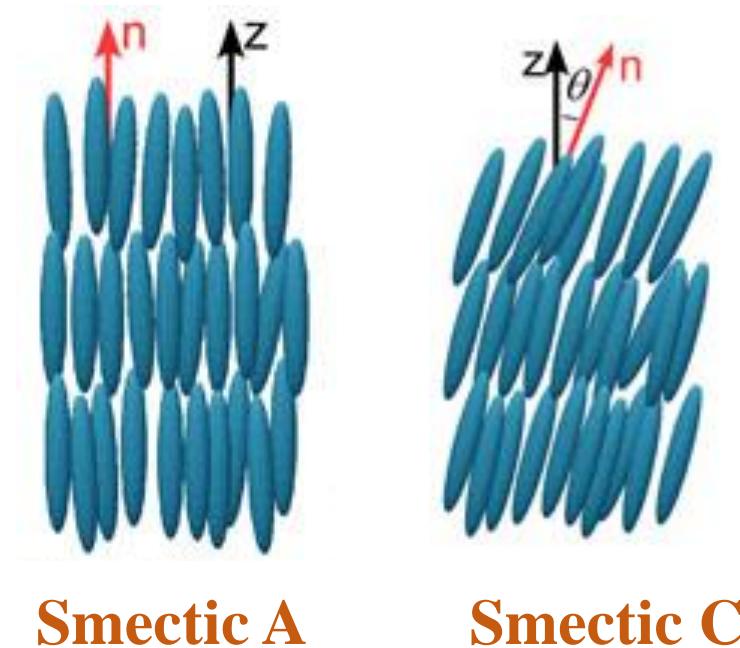
## Smectic Phase:

Increasing temperature, solid crystal first converts to Smectic phase

All molecules are unidirectional

No correlation of the molecular position from one layer to the next

Consequently, well ordered layers can slide over one another in a manner similar to soap



Types →

**Smectic A phase:** Molecules are oriented along the director

**Smectic C phase:** Molecules are tilted away from the director

## Nematic Phase

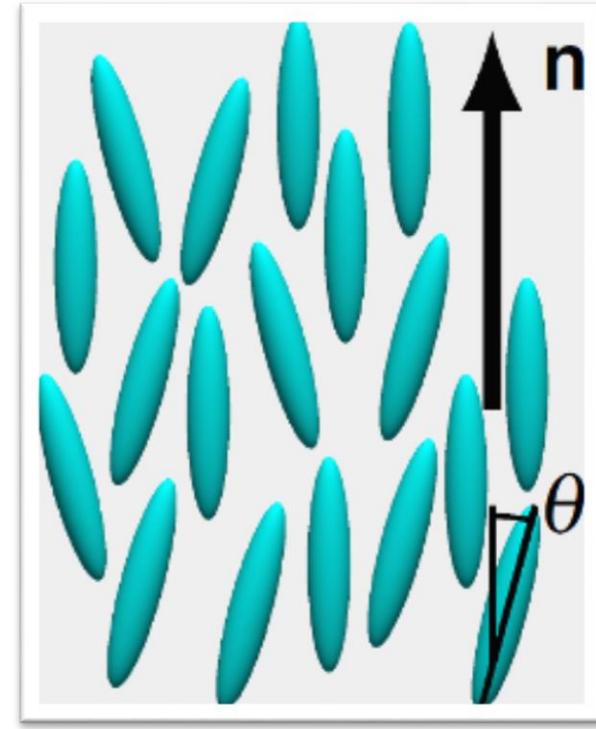
Most common **liquid crystal** phase

All the molecules are not unidirectional

Molecules maintain parallel or nearly parallel arrangement to each other along the director

Molecules have orientation but no long range positional order

Structure can be altered by using external electric and magnetic field



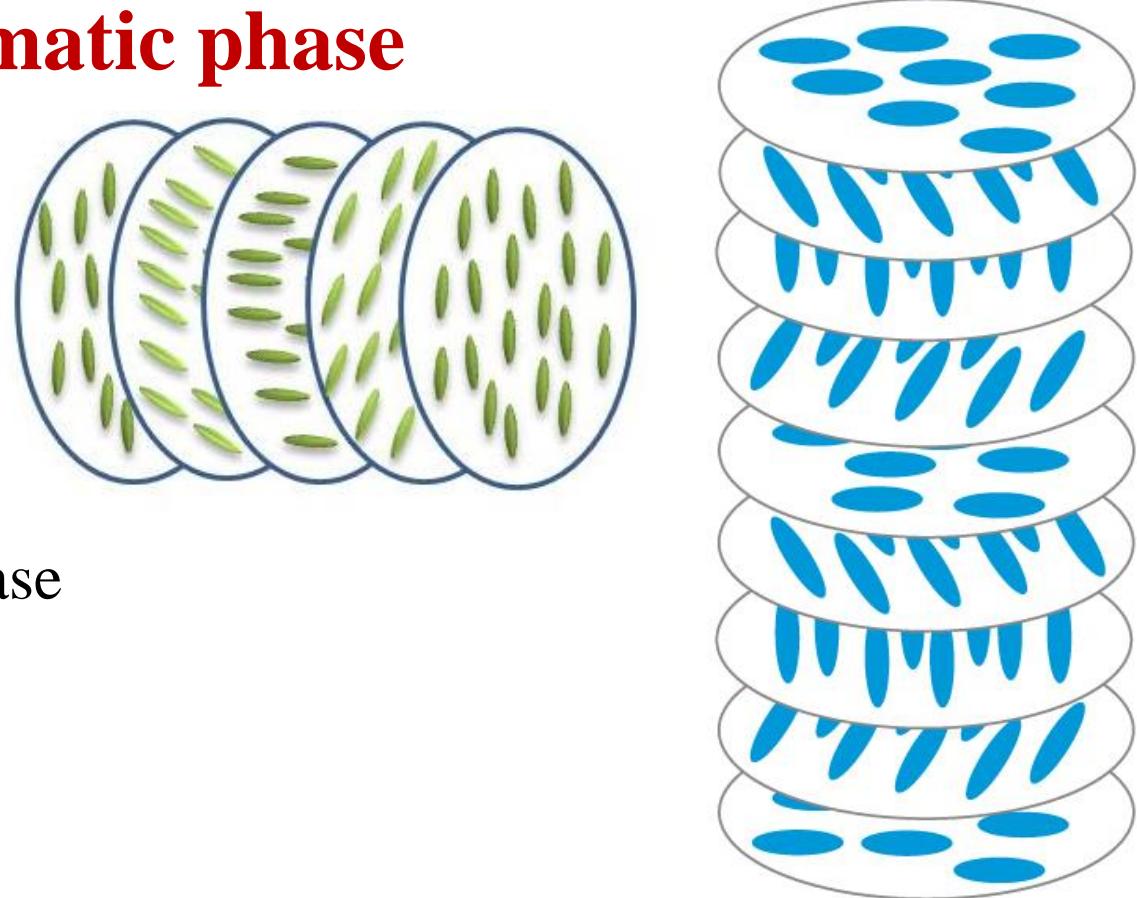
## Cholesteryl phase or Chiral Nematic phase

This phase exhibits chirality

First observed for cholesterol derivatives

Only chiral molecules can give rise to this phase

The director is helical in nature



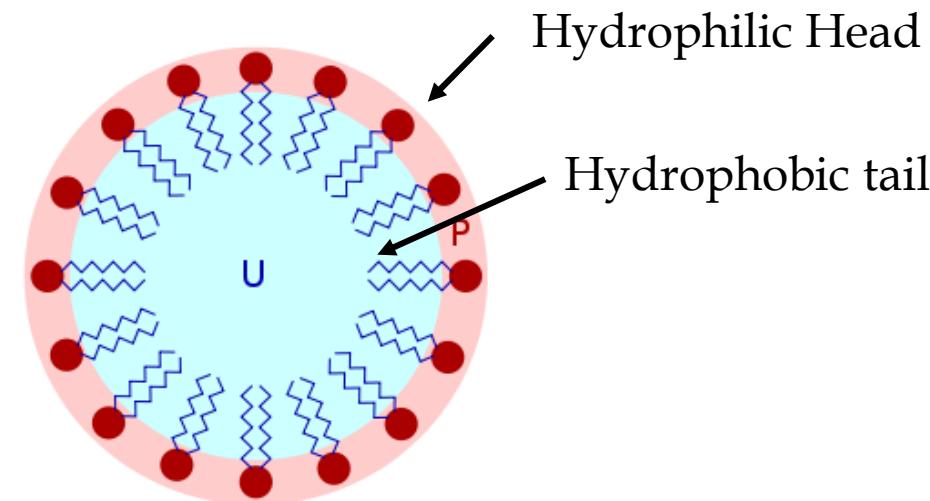
**Pitch:** The distance over which the director makes one complete turn

**Pitch is affected by:** Temperature, pressure, electric and magnetic field

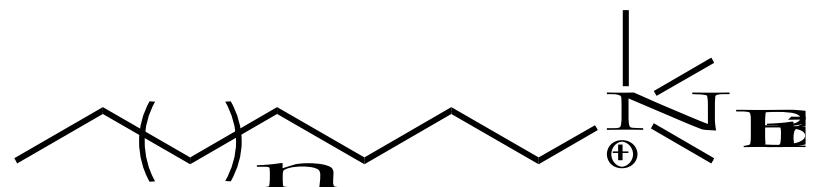
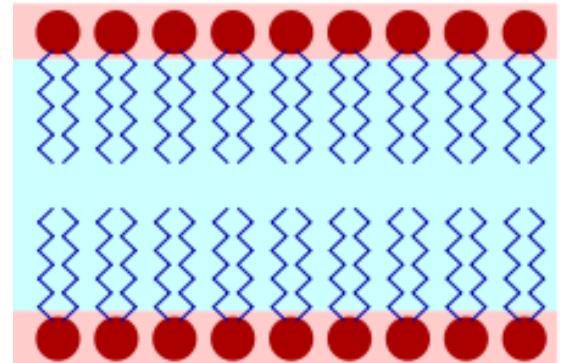
## 2. Lyotropic Liquid Crystal

Lyotropic LCs have two component

1. Hydrophilic Polar Head
2. Hydrophobic Non-polar Tail

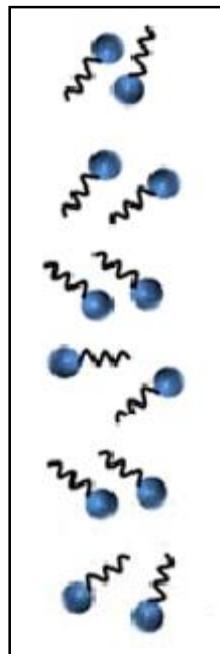


- Lyotropic phase shows LC properties only at certain concentrations
- Extra solvent phase is required to provide fluidity to the system
- Phase of LC changes with change in concentration and solvent
- Soaps, detergents are good examples of Lyotropic LC



# Change in Phase with Change in Concentration

Low  
Concentration



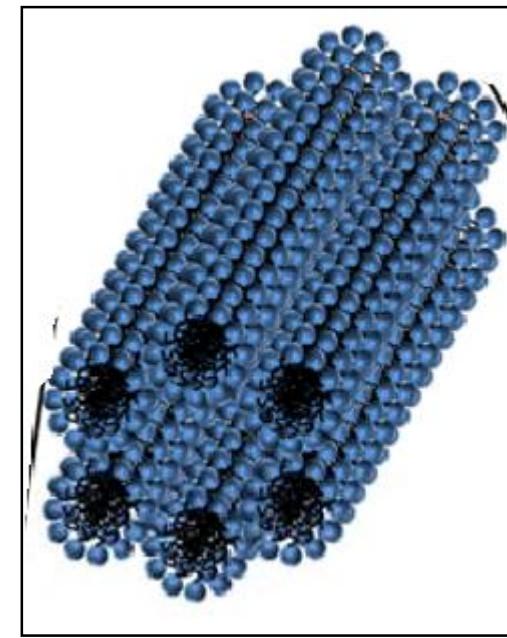
Free  
Molecules

Slightly higher  
Concentration



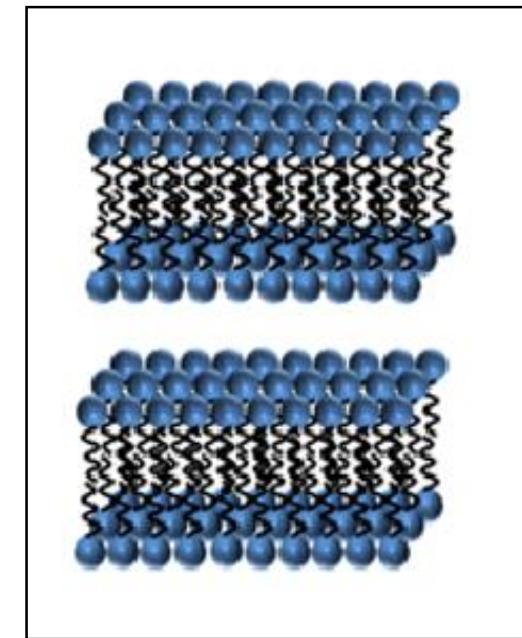
Micelle  
Formation

Higher  
Concentration



Hexagonal  
Columnar Phase

More Higher  
Concentration



Lamellar Phase



With increase in Concentration, phases are changing

# Application: Liquid Crystal Display (LCD)

First synthesized LCD for commercial purpose is a chemically stable substances, **Cyanobiphenyls**; by George Gray in 1973

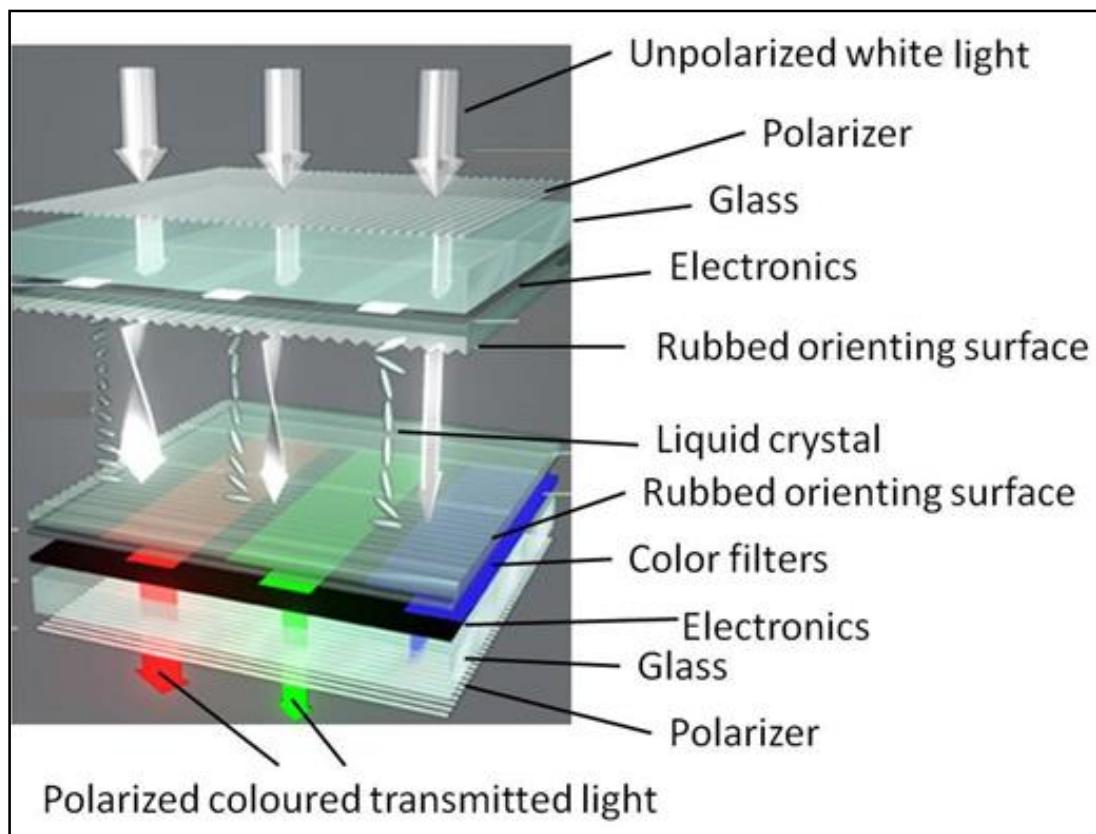
Because of two unique characteristics, LC are used in LCD

- ✓ Can rotate plane polarize light due to the unique direction of molecules
- ✓ Change orientation in presence of applied Electric Field

Nematic LCs are mostly used in LCD

## Functioning LC in LCD

- In LCD, LC layer is placed between an electric field
- With change in potential difference, molecules change their orientations
- Allow only one plane of light to pass through





## Fuel Cells

Convert chemical energy to electrical energy  
Convert hydrogen and oxygen into water, and produces electricity

Environmentally friendly

A battery has all of its chemicals stored inside, and it converts those chemicals into electricity when required

Battery eventually "goes dead"

# Battery



## In Fuel Cell

Chemicals constantly flow into the cell so it never goes dead

As long as there is a flow of chemicals into the cell, electricity flows out of the cell

Most fuel cells in use today, use **hydrogen** and **oxygen** as the chemicals

# Fuel Cell

## Anode

Negative post of the fuel cell.

Conducts the electrons that are freed from the hydrogen molecules so that they can be used in an external circuit.

Etched channels disperse hydrogen gas over the surface of catalyst.

## Cathode

Positive post of the fuel cell

Etched channels distribute oxygen to the surface of the catalyst.

Conducts electrons back from the external circuit to the catalyst

Recombine with the hydrogen ions and oxygen to form water.

## Electrolyte

Proton exchange membrane or even electrolyte solution

Specially treated material, only conducts positively charged ions.

Membrane blocks electrons.

## Fuel Cell

## Catalyst

Special material that facilitates reaction of oxygen and hydrogen

Usually platinum powder very thinly coated onto carbon paper or cloth

Rough & porous maximizes surface area exposed to hydrogen or oxygen

The platinum-coated side of the catalyst faces the PEM

## Basic operating principle

An input fuel is catalytically reacted (electrons removed from the fuel elements) in the fuel cell to create an electric current.

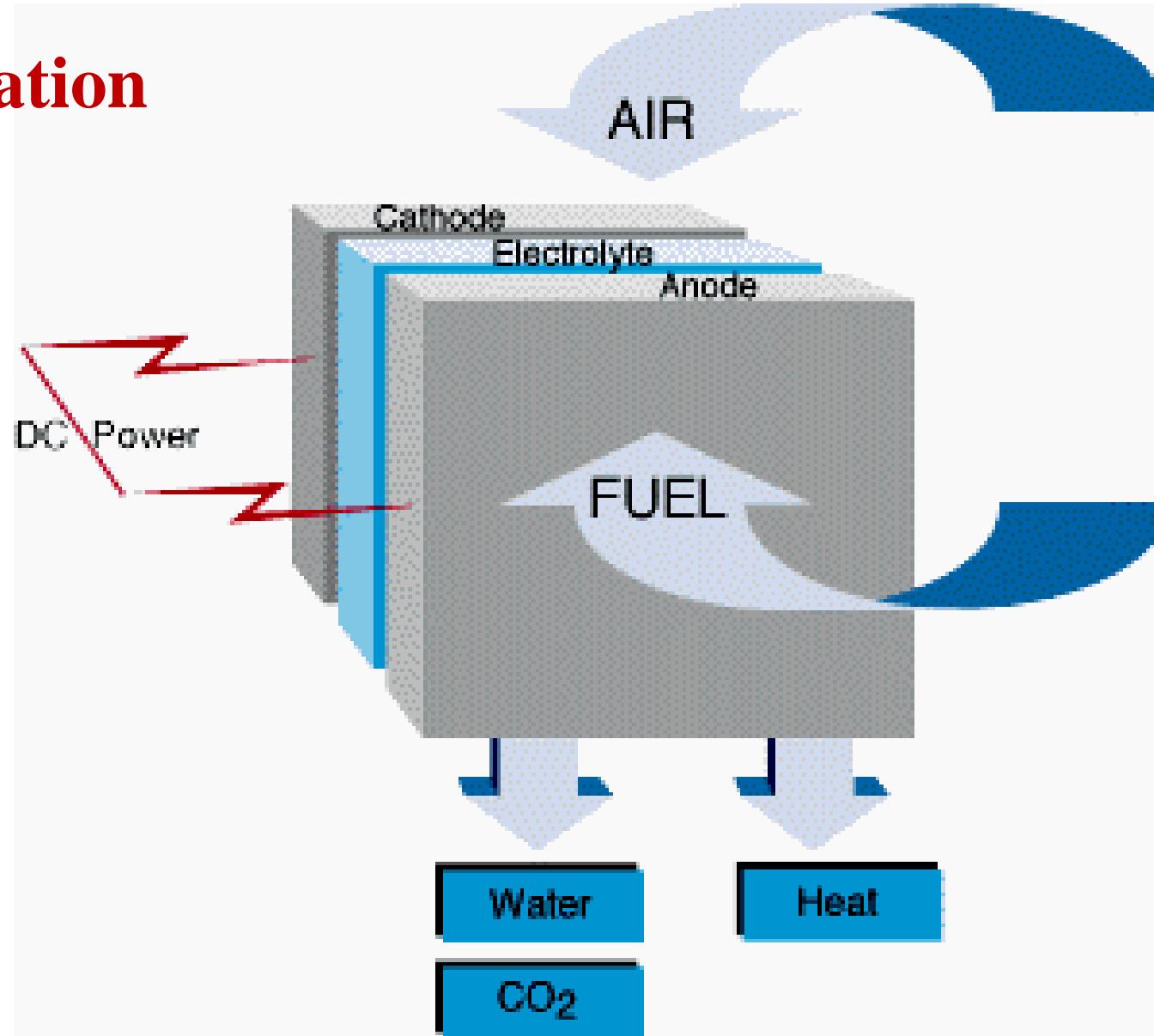
Fuel cells consist of an electrolyte material which is sandwiched in between two thin electrodes (porous anode and cathode).

The input fuel passes over the anode (and oxygen over the cathode) where it catalytically splits into ions and electrons.

Electrons go through an external circuit to serve an electric load while the ions move through the electrolyte toward the oppositely charged electrode.

Depending on the input fuel, different chemical reactions are takes place at the electrode and by-products e.g.  $\text{H}_2\text{O}$  or  $\text{CO}_2$  formed.

# Basic Configuration



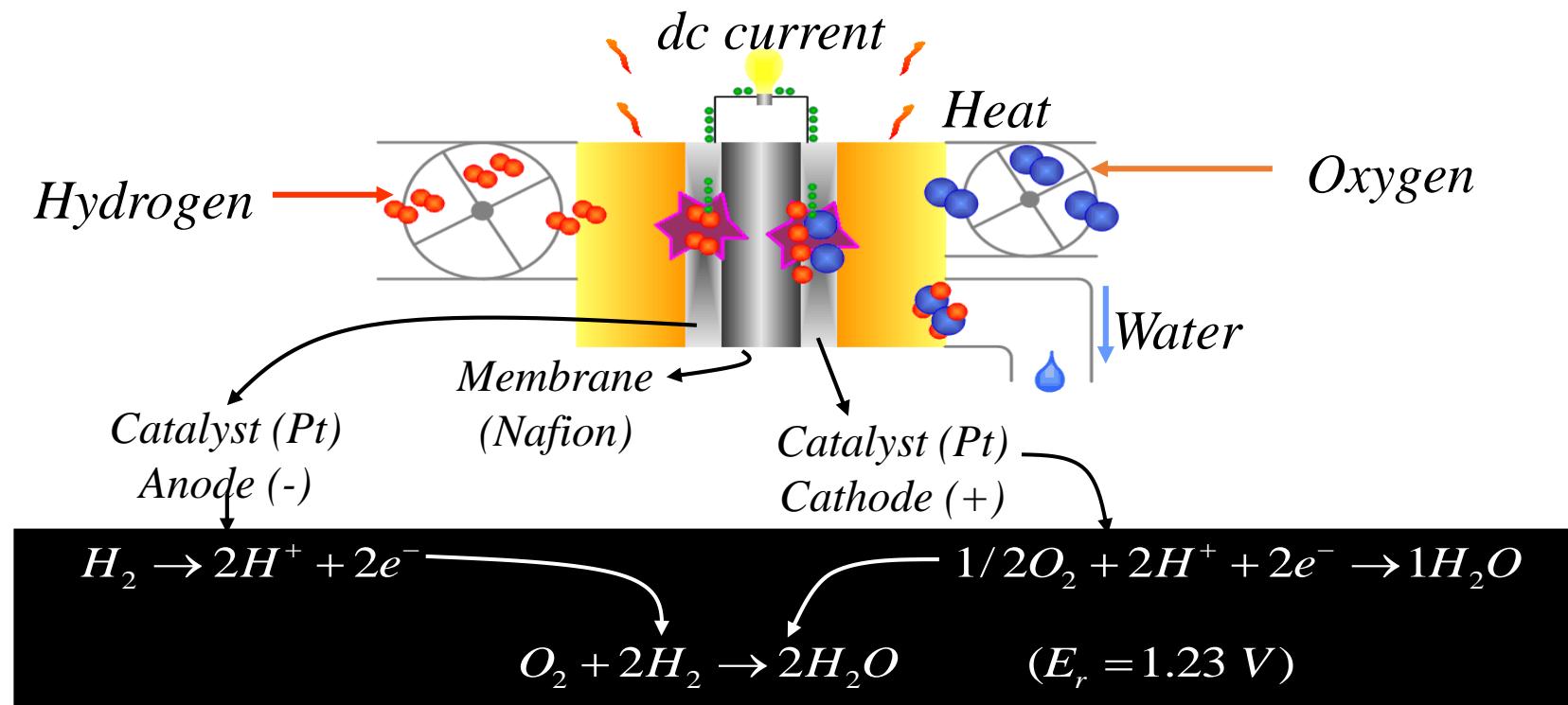
# Types of fuel cells:

- Proton exchange membrane (PEMFC)
- Solid-oxide fuel cell (SOFC)
- Direct Methanol fuel cell (DMFC)
- Alkaline fuel cell (AFC)
- Phosphoric acid fuel cell (PAFC)
- Molten-carbonate fuel cell (MCFC)

# 1. Proton exchange membrane (PEMFC)

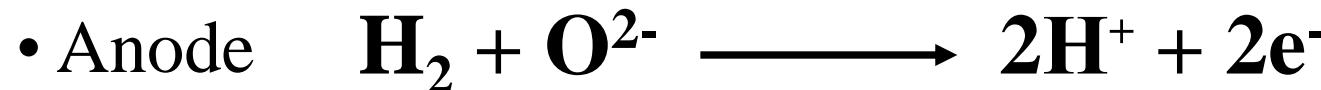
The hydrogen atom's electron and proton are separated at the anode

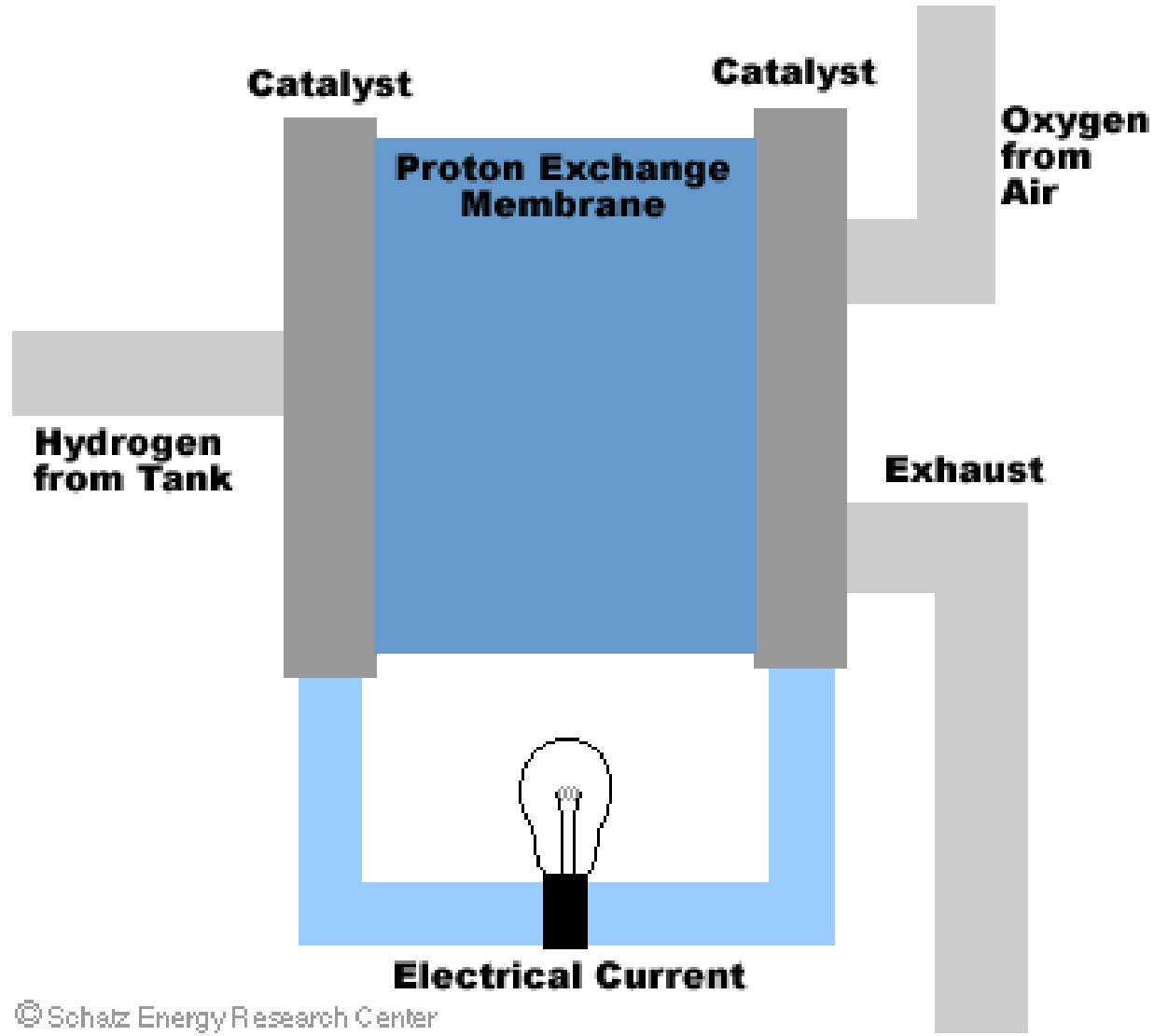
Only the protons can go through the membrane (thus, the name proton exchange membrane fuel cell).



# Cell reaction PEMFC

## Reactions:





© Schatz Energy Research Center

## **Proton Exchange Membrane Fuel Cell Technology and issues**

Expected life of PEMFC is very short (5,000 hours)

The most commonly used catalyst (Pt) is very expensive.

The most commonly used membrane (Nafion – a sulfonated tetrafluorethylene copolymer is also very expensive).

**CO poisoning diminishes the efficiency.** Carbon monoxide (CO) tends to bind to Pt. Thus, if CO is mixed with hydrogen, then the CO will take out catalyst space for the hydrogen.

Hydrogen generation and storage is a significant problem.

## 2. Solid Oxide Fuel Cells (SOFCs)

One of the main advantages is the variety of fuels and catalyst than can be used.

### Reactions:

- Anode  $\text{H}_2 + \text{O}^{2-} \longrightarrow \text{H}_2\text{O} + 2\text{e}^-$
- Cathode  $\frac{1}{2}\text{O}_2 + 2\text{e}^- \longrightarrow \text{O}^{2-}$

**Anode:** Porous metallic nickel (Ni)

**Cathode:** Strontium-doped lanthanum manganite  $(\text{La}_{0.84}\text{Sr}_{0.16})\text{MnO}_3$ , semiconductor

# Solid Oxide Fuel Cells : Design and Operation

It consists of three components - /cathode /anode /electrolyte is sandwiched between the two.

Oxygen from the air flows through the cathode

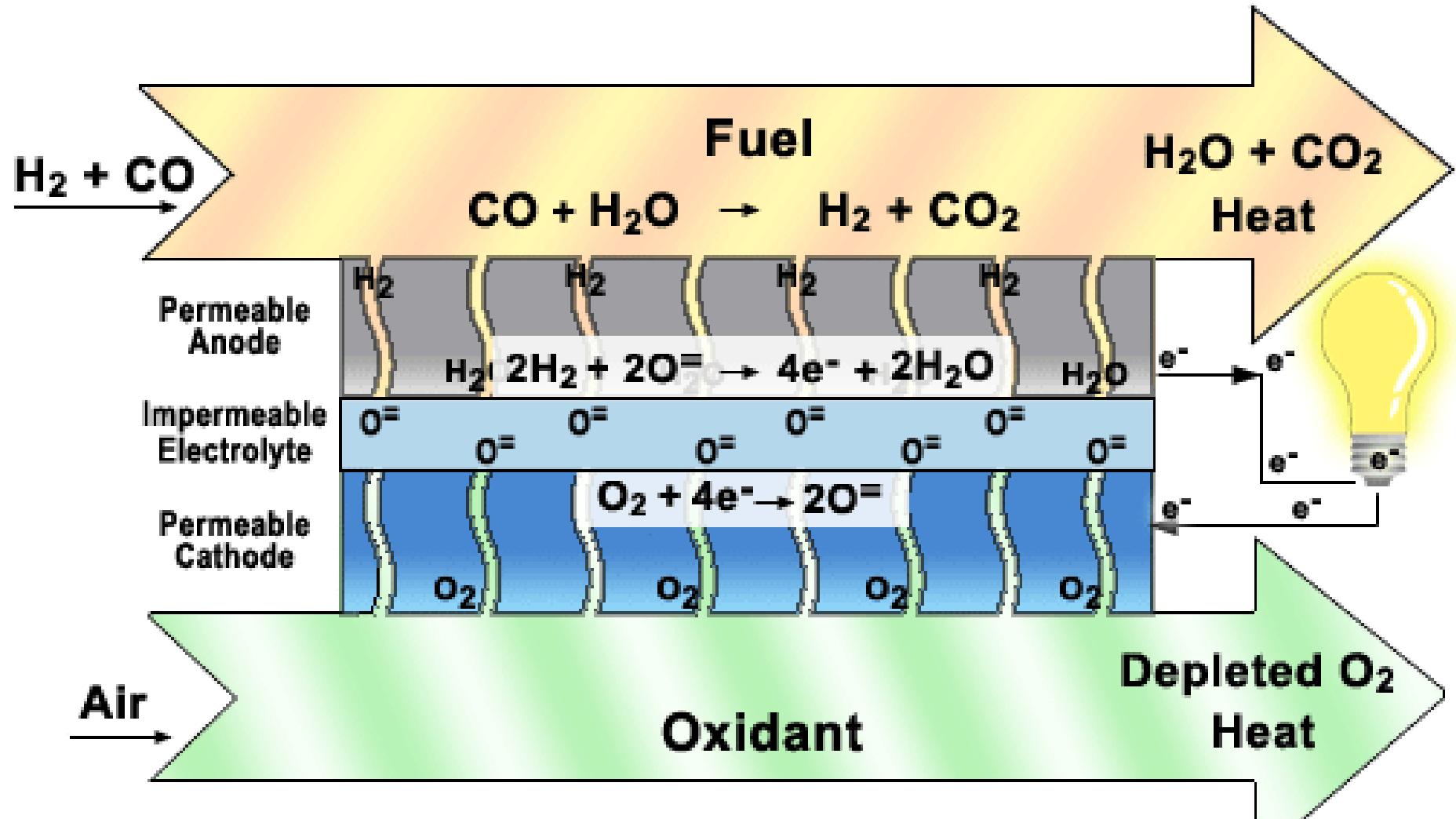
A fuel gas containing **hydrogen**, such as **methane**, flows past the anode.

Negatively charged oxygen ions migrate through the electrolyte membrane react with the hydrogen to form water

Similarly, oxygen ions reacts with the methane to form hydrogen ( $H_2$ ) & carbon dioxide ( $CO_2$ ).

- The electrochemical reaction generates electrons, which flow from the anode to an external load and back to the cathode
- a final step that both completes the circuit and supplies electric power
- To increase voltage output, several fuel cells are stacked together to form the heart of a clean power generator.

# Solid Oxide Fuel Cell



A functioning cell in a Solid Oxide Fuel Cell stack

# Solid Oxide Fuel Cells: Technology and issues

They operate at high temperature

They are not sensitive to CO poisoning

They have a relatively low cost

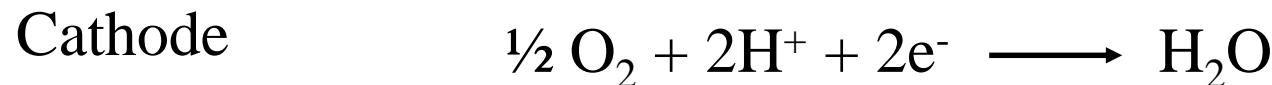
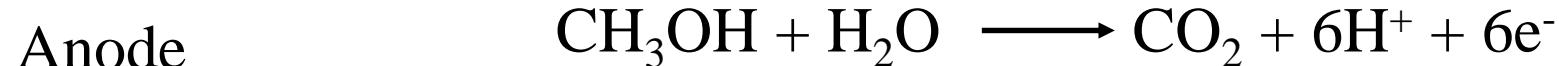
They have a relatively high efficiency

They have a fast startup

### 3. Direct Methanol Fuel Cells (DMFC)

The main advantage is that they use a liquid fuel.

#### Reactions:



Voltages: 0.046 V at anode, 1.23 V at cathode, 1.18 V overall.

Methanol has high energy density so DMFC are good for small portable applications

#### Issues:

Cost

Excessive fuel crossover (methanol crossing the membrane)

Low efficiency caused by methanol crossover

CO poisoning

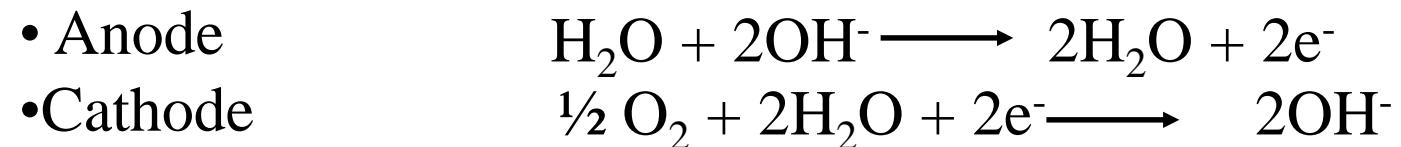
Low temperature production

Considerable slow dynamic response

## 4. Alkaline Fuel Cells (AFCs)

- The main advantage is that their cost is relatively low (when considering the fuel cell stack only without “accessories”).

- Reactions:



- Developed for the Apollo program.
- **Very sensitive to CO<sub>2</sub> poisoning.** So these FCs can use impure hydrogen but they require purifying air to utilize the oxygen.

### Disadvantages:

/ Cost / Short life (8000 hours) / Relatively low heat production

## **5. Phosphoric Acid Fuel Cells (PAFC)**

The PAFC uses liquid phosphoric acid as the electrolyte

Platinum catalyzed, porous carbon electrodes are used on both the fuel (anode) and oxidant (cathode) sides of the electrolyte

The phosphoric acid is contained in a Teflon bonded silicone carbide matrix

# Electrochemical reactions in PAFC



## Anode reaction:

Hydrogen is split into two hydrogen ions ( $\text{H}^+$ ), and pass through the electrolyte to the cathode. Two electrons are generate during the reaction and pass through the external circuit to the cathode.

## Cathode reaction:

Hydrogen, electrons and oxygen combine to form water

## PAFCs Technology and issues

Long life in the order of 40,000 hours.

Phosphoric acid serves as the electrolyte.

Reversible voltage is 1.23 V

Catalyst support CO poisoning better than PEMFC

Relative high cost is an important issue

## 6. Molten Carbonate Fuel Cells (MCFC)

A molten carbonate salt mixture is used as its electrolyte.

Molten carbonate salt mixture is mainly used as electrolyte (lithium carbonate and potassium carbonate)

At the operating temperature of about  $650^{\circ}\text{C}$  ( $1200^{\circ}\text{F}$ ), the salt mixture is liquid and a good ionic conductor.

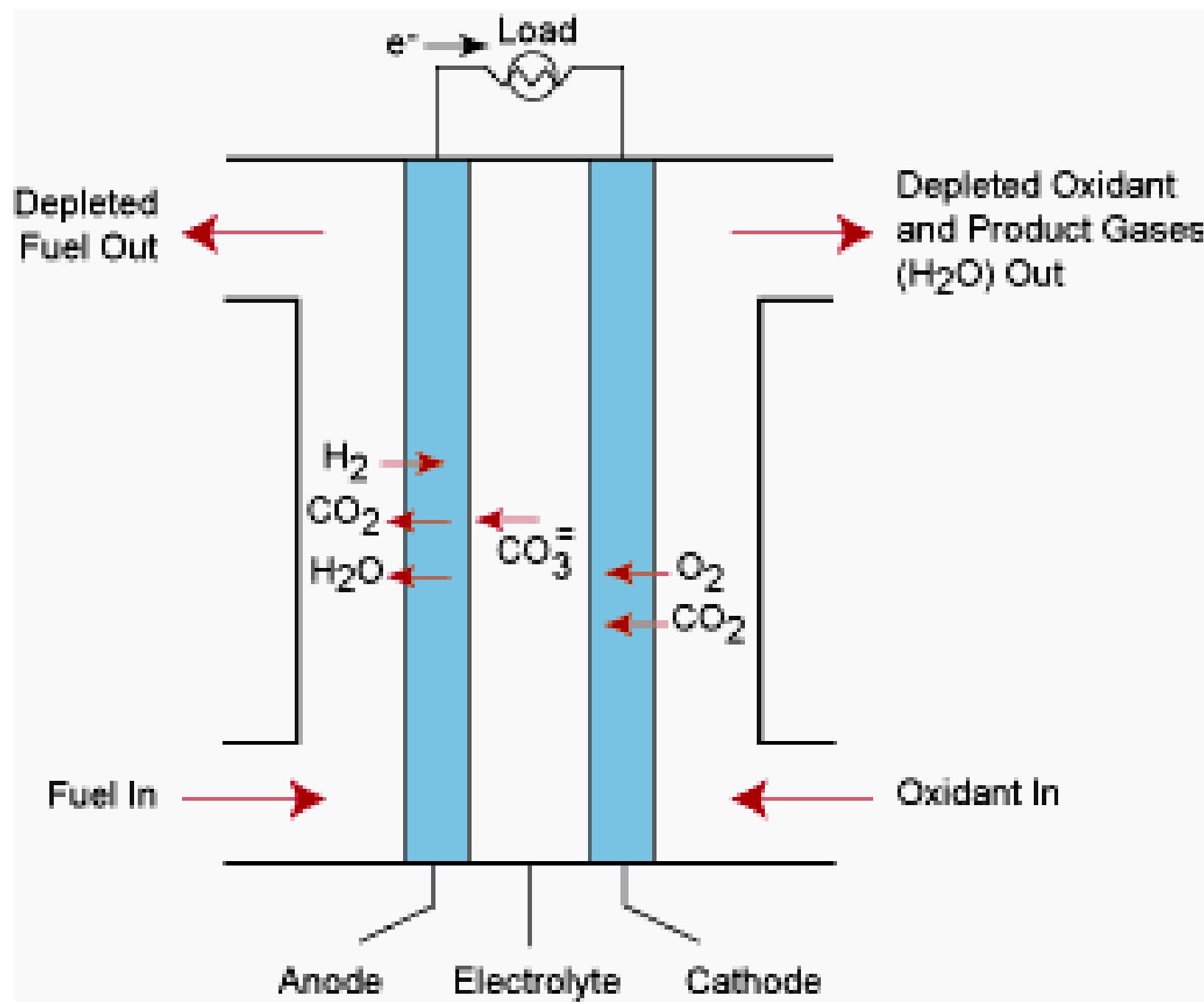


The **anode process** involves a reaction between hydrogen and carbonate ions ( $\text{CO}_3^{=}$ ) from the electrolyte.

The reaction produces water and carbon dioxide ( $\text{CO}_2$ ) while releasing electrons to the anode.

The **cathode process** combines oxygen and  $\text{CO}_2$  from the oxidant stream with electrons from the cathode to produce carbonate ions which enter the electrolyte.

The need for  $\text{CO}_2$  in the oxidant stream requires a system for collecting  $\text{CO}_2$  from the anode exhaust and mixing it with the cathode feed stream.



## MCFC Technology and issues

They operate at high temperature. On the plus side, this high temperature implies a high quality heat production. On the minus side, the high temperature creates reliability issues.

They are not sensitive to CO poisoning.

Issues:

Extremely slow startup

They have a relatively low cost.

Very slow dynamic response

# Fuel cell technologies

## Comparison of the most common technologies

	PEMFC	DMFC	AFC	PAFC	MCFC	SOFC
Fuel	H <sub>2</sub>	CH <sub>3</sub> OH	H <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> , CO, CH <sub>4</sub> , hydrocarbon	H <sub>2</sub> , CO, CH <sub>4</sub> , hydrocarbon
Electrolyte	Solid polymer (usually <i>Nafion</i> )	Solid polymer (usually <i>Nafion</i> )	Potassium hydroxide (KOH)	Phosphoric acid (H <sub>3</sub> PO <sub>4</sub> solution)	Lithium and potassium carbonate	Solid oxide (yttria, zirconia)
Charge carried in electrolyte	H <sup>+</sup>	H <sup>+</sup>	OH <sup>-</sup>	H <sup>+</sup>		O <sup>2-</sup>
Operational temperature (°C)	50 – 100	50 - 90	60 - 120	175 – 200	650	1000
Efficiency (%)	35 – 60	< 50	35 – 55	35 – 45	45 – 55	50 – 60
Unit Size (KW)	0.1 – 500	<< 1	< 5	5 – 2000	800 – 2000	> 2.5
Installed Cost (\$/kW)	4000	> 5000	< 1000	3000 – 3500	800 – 2000	1300 - 2000