UNIT - I
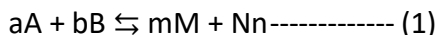# THERMODYNAMICS - III

1. Van't Hoff reaction isotherm:

Van't Hoff isotherm relates equilibrium constant and free energy of a reaction

$\Delta G° = -2.303 RT \log K_p$

Let us consider a reversible reaction

$aA + bB \leftrightharpoons mM + Nn$------------- (1)

where a, b, m and n are the stoichiometric coefficients of A, B,
M and N respectively.

Free energy of the reactants,

$G_{reactants} = a\mu_A + b\mu_B$ ------------(2)

μ_A **and** μ_B **= Chemical potential of species A and B**

Similarly free energy of products,

$G_{products} = m\mu_M + n\mu_N$ ---------------------(3)

$\Delta G_{reaction} = G_{products} - G_{reactants}$

$\Delta G_{reaction} = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B)$ ------ (4)

$\Delta G_{reaction} = 0$

Therefore, $(m\mu_M + n\mu_N) - (a\mu_A + b\mu_B) = 0$-------(5)

We know that,

$\mu_i = \mu_i° + RT \ln P_i$ -----------(6)

Where P_i **= partial pressure of** i^{th} **component**

$\mu_i°$ **= standard chemical potential**

Therefore, equation (5) becomes

$[m(\mu_M° + RT \ln P_M) + n(\mu_N° + RT \ln P_N)]-$
   $[a(\mu_A° + RT \ln P_A) + b(\mu_B° + RT \ln P_B)] = 0$

$RT \left[\ln \dfrac{P_M^m . P_N^n}{P_A^a . P_B^b} \right] = -[(m \mu_M° + n \mu_N°) - (a \mu_A° + \mu_B°)]$

$RT \left[\ln \dfrac{P_M^m . P_N^n}{P_A^a . P_B^b} \right] = -[G°_{products} - G°_{reactants}]$

$RT \ln K_p = -\Delta G°$

Where $K_p = \left[\ln \dfrac{P_M^m . P_N^n}{P_A^a . P_B^b} \right]$

ie $\Delta G° = -RT \ln K_p$--------- (7)

$\Delta G° = -2.303 \log K_p$ --------(8) **Equation (8) is Van't Hoff isotherm**

Significance of Van't Hoff's isotherm:

  i.   van't Hoff's isotherm relates equilibrium constant and free energy change of a reaction.

ii.   The magnitude of Kp depends on the value of ΔG°. More the –ve value of ΔG°, more will be +ve value of Kp.

iii. Using the reaction isotherm, we can work out the condition for maximum yield.

iv.   Since ΔG is related to ΔS and ΔH as ΔG = ΔH – TΔS. The value of ΔS (increase in entropy) makes Kp positive.

2. Van't Hoff isochore equation:
(Effect of temperature on chemical equilibria)

We know that
$\Delta G° = - RT \ln Kp$ ––––––––––––––––(1)
where Kp is the equilibrium constant at constant pressure.

Differentiating equation (1) w.r.t. temperature treating pressure as constant then

$$\left[\partial \frac{(\Delta G°)}{\partial T}\right]_P = -R\ln K_p - RT\left[\frac{\partial(\ln K_P)}{\partial T}\right]_p \text{ -------------- (2)}$$

Multiply by T,

$$T\left[\partial \frac{(\Delta G°)}{\partial T}\right]_P = -RT\ln K_p - RT^2\left[\frac{\partial(\ln K_P)}{\partial T}\right]_p \text{ --------(3)}$$

Therefore, $\Delta G° = - RT \ln Kp$; $\left[\partial \frac{(\Delta G°)}{\partial T}\right]_P = -\Delta S°$

Substitute in equation (3)

$-T\Delta S° = \Delta G° - RT^2\left[\frac{\partial(\ln K_P)}{\partial T}\right]_p$ **(or)** $\Delta G° + T\Delta S° = RT^2\left[\frac{\partial(\ln K_P)}{\partial T}\right]_p$

(or) $\Delta H° = RT^2\left[\frac{\partial(\ln K_P)}{\partial T}\right]_p$ $\Delta G° = \Delta H° - T\Delta S°$

At constant P, $\Delta H° = RT^2\left[\frac{d(\ln K_P)}{dT}\right]$

(or) $\left[\frac{d(\ln K_P)}{dT}\right] = \frac{\Delta H°}{RT^2}$ ----------- (4)

Since ΔH does not vary with P, **ΔH° = ΔH**
$$\left[\frac{d(\ln K_P)}{dT}\right] = \frac{\Delta H}{RT^2} \text{----------- (5)}$$
Integrated form of eqn (5)

$d(\ln K_P) = \frac{\Delta H}{R}\frac{dT}{T^2}$

On integrating both sides,

$$\int_{K_{P_1}}^{K_{P_2}} d(\ln K_P) = \frac{\Delta H}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\ln \frac{(K_P)_2}{(K_P)_1} = \frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ ; } \ln \frac{(K_P)_2}{(K_P)_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{(K_P)_2}{(K_P)_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \text{--------(6)}$$

It is Van't Hoff's Isochore.

3. **Signficance of Clausius Clapeyron equation**
Calculation of molar heat of vapourisation (Hv)

The molar heat of vapourisation, Hv of a liquid can be calculated if its vapour pressures at two different temperatures are known.

Effect of temperature on vapour pressure of a liquid:

If vapour pressure of a liquid at one temperature is known, then the vapour pressure at another temperature can be calculated.

Effect of pressure on boiling point:

If the boiling point of a liquid at one pressure is known, then the boiling point at another pressure can be calculated.

It is used to determine the molar elevation constant (Kb), molar depression constant (Kf).

Clausius – Clapeyron equation is used in phase rule to study water and sulphur system.

4. **Nernst Heat theorem:**

According to Nernst heat theorem the value of $\left[\partial \frac{(\Delta G)}{\partial T}\right]$ approaches zero gradually as the temperature is lowered towards the absolute zero.

Mathematically, $\lim_{T \to 0}\left[\partial \frac{(\Delta G)}{\partial T}\right] = \lim_{T \to 0}\left[\partial \frac{(\Delta H)}{\partial T}\right] = 0$ -----(1)

Therefore, $\left[\partial \frac{(\Delta G)}{\partial T}\right]_P = -\Delta S$; $\left[\partial \frac{(\Delta H)}{\partial T}\right] = \Delta C_P$

Substitute in (1)

$\lim_{T \to 0} \Delta S = 0 \ and \ \lim_{T \to 0} \Delta C_P = 0$

At the vicinity of absolute zero, all process should occur without any change in entropy and heat capacity.

Application:
i. It is used to determine the transition temperature (Tf) of sulphur.

$\Delta H° = \Delta H - \frac{\beta}{2}T_f^2$; $\beta = \frac{\Delta C_P}{T}$

ii. $\Delta G = -nFE$ to determine the emf of cells $\Delta G = \Delta H° - T(\Delta C_P \ln T)$

Limitation:
It is applicable only for pure solids but not for gases.

5. **Statements of third law of thermodynamics:**
Planck statement:
The entropy of a solid or liquid becomes zero at absolute zero.

T→0, S=0

Lewis and Randell statement:

Every substance has a finite positive entropy. At absolute zero, the entropy may become zero and it does become zero for perfectly crystalline solids.

Statement III:

At 0 K, the entropy of a perfectly crystalline solid is equal to zero.

6. Exception to the third law:

CO:

In CO molecules the value of Sspec (spectroscopic entropy ie the value obtained on the basis of spectroscopic data by means of statistical formula) is greater than Scal or thermal entropy (calculated using III law) by 4.5J. This can be explained on the basis of frozen in randomness of orientation in crystal.

When CO crystal grows in the presence of a liquid, the molecule is condensed with two equally probable orientations CO and OC.

CO OC CO OC
OC CO CO CO
CO OC CO OC
Hence the crystal does not have definite structure.
S = 5.76 JK-1 mol-1

NO (Nitric oxide)
It exists as a dimer N_2O_2. Two orientations are possible
N O O N
O N N O
Since there are N/2 dimer molecule per mole of Nitric oxide.
S = klnW
=2.88 J K^{-1}mo l^{-1}

Ortho and para hydrogen:

In hydrogen molecule, the difference between Scal and Sspec is 11.5J. This is due to the fact that ordinary hydrogen at lower temperature is a mixture of two forms ortho and para hydrogen in the proportion 3:1. These two differ in their nuclear spin. Therefore, the entropy of molecular hydrogen is larger than Scal values.

Ice:
In ice (H_2O), the entropy (Sspec) is higher than Scal by 3.375 Joules. The is due to
   i.   rotational motion of molecule in the solid state.
   ii. uncertainity of position of hydrogen bonding in the crystal.

7. Gibbs Duhem equation
Gibbs Duhem equation relates change in chemical potential with composition.
$\sum n_i d\mu_i = 0$
Derivation
For binary system at constant T and P
$(dG)_{T, P} = \mu_1 dn_1 + \mu_2 dn_2$ --------- (1)
$(G)_{T, P} = \mu_1 n_1 + \mu_2 n_2$ ------------------- (2)
Differentiate eqn (2), $(dG)_{T, P} = (\mu_1 dn_1 + n_1 d\mu_1) + (\mu_2 dn_2 + n_2 d\mu_2)$
$(dG)_{T, P} = (\mu_1 dn_1 + \mu_2 dn_2) + (n_1 d\mu_1 + n_2 d\mu_2)$ ---------(3)
Comparing equations (1) and (3),
$n_1 d\mu_1 + n_2 d\mu_2 = 0$ ------ (4)
In general, $\sum n_i d\mu_i = 0$ ------- (5)
Equation (5) is Gibbs- Duhem equation.

Application:

1. For system having only two components,

   $n_1 d\mu_1 + n_2 d\mu_2 = 0$

   $n_1 d\mu_1 = - n_2 d\mu_2$

   $d\mu_1 = - (n_1 / n_2) d\mu_2$

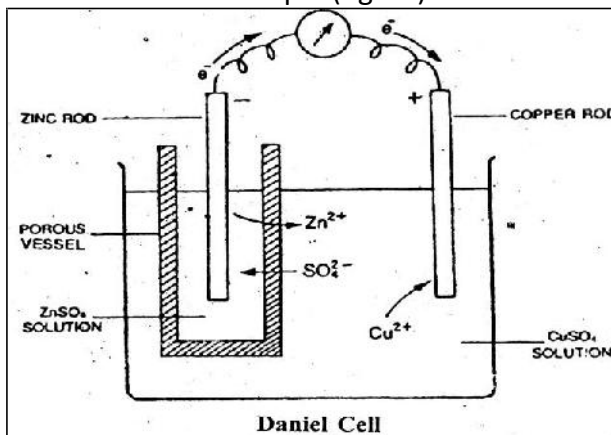2. Gibbs Duhem equation is used in heterogeneous equilibrium. Eg. Liquid-vapour system.

UNIT - II
ELECTROCHEMISTRY

1. EMF and Electrode potential:

The electrode potential, the electrode reaction, the cell reaction and EMF of the cell can be explained by taking Daniel cell as an example (figure)
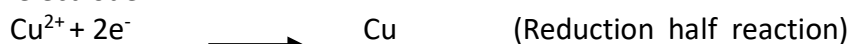

Daniel Cell

It consists of a Zn – electrode dipped in $ZnSO_4$ solution and a Cu-electrode dipped in $CuSO_4$ solution. Both these solutions are separated by porous vessel.

When both the electrodes are connected by a wire externally, chemical reaction occurs. Oxidation reaction takes place at the Zn-electrode (i.e) Zn-rod dissolves in the solution producing Zn^{2+} ions.

$Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)

Thus Zn-electrode is called –ve electrode and sends electrons with the outer circuit.

Reduction reaction occurs at the Cu-electrode (i.e) Cu^{2+} ion from the solution undergoes reduction by taking two electrons to form Cu-metal and deposited on the Cu-electrode.
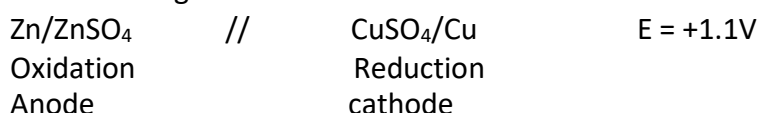
$Cu^{2+} + 2e^- \longrightarrow Cu$ (Reduction half reaction)

Cell reaction:

The net chemical reaction obtained by adding the two half reactions is called the cell reaction.

$Zn \rightarrow Zn^{2+} + 2e^-$

$Cu^{2+} + 2e^- \rightarrow Cu$

$Zn + Cu^{2+} \leftrightarrows Zn^{2+} + Cu$
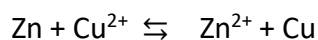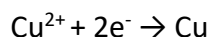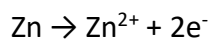
Cell representation:

The Daniel cell may be represented by writing the anode at left hand side and the cathode at right hand side.

Zn/ZnSO₄	//	CuSO₄/Cu	E = +1.1V
Oxidation		Reduction	
Anode		cathode	

2. Cell Potential (or) EMF

The electrons are flowing from Zn electrode to the Cu-electrode through the outer circuit. This causes the flow of current and it is determined by thepush of electrons at the anode and attraction of electrons at the cathode. These two forces produced the driving force. This driving force is called the Electromotive force (EMF) or the cell potential. It isexpressed in volts.

Standard cell:

A cell which has the following characters is known as standard cell.

i. Its potential (emf) must be reproducible.
ii. Its emf remains constant for a long period.
iii. The cell should be reversible
iv. It should not be damaged by the passage of current through it.
v. Its temperature coefficient must be very low.

Single electrode potential

Each cell is made up of two electrons. One electrode is called –ve electrode where oxidation takes place and other electrode is +ve electrode where reduction takes place.

Example: $Zn / Zn^{2+} // Cu^{2+} / Cu$

Halfcell   Half cell
(-ve electrode)   (+ve electrode)

Each electrode which is in contact with its own ion in solution is called half cell (or) single electrode.

The tendency of an electrode to lose or gain electrons (oxidation or reduction) when it is in contact with its own ions in solution is called single electrode potential or electrode potential.

The potential of an electrode which undergoes oxidation is called oxidation potential and the potential of an electrode which undergoes reduction is called reduction potential.

Standard electrode potential:

If the concentration of the ions is unity and temperature is 25ºC, the single electrode potential obtained is called standard electrode potential (E^0) and such electrode is called standard electrode.

Example:
Standard Hydrogen Electrode

(SHE) is, $H_2(g)$ (Pt) / H^+(C = 1)
The E^0 for SHE is zero volt at 25ºC
(i.e) E^0_{SHE} = 0 volt.

3. Reference Electrodes:
Hydrogen electrode:

It is a primary standard electrode or a primary reference electrode. It consists of a Pt – wire coated with Pt-black to absorb hydrogen gas. It is surrounded by an outer glass tube containing an inlet for hydrogen gas at the top. This set up is placed in a dilute solution of an acid.

Hydrogen electrode:
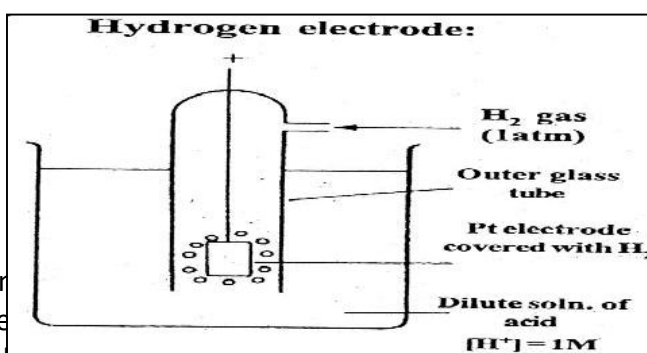
When pure hydrogen ... heric pressure, a part of it is covered (absorbe ... hed between the absorbed hydrogen gas on the surface of the electrode and the H ion of the acid solution. The electrode reaction is
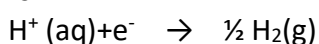
H^+ (aq)+e^- → ½ $H_2(g)$
The electrode is reversible w.r.to hydrogen ion.

The electrode is represented as

Pt, $H_{2(g)}$, / H^+
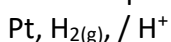
At 25ºC, when the pressure of H_2 gas is 1 atmosphere, the concentration of H^+ ion is 1 g.mole / lit, now it is known as Standard Hydrogen Electrode (SHE). The potential of SHE is fixed as zero volt at 25ºC.

Advantages:
i.   It can be used as a wide range of pH.
ii. It exhibits no salt error
iii. It is the fundamental electrode. Its potential is zero volt at 25ºC.

Disadvantages:
i.   Presence of impurities in H_2 gas may poison the electrode.
ii. To maintain the H_2 gas pressure at 1 atmosphere is difficult.
iii. It cannot be used for solution containing strong oxidizing agent.

Calomel electrode:

Calomel electrode is a secondary standard or a secondary reference electrode. It consists of a narrow central glass tube in which mercury and solid calomel (Hg_2Cl_2) are held by a porous plug. For electrical contact, a platinum wire dips into the mercury. The potassium chloride solution (0.1N or 1.0N or saturated) contained in the electrode makes contact with other electrode through a sintered glass disc. The disc function as a salt bridge (between the two electrode solutions).

This electrode is represented as
Hg, $Hg_2Cl_{2(s)}$ (solution), KCl
The electrode reaction is

$$Hg_2Cl_{2(s)} + 2e^- \leftrightarrows 2\,Hg\,(l) + 2Cl^-\,(aq)$$
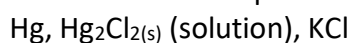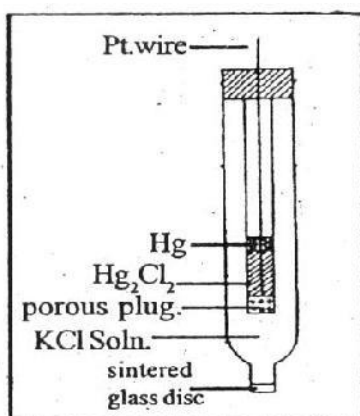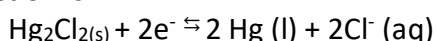
Calomel electrode is reversible with respect to the Cl^-

Name of the calomel electrode	[KCl]	EMF (in volt)
Decinormal calomel electrode (DNCE)	0.14N	0.333

Normal Calomel Electrode (NCE)	1N	0.281
Saturated Calomel Electrode (SCE)	saturated	0.242

4. Electrochemical series

With reference to the standard hydrogen electrode, the electrodes are arranged in the decreasing order of their standard reduction potentials at 25°C. This is called electro chemical series.
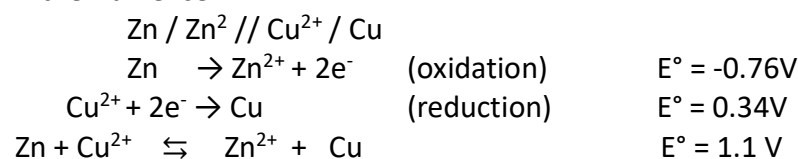
Electrode	E^0 volts
Au^{3+}, Au	+ 1.50
Hg^{2+}, Hg_2^{2+}, (Pt)	+ 0.92
Ag^+, Ag	+ 0.80
$Fe^{3+,}$ Fe^{2+}, (Pt)	+ 0.77
Cu^{2+}, Cu	+ 0.34
$2H^+$, H_2, (Pt)	0.00
Pb^{2+}, Pb	- 0.13
Sn^{2+}, Sn	- 0.15
Fe^{2+}, Fe	- 0.44
Zn^{2+}, Zn	- 0.70
Na^+, Na	- 2.71

Applications or Significance:

1. A high positive value of E^0 indicates that the electrode undergoes reduction (by accepting electrons). A high negative value of E^0 indicates that the electrode undergoes oxidation (by donating electrons).

The emf of the cell reaction can be easily determined with the help of E^0 values.
Example: In the Daniel cell

$$Zn / Zn^2 // Cu^{2+} / Cu$$

$$Zn \rightarrow Zn^{2+} + 2e^- \quad \text{(oxidation)} \quad E° = -0.76V$$
$$Cu^{2+} + 2e^- \rightarrow Cu \quad \text{(reduction)} \quad E° = 0.34V$$
$$Zn + Cu^{2+} \leftrightarrows Zn^{2+} + Cu \quad E° = 1.1 V$$

E_{cell} = Redn.potential of RHS – Redn. potential of LHS
E_{cell} = E^0_R–E^0_L = 0.34 – (-0.76)   = + 1.10V

2. The feasibility of the cell reaction can also be predicted with the help of E^0values. From E^0 values, emf of the cell is calculated.

E_{cell} = $E°_R$ - $E°_L$
If, E_{cell} is –ve, the reaction will be
feasible. If, E_{cell} is –ve, the reaction will
not be feasible
Example: Predict the following reaction is feasible (or)
not. $\longrightarrow$
$2Ag+ Zn^{2+}$ $2Ag^+ + Zn$
The half cell reactions are
Anode $2Ag \rightarrow 2Ag^+ + 2e^-$; E^0 = 0. 80V
(oxidation)
Cathode $Zn^{2+} + 2e^- \longrightarrow Zn$;   E° = -
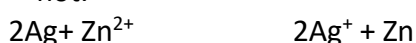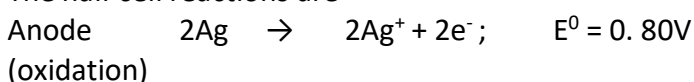
0.76V
(Reduction)

The Cell reaction is,

$$2Ag + Zn^{2+} \leftrightarrows 2Ag^+ + Zn$$

E_{cell} = $E^0_R - E^0_L$ = -0.76 - 0.80 = -1.56V

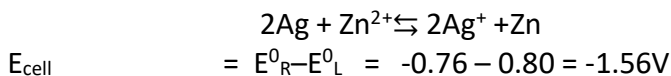Since, the value of E_{cell} is –ve. Thus, the reaction is not feasible.

3. The metal will displace another metal from its salt solution or else it can be predicted by electrochemical series. Generally, a metal lower down the electrochemical series can precipitate the one higher up the series.

4. The metal will displace hydrogen from a dilute acid or else it can be predicted by electro chemical series. (i.e.) Any metal above the hydrogen in the series is a weaker reducing agent and cannot reduce H^+ and H_2 gas. Any metal lying below the hydrogen in the series is a stronger reducing agent and can reduce H^+ to H_2 gas.

Example: Zn can liberate H_2 gas from dil.H_2SO_4 but Cu cannot. The reason is Zn is lying below and Cu is lying above the hydrogen in the electro chemical series.

$Zn + 2H^+$ ⟶ Zn^{2+} +
$H_2\uparrow$ (dil.H_2SO_4)
$Cu + 2H^+$ ⟶̷ Cu^{2+} +
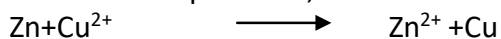$H_2\uparrow$ (dil.H_2SO_4)
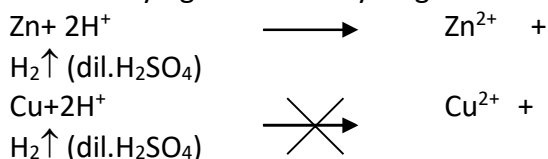
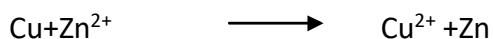## 5. CELLS
REVERSIBLE CELL:

A cell which has the following conditions is known as reversible cell. The external emf equal to that of the cell emf is applied in opposite direction, no reaction should occur on either of the electrodes. The external emf is infinitesimally increased, the current will start to flow into the cell and the cell reaction gets reversed.

Eg: Daniel cell
The normal equation is,
$Zn + Cu^{2+}$ ⟶ Zn^{2+} + Cu
If an external emf is increased infinitesimally, the cell reaction is reversed
$Cu + Zn^{2+}$ ⟶ Cu^{2+} + Zn
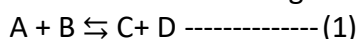Thus, the Daniel cell is a reversible cell.

IRREVERSIBLE CELL

A cell which does not satisfy the condition of reversibility is known as irreversible cell (i.e.) its chemical reaction cannot be reversed by the application of external emf.

6. Nernst Equation for emf of cells:
Consider the following cell reaction
A + B $\leftrightarrows$ C + D --------------(1)
Applying law of mass action,

$$K = \frac{[C][D]}{[A][B]}$$

We know that , $\Delta G = -nFE$ and $\Delta G° = -nFE°$

$E \rightarrow$ EMF of the cell; $E°$ = Standard emf of the cell at 25°C.

According to Van't Hoff reaction isotherm,

$\Delta G = \Delta G° + RT\ln K$ ------(2)

Substitute the value of ΔG and $\Delta G°$ in eqn (2)

$-nFE = -nFE° + RT\ln K$

$-nFE = -nFE° + RT\ln\frac{[C][D]}{[A][B]}$

$nFE = nFE° - RT\ln\frac{[C][D]}{[A][B]}$

$E = E° - \frac{RT}{nF}\ln\frac{[C][D]}{[A][B]}$

$E = E° - \frac{2.303RT}{nF}\log\frac{[C][D]}{[A][B]}$ ---------(3)

This is the Nernst equation for emf of cells.

At 25°C the value of $\frac{2.303RT}{nF}$ = 0.0591

Therefore, the equation becomes,

$E = E° - \frac{0.0591}{F}\log\frac{[C][D]}{[A][B]}$ **at 25°C**

Significance:

Nernst equation is used to calculate the cell emf, single electrode potential and the equilibrium constant for the cell reaction.

Example

To calculate the cell emf, $\qquad$ $Zn / Zn^{2+} // Cu^{2+} / Cu$

The cell reaction is, $\qquad$ $Zn + Cu^{2+} \leftrightarrows Zn^{2+} + Cu$

The emf of the cell at 25°C is given by the Nernst equation.

$E = E° - \frac{0.0591}{F}\log\frac{[Zn^{2+}][Cu]}{[Zn][Cu^{2+}]}$

Since the concentration of metal is unity, the equation becomes,

$E = E° - \frac{0.0591}{F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$ **at 25°C**

7. Potentiometric titrations

Titrations in which the end point is determined by measurement of electrode potential are known as potentiometric titrations. Three types of potentiometric titration are possible.

    a. Acid-base titrations
    b. Oxidation-reduction (Redox) titrations
    c. Precipitation titrations

a. Acid-base titrations

The acid-base titration involves changes in the concentration of H^+ ions or changes in the pH of the solution.

Hydrogen electrode (or) glass electrode is immersed in the known volume of the acid solution whose strength is to be determined. The indicator electrode is connected to a standard calomel electrode (reference) to form a galvanic cell.

It may be represented as

Pt, H_2 (1 atm), H^+ (unkonwn) || KCl (sat soln), Hg_2Cl_2 (s),
Hg Hydrogen electrode || SCE

The EMF of the cell is measured potentiometrically. It is given
by $E = E_R - E_L = E_{calomel} - E_{hydrogen}$
$= 0.2422 + 0.0591$ pH

Example: HCl × NaOH

When NaOH is added, the H^+ ion concentration goes on decreasing ie pH of the solution goes on increasing. Hence the emf of the cell (E) rises gradually. Near the end point the emf rises sharply. After the end point, the emf changes slightly on the addition of excess of alkali.

The emf of the cell (E) is plotted against the volume of alkali added. The type of curve obtained for the titration of strong acid against strong base (HCl vs NaOH) is shown in the Figure. The steepest portion of the curve indicates the end point. For every dilute solutions, or weak acids or weak bases, the end point detection is very difficult. In such cases,

$\Delta E/\Delta V$ is plotted against volume of the alkali added (Figure). The maximum of the curve indicates the end point.
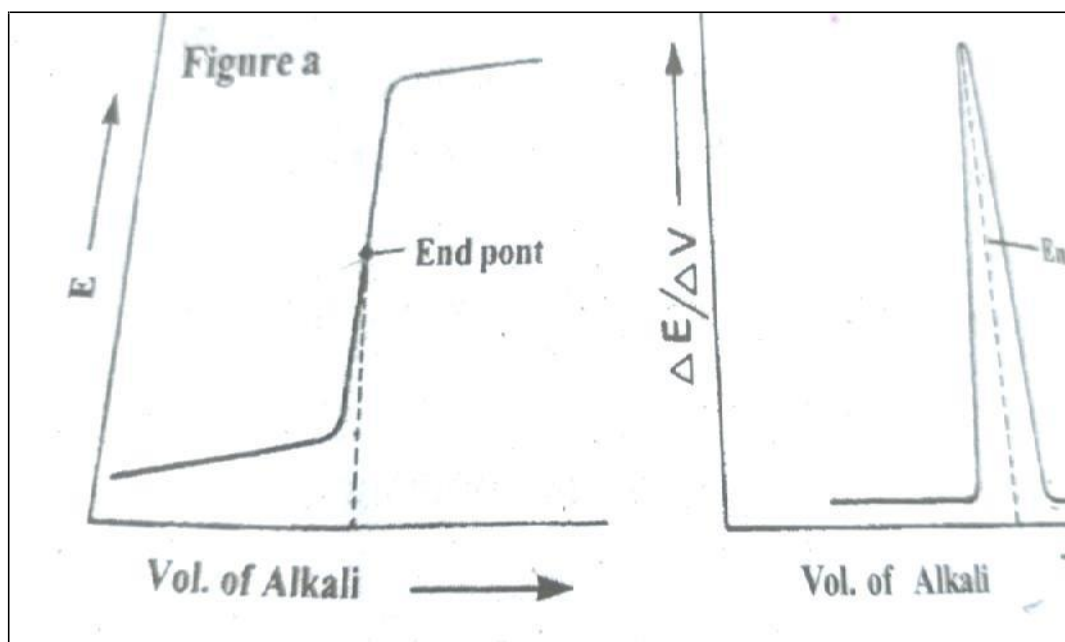
b. Redox Titrations

Consider the titration of $FeSO_4$ against $KMnO_4$. The platinum electrode is coupled with the calomel electrode and immersed in the known volume of $FeSO_4$ solution. The complete cell thus formed is

Pt/Fe^{2+} , Fe^{3+} // Calomel electrode

When $KMnO_4$ is added from the burette, the emf rises. Near the end point the emf rises sharply. The end point of this titration is determined by plotting $\Delta E/\Delta V$ against volume of $KMnO_4$ added.

Volume of KMnO4 added   →
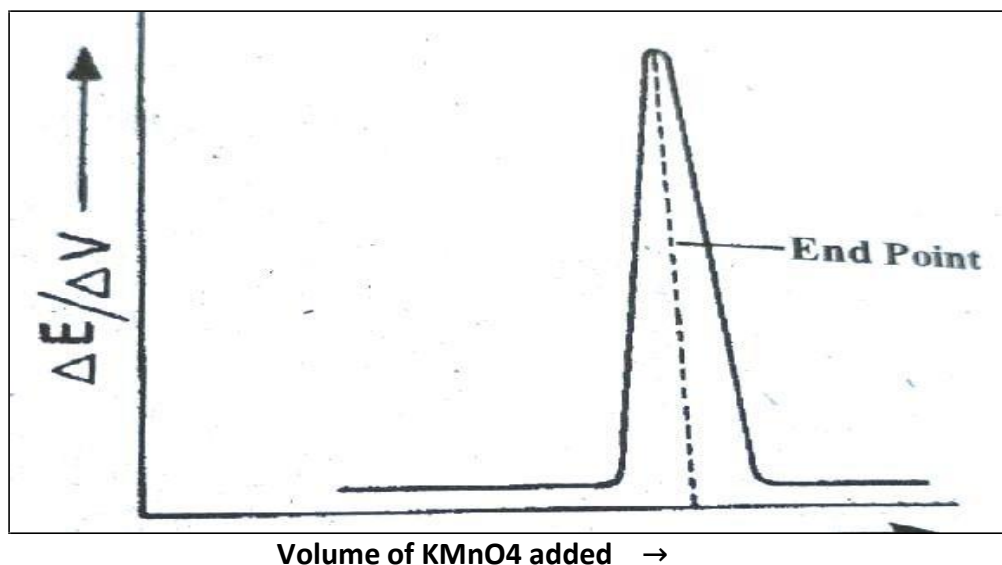
c. Precipitation titration

Consider the titration of $AgNO_3$ with NaCl solution. A silver electrode (indicator electrode) is dipped in the unknown sodium chloride. It is conn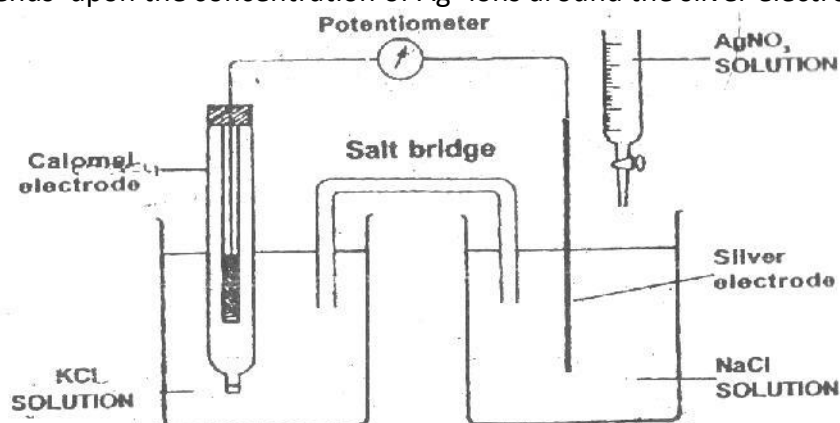ected to a calomel electrode (reference electrode) through a salt bridge as shown in the figure. The emf (E) of the cell depends upon the concentration of Ag^+ ions around the silver electrode.

Initially the concentration of Ag^+ ions will be zero. When the $AgNO_3$ solution is added from the burette, AgCl is precipitated. Now a reversible silver – silver chloride electrode is setup. As a result, the solution contains a small concentration of Ag^+ ions and the emf (E) will rise gradually. The end point of this titration is determined by plotting $\Delta E / \Delta V$ against volume of the $AgNO_3$ added.
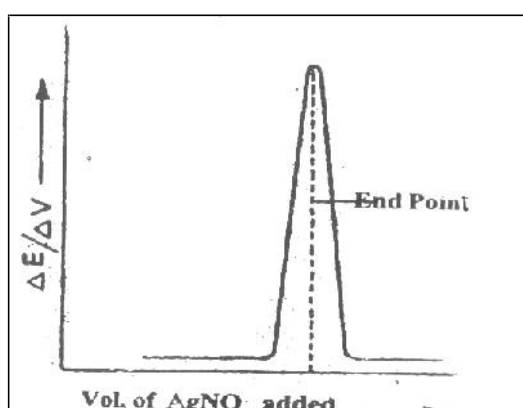
Advantages of potentiometric titrations:

i.   Used to find out the end point of coloured solutions where no indicator is effective.
ii. In oxidation – reduction titrations, the use of external indicator is eliminated.
iii. Used in acid – base titrations where no suitable indicator is found to work

Example: weak acid Vs weak base.

UNIT – III
SURFACE CHEMISTRY

1. Distinction between physisorption and chemisorptions

Sr	Physisorption	Chemisorption
1	Reversible physical process	Irreversible chemical process
2	The gas molecules are held on solid surface by weak Vander Waal's forces	The gas molecules are held on solid surface by strong chemical bonds
3	It occurs appreciably at low temperatures.	It can occur at all temperatures
4	Rate of adsorption increases with increase in pressure	Rate of adsorption is independent of pressure
5	Rate of adsorption decreases with increase in temperature	Rate of adsorption increases with increase in temperature.
6	Involves low heat of adsorption	Involves very high heat of adsorption
7	Adsorption is multilayer	Adsorption is only monolayer
8	Physisorption is non-specific	Chemisorption is highly specific
9	It involves no compound formation	It involves compound formation
10	Physical adsorption is instantaneous	Chemisorption is very slow

2. Langmuir adsorption isotherm

Definition

Langmuir deduced the following equation for type I isotherms. This is known as Langumuir adsorption isotherm.

$$\frac{x}{m} = \frac{aP}{1+bP}$$

Derivation:

Langmuir derived the above equation based on the following assumptions:

i) An adsorbent site can adsorb only one molecular species of adsorbate.
ii) Adsorption of other molecules of adsorbate at this site does not take place.
iii) Thus, the adsorbed gas is unimolecular in thickness.
iv) There is no interaction between the adsorbate molecules.
v) The heat of adsorption is same for all the adsorbent sites.
vi) A dynamic equilibrium exists between the processes of adsorption and desorption.

Consider a surface area = $1.0 \, cm^2$
Surface area covered by gas molecules = θ
Rate of adsorption r_1 is directly proportional to the pressure P of the gas and the free surface area $(1-\theta)$

$r_1 \, \alpha \, P(1-\theta);$ $\qquad$ $r_1 = k_1 P(1-\theta)$

The rate of desorption r_2 is directly proportional to the surface area covered by gas molecules (θ)

$\qquad$ $r_2 \, \alpha \, \theta;$ $\qquad$ $r_2 = k_2\theta$

$\qquad$ At equilibrium, $r_1 = r_2$

$\qquad$ $k_1 P(1-\theta)$ $\qquad$ $= k_2\theta$

$\qquad$ $k_1 P - k_1 P \theta$ $\qquad$ $= k_2\theta$

$k_1 P = k_1 P\theta + k_2\theta$

$$= (k_2 + k_1 P) \, \theta$$

$$\theta = \frac{k_1 P}{k_2 + k_1 P} \text{------- (1)}$$

$$\theta = \frac{\frac{k_1}{k_2} P}{\frac{k_2}{k_2} + \frac{k_1}{k_2} P}; \quad \theta = \frac{bP}{1 + bP} \text{-------(2)} \qquad \left[\frac{k_1}{k_2} = b\right]$$

The mass of gas adsorbed per unit mass of adsorbent (x/m) is directly proportional to the fraction of surface area covered by gas molecules.

$$\frac{x}{m} \, \alpha \, \theta \; ; \quad \frac{x}{m} = k \, \theta$$

Substituting the value of θ from equation (2)

$$\frac{x}{m} = \frac{kbP}{1 + bP} \; ; \quad \boxed{\frac{x}{m} = \frac{aP}{1 + bP}} \quad [kb = a]$$

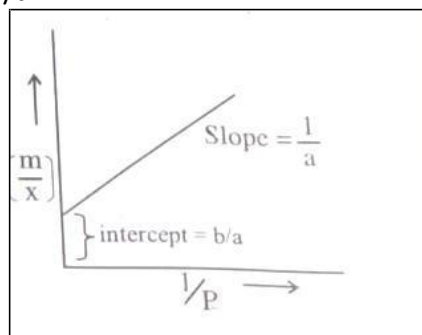**It is Langmuir adsorption isotherm.** a & b are constants.

   c) **Validity of Langmuir isotherm**

$$\boxed{\frac{x}{m} = \frac{aP}{1 + bP}}$$

By rearranging,

$$\frac{m}{x} = \frac{1}{aP} + \frac{bP}{aP} \; ; \qquad \frac{m}{x} = \frac{1}{aP} + \frac{b}{a}$$

This is straight line equation. A plot of m/x against 1/P gives a straight line with a slope of 1/a and a intercept of b/a.

Interpretation of Langmuir isotherm

1. When the gas pressure P is very low

    At very low P, bp<<1 $\frac{x}{m} = aP$; Therefore, $\frac{x}{m} = P$

    Thus, at low P the adsorption follows I order kinetics.

2. When the gas pressure is very high

    At very high Pressure bP>>1.

$$\frac{x}{m} = \frac{aP}{bP} = \frac{a}{b}$$

    It becomes independent of P and follows zero order kinetics.

3. Freundlich adsorption isotherm

Definition:

   He gave an empirical relationship between the quantity of gas adsorbed by a given amount of solid adsorbent surface and pressure at a particular temperature.

$$\frac{x}{m} = kP^{\frac{1}{n}} \quad \ldots\ldots(1)$$

   x= mass of gas adsorbed, m= mass of adsorbent P= pressure of gas

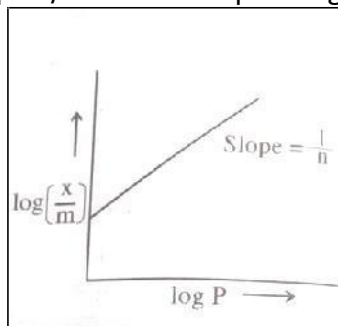   k and n = constants, depend upon adsorbent, adsorbate and temperature.

   It is called Freundlich adsorption isotherm.

Validity:

On taking log on both sides of equation (1),

$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$. This is a straight line equation. A plot of $\log \frac{x}{m}$ against $\log P$ gives a straight line with slope 1/n and intercept of log k.

Significance and Limitations

  i.   It is applicable only for small ranges of pressure
  ii. It is purely empirical.
  iii. The constants k and n vary with temperature.

4.B.E.T adsorption isotherm

The following are the assumptions of B.E.T theory.

  i.   The solid surface possesses uniform, localized sites.
  ii. Adsorption at one site does not affect the adsorption at neighbouring sites.
  iii. The molecules can be adsorbed in second, third and n^{th} layers.
  iv. The surface area available for the nth layer is equal to the coverage of the $(n-1)^{th}$ layer.
  v.   The energy of adsorption in the first layer (E_1) is a constant.
  vi. The energy of adsorption in succeeding layer is equal to the energy of liquefaction of the gas. (E_L)

Based on this Brunauer, Emmett and Yeller derived the following equation.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{c-1}{V_m c}\left(\frac{P}{P_0}\right)$$

This is known as BET equation.

V   = Volme of gas adsorbed at a pressure P

V_m = Volume of gas adsorbed for the formation of monolayer.

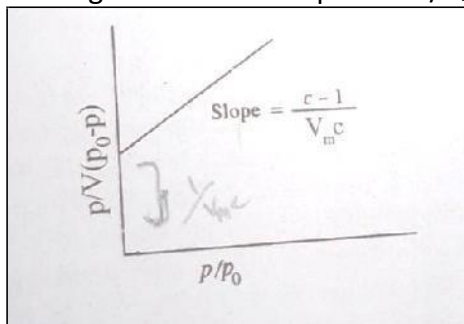c   = Constant depends on the nature of gas.

P_0 = Saturation Pressure

Validity:

The validity of BET can be tested by plotting $P/V(P_o - P)$ against P/P_o

The plot obtained will be straight line with a slope of $c-1/V_mc$.

Significance:

Using B.E.T equation, the surface area of the adsorbent (solid) can be easily calculated.

5. Applications of adsorption:

1. The manufacture of compounds like NH_3, H_2SO_4 etc., takes place on solid catalysts such as Fe and Pt/V_2O_5 respectively. This involves the principle of adsorption.
2. Oils can be hydrogenated using finely divided nickel as the solid surface.
3. Animal charcoal is used as delocaliser in the manufacture of cane-sugar.
4. Process of dyeing involves the adsorption of colouring matter on the solid surfaces.
5. Concentration of ores by froath floatation process using vegetable oil is based on adsorption.
6. Activated charcoal is used to create high vacuum.
7. Soaps and detergents remove the dirty materials by the principle of adsorption.
8. Adsorption indictors are used to find out the end point in precipitation titrations.
9. Activated charcoal is used in gas masks to remove the poisonous gases present in atmospheric air.
10. Silica and alumina gels are used as adsorbents to remove moisture and to control the humidity.

6. Characteristics of Catalytic reactions:

1. A catalyst remains unchanged in mass and chemical composition at the end of the reaction, though a change in its physical state, colour etc., may occur.
   Example : Granular MnO_2 used as the catalyst in the decomposition of $KClO_3$ becomes a fine powder at the end of the reaction.
2. A small amount of catalyst is sufficient to bring about an appreciable change in the velocity of reaction.
   Example: The presence of even 1mg of fine platinum powder is enough to catalyse the combination of 2.5 litres of mixture of H_2 and O_2 to form H_2O.
3. A catalyst is specific in its action, like a key can open a particular lock.
   Example: MnO_2 can catalyse the decomposition of $KClO_3$ but not KNO_3 or other substances.
4. A catalyst is more effective when finely divided.
   Example: In the decomposition of H_2O_2, finely divided Pt is a better catalyst than lumps of Pt.
5. A catalyst cannot start a reaction, but can only decrease or increase its speed.
6. A catalyst does not affect the final state of the equilibrium, since it shortens the time required to establish the equilibrium. A catalyst is more active at a particular temperature, called the optimum temperature.

7. The addition of a small amount of foreign substances, which are not themselves catalytically active, sometimes increases the activity of the catalyst.
   Example: In the manufacture of ammonia by Haber's Process, finely divided iron acts as a catalyst while Mo acts as a promoter.

8. The activity of a catalyst is inhibited or completely destroyed by the presence of even minute traces of certain substances, called catalytic poisons or anti-catalysts.
   Example: In the manufacture of sulphuric acid by the Contact Process, a trace of As_2O_3 destroys the catalytic activity of platinum. Hence As_2O_3 acts as a catalytic poison.

UNIT – IV
GROUP THEORY

1. Group Theory:

Symmetry element	Symmetry Operation
a. Identity (E)	The operation leaves the molecule unchanged.
b. Proper axis of rotation (C_n)	Rotation by an angle $\theta = 2\pi/n$
c. Plane of symmetry (σ)	Reflection in the plane.
d. Improper axis of rotation (S_n)	Rotation about the axis followed by reflection.
e. Centre of symmetry(i)	Inversion of all atoms in the molecule through the inversion centre.

2. Groups and their basic properties

Definition: A group is a complete set of elements which are related to each other by certain rules. They are

i) Closure property:

   The product of any two elements must be element of the group. i.e. if A and B are the elements of the group, then its product AB= C, which is also an element of the group. If AB = BA , the elements of the group A and B are said to commute.

   An element combines with itself to form another element of the group.

ii) Identity:

   The group must contain the identity element E which commutes with all the elements and does not produce any change.

   EA = AE = A

   EB = BE =B

iii) Inverse:

   Every element A of the group has an inverse A^{-1} which is also an element of the group. $AA^{-1} = A^{-1}A = E$.

iv) Associative Property:

   Every element of the group obeys the associative laws of combination.

   A(BC) = (AB)C

3. Order of a group:

   The total number of elements present in a finite group is called its order. It is represented by the symbol 'h'. Example: The order of H_2O molecule is 4.

   i.e. E, C_2, σ_v and σ_v'

4. Sub group:

   A subgroup is defined as a subset of the elements of a group which satisfies all the definitions of a group. The condition for a subgroup is   h/g = k

Where, h = order of the group, g = order of the subgroup, k = integer. When k =1, it is known as trivial group.

5. Class:

A class is defined as a set of elements which are conjugate to each other. They have same character. In NH_3 molecule, there are three classes E, $2C_3$ and $3\sigma_v$.

6. Abelian group:

A group is said to abelian or commutative if all the symmetry elements commute. $AB = BA$. Example: Water molecule

7. Non-abelian group:

A group is said to be non abelian or non-commutative if all the symmetry elements do not commute. $AB \neq BA$
Example: NH_3 molecule

8. Show that H_2O is an abelian group

Proof: H_2O molecule possesses four symmetry operations.
They are E, C_2, $\sigma_v(xz)$, $\sigma_v'(yz)$
If H_2O is an abelian group, it follows the following conditions.

i) Closure property:

$EC_2 = C_2$
$C_2 . \sigma_v(xz) = \sigma_v'(yz)$
$C_2 . \sigma_v'(yz) = \sigma_v(xz)$
$C_2 . C_2 . = E$ and so on.

ii) Identity:

There is an identity element 'E' in H_2O molecule.

iii) Inverse:

Since $C_2 . C_2 . = E$, inverse of C_2 is equal to C_2.
i.e. $C_2^{-1} = C_2$ or C_2 is its own inverse.

iv) Associative Property:

It means ABCD is the same as (AB) (CD), (A)(BCD) or (ABC)(D).
In H_2O molecule
$C_2 \sigma_v E \sigma_v' = (C_2 \sigma_v) (E\sigma_v')$
$= \sigma_v' \sigma_v' = E$ (or)
$C_2 \sigma_v E \sigma_v' = C_{2(} \sigma_v E \sigma_v') = C_2 C_2 = E$

v) Commutative property:

It means $AB = BA$. ie. $E C_2 = C_2$; $C_2E = C_2$. Thus, H_2O molecule is an abelian group.

9. Cyclic groups:

A group is said to be cyclic, if all its elements can be generated from the symmetry element. Thus, A, A^2, A^3 ----- A^n form the elements of a cyclic group, here $A^n = E$, the identity element. All the cyclic groups are abelian.

10. Group Multiplication table:
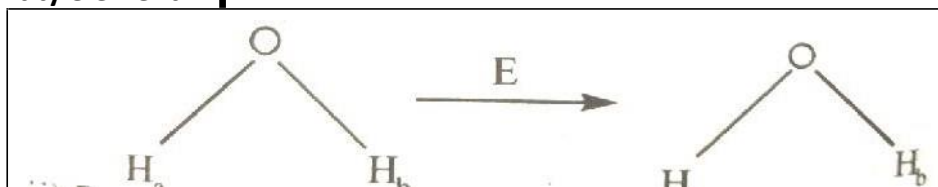
Multiplication table for H_2O molecule:
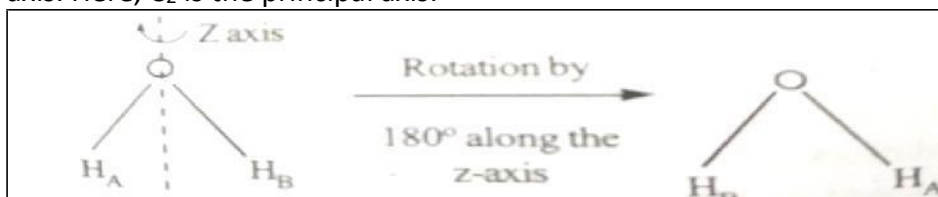It is a V – shaped molecule
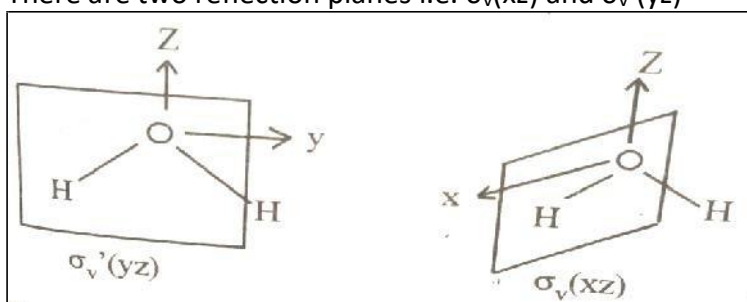
i) Identity element 'E'

ii) Proper axis of rotation

An axis passing through the O atom and parallel to the molecular plane is the C_2 – axis. Here, C_2 is the principal axis.

iii) Plane of symmetry:

There are two reflection planes i.e. $\sigma_v(xz)$ and $\sigma_v'(yz)$

iv) Improper axis of rotation:

There is no S_n in H_2O molecule.

v) Centre of symmetry: There is no inversion.

The symmetry elements of H_2O molecule are E, C_2, σ_v and σ_v'

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

Here, $C_2 . C_2 = E$; $C_2 . \sigma_v = \sigma_v'$; $C_2 . \sigma_v' = \sigma_v$

11. Multiplication Table of C_{3v} group

C_{3v}	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E	σ_v'	σ_v''	σ_v
C_3^2	C_3^2	E	C_3^1	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3^1
σ_v'	σ_v'	σ_v	σ_v''	C_3^1	E	C_3^2
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3^1	E

Molecular point groups

Point group	Symmetry elements	Examples
C_1	E	CHClFBr
C_2	E, C_2	H_2O_2
C_3	E, C_3	C_2H_6
C_{2v}	E, C_2, $2\sigma_v$	H_2O, $CH_2=O$
C_{3v}	E, C_3, $3\sigma_v$	NH_3, $CHCl_3$, PH_3
$C_{\infty v}$	E, C_∞, $\infty\sigma_v$	HCl, CO

Point group	Symmetry elements	Examples
C2h	E, C2, σ_h, i	Trans- dichloro ethylene
D_{2h}	E, $3C_2$, 3σ, i	Ethylene, naphthalene
D_{3h}	E, $2C_3$, $3C_2$, $3\sigma_v$, σ_h, $2S_3$	BF_3
D_{4h}	-	$[PtCl_4]^{2-}$
D_{6h}	-	C_6H_6
T_d	-	CH_4
O_h	-	SF_6

UNIT - V
SPECTROSCOPY - I

1. Spectroscopy - I

Spectroscopy is the study of interaction of electromagnetic radiation with matter. Spectroscopy is broadly classified into
    i. Atomic spectroscopy
    ii. Molecular spectroscopy

i. Atomic spectroscopy

It is the study of interaction of EMR with atoms.

ii. Molecular spectroscopy

It is the study of interaction of EMR with molecules.

2. Types of molecular energies

Molecules possess different types of energies. They are
  i) Translational energy (Etrans)
      It is the energy due to the translational motion of the molecule.
  ii) Rotational energy:
      It is the energy associated with the rotation of the molecule about its centre of gravity.
  iii) Vibrational energy:
      It is the energy associated with the vibrations of the constituent atoms.
  iv) Electronic energy:
      It is the energy associated with the transition of an electron from one level to another energy level.

3. Born- Oppenheimer approximation:

The total energy of a molecule can be written as the sum of the translational, rotational, vibrational and electronic energies on motion.

$E_{total} = E_{tr} + E_{rot} + E_{vib} + E_{el}$

Where E_{tr}, E_{rot}, E_{vib} and E_{el} are the translational, rotational, vibrational and electronic energies respectively.

Also, $E_{el} > E_{vib} > E_{rot} > E_{tr}$

The translational energy is not quantized and hence it is negligible compared with other energies. Therefore,

$E_{tot} = E_{el} + E_{vib} + E_{rot}$

4. Types of Molecular spectroscopy:

  1. Nuclear magnetic resonance (NMR) spectroscopy

      The energy involved in this spectroscopy is 5-100MHz. In NMR spectroscopy a nucleus possessing nuclear spin , when placed in an external magnetic field (Zeeman field) , undergoes transitions between the nuclear levels when radiofrequency radiation is applied.

  2. Electron spin resonance (ESR) spectroscopy

      The energy involved in ESR is 2000-36,000 MHz. In ESR spectroscopy, a system containing an odd number of electron, when placed in a Zeeman field, undergoes

transitions between the electronic spin energy levels when microwave frequency radiation is applied.

3. **Pure rotational (Microwave) spectroscopy**

   In rotational spectroscopy, the transitions are observed between the rotational energy levels of a molecule containing permanent dipole moment occur in the microwave region or the IR region. The energy range involved is 1-100cm^{-1}.

4. **Vibrational (Infrared) and vibrational rotational spectroscopy**

   In this type of spectroscopy, the transitions are observed between the vibrational energy levels of a molecule on the application of infrared (IR) radiation. The energy range involved is 200-4000cm^{-1}.

5. **Raman spectroscopy**

   This spectroscopy is based on scattering of radiation and not on the absorption of radiation by the sample. The spectrum is observed in the visible region. (12,500-25,000 cm^{-1}).

6. **Electronic spectroscopy**

   This branch of spectroscopy deals with transition between the electronic energy levels of a molecule brought about by absorption of ultraviolet (uv) or visible radiation. The energy range involved is 12,500 -25,000cm^{-1} for visible region, 25,000-66,500cm^{-1} for uv region and 66500 -2x10^6 cm^{-1} for vacuum ultra violet region.

5. Rotational Spectra or microwave spectra, electronic spectra and Vibrational spectra

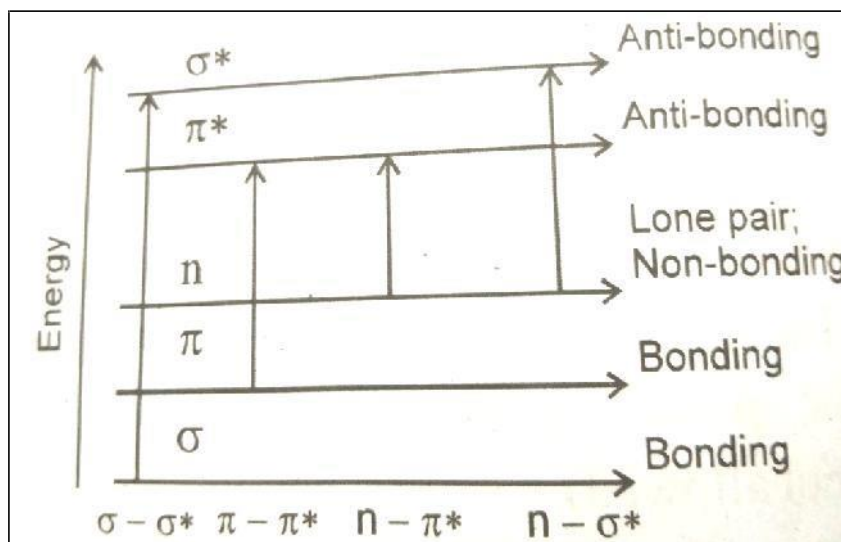| Type	Origin	Condition	Selection rule
Rotational spectra	• Radiation of wavelength 10^{-2} to 10 cm	Molecule should possess permanent dipole moment.	ΔJ = ±1 where J= rotational quantum number ΔJ= +1 – Absorption ΔJ= -1 - Emission
	• Due to rotational transition of the molecule	**Case I** Molecules like H_2, N_2, O_2, CO_2 etc have no charge separation and so they possess zero dipole moment. Therefore, Microwave inactive.	
	• It is observed in Far IR region or microwave region		
		Case II Heteronuclear diatomic molecules like HBr, HCl , CO, NO have permanent charge separation and they possess permanent dipole moment. Therefore, microwave active	

Electronic spectra	• 12500-2500cm^{-1} visible region.		• Spin of the two states involved should be same for allowed transition. $\Delta S = 0$	
	• 25000-66500cm^{-1} uv region			
	• Electronic transition		• Transitions in which the change in angular momentum along the internuclear axis is either 0 or ±1 are allowed	
	• UV or			
	Visible region		• Transitions in	
			• s→s, p→p, d→d and u→uare not allowed.	
			• s→p, g→u are allowed	
Vibrational spectra	• Radiation of wavelength 10^{-3} to 10^{-5}cm	Case I • Molecules like H_2, N_2, O_2 etc., have stretching motion and no bending motion. • Dipole moment does not change. • IR inactive		Δv =±1, Where vibrational quantum number v = =0, 1,2 .... Δv = +1
	• Due to vibrational transition			
	• Mid and near IR region			
		Case II • Heteronuclear diatomic molecules like CO, NO etc and polyatomic molecules like CO_2, H_2O, CH_4 etc., possess change in dipole moment. • IR active		

			— Absorption $\Delta v = -1$ — emission

6. Electronic spectroscopy:

Types of electronic transitions:

When a molecule is excited by a radiation energy, the electrons can be excited from a bonding (σ, π) or non – bonding (n) orbital to a higher energy antibonding orbitals ($\sigma *, \pi *$) which are vacant in the ground state. This produces $\sigma \rightarrow \sigma*$, $\pi \rightarrow \pi$, $n \rightarrow \sigma*$ and $n \rightarrow \pi*$ electronic transitions.

The energy of transition is in the following order.
$\sigma \rightarrow \sigma* > n \rightarrow \sigma* > \pi \rightarrow \pi* > n \rightarrow \pi*$

Types of transitions and the energy of n,π, σ electrons.

a) σ→σ* transitio

The transition of an electron occurs from a bonding sigma orbital of molecule to the higher energy antibonding sigma orbital is known as σ→σ* transition. Thes transitions occur at the highest excitation energy than the others. These transitions are mainly observed in saturated hydrocarbons and their characteristic bands appear in the "vacuum UV region" (below 200nm)

Example: Methane λ_{max} -122nm Ethane λ_{max} - 135nm

b) π→π* transitic

The transition of an electron occurs from π bonding orbital to π* orbital is known as π→π* transition. These transitions are observed in unsaturated compounds such as alkenes, alkynes, carbonyl compounds etc., Their bands appear in the near UV region.

Example: 1,3- butadiene λ_{max} -217nm

c) n→σ* transition

The transition of an electron occurs from the non-bonding orbital of the ground state to the antibonding sigma orbital is known as n→σ* transition. These transitions are observed in saturated halides, amines, alcohols etc., Their bands appear in the vacuum region.

Example: methyl alcohol λ_{max} – 174nm

d) n→π* transition

The transition of an electron occurs from the non-bonding orbital of the ground state to the antibonding π* orbital. These transitions occur at the lowest energy than the others. These transitions are mainly observed in saturated aliphatic ketones and aldehydes. Their bands appear in the near UV region.

Example: Acetone λ_{max} - 270nm

7. Applications:

i) Quantitative analysis

UV spectroscopy is generally used for the quantitative determination of compounds that absorb UV. This determination is based on Beer Lambert's law.

ii) Study of charge transfer reaction

When benzene and iodine are brought together in the molar ratio of 1:1, a new absorption band is obtained. This is due to the formation of a charge transfer complex between the donor molecule (benzene) and the acceptor molecule(iodine).
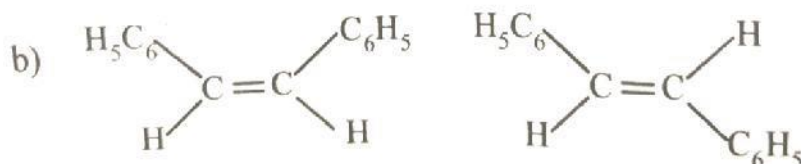
iii) Chemical kinetics

Several chemical reactions can be followed spectrophotometrically in the UV region. By measuring the intensities of characteristic absorption peaks from time to time, the rate of a reaction is calculated. Reaction intermediates can also be characterized in a few reactions.

iv) Determination of geometrical isomers

The λ_{max} for the trans isomer is generally higher than those of the cis- form.
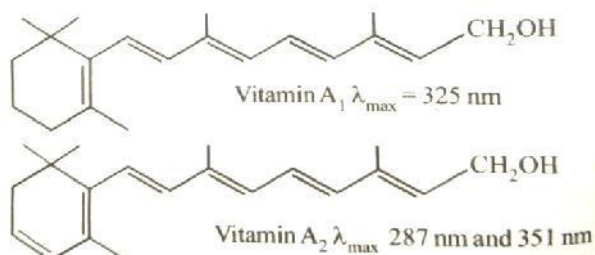Example: a.cis-2-alkenes λ_{max} = 176nm ; trans-2-alkenes λ_{max} =179nm

b)

$$H_5C_6 \diagdown \atop H \diagup C=C \diagup {}^{C_6H_5} \atop \diagdown H \qquad H_5C_6 \diagdown \atop H \diagup C=C \diagup {}^{H} \atop \diagdown C_6H_5$$

b. cis-stilbene (λ_{max} =280nm); trans –stilbene (λ_{max} =296nm)

v) Elucidation of vitamin A and K

Electronic spectra are very much useful in elucidating the structures of Vitamin A_1 and A_2 and K_1 and K_2.

Vitamin A_1 λ_{max} = 325 nm

Vitamin A_2 λ_{max} 287 nm and 351 nm

Vitamin A_1 absorbs at 325nm while Vitamin A_2 absorbs at 287 and 351nm.The longer wavelength is due to the presence of extra double bond

vi. Study of conjugation

UV spectra can be used to distinguish conjugated dienes from non conjugated dienes. Acyclic conjugated dienes show intense $\pi \rightarrow \pi^*$ absorption band more than 217nm.
Example $CH_2=CH-CH=CH-CH_3$ 1,3- pentadiene λ_{max} -223 nm
$CH_2=CH-CH_2-CH=CH_2$ 1,4-pentadiene λ_{max} -182nm
When the number of conjugated double bonds increases, the λ_{max} also increases. The absorption band shifts to the longer wavelength.

Compound	Formula	λ_{max} (nm)
Ethylene	$CH_2=CH_2$	165
1,3 butadiene	$CH_2=CH-CH=CH_2$	217
1,3-pentadiene	$CH_2=CH-CH=CH-CH_3$	223
1,3,5-hexatriene	$CH_2=CH-CH=CH-CH=CH_2$	254

8. Vibrational spectroscopy

A molecule may be considered as a system of balls (atoms) and spring (bonds). When a molecule absorbs IR radiation, it undergoes vibrations. There are two types of normal modes of vibrations.

    a. Stretching
    b. Bending

a. Stretching vibrations:

In this type , the distance between the two atoms(bond length) increases or decreases but the atoms remain in the same bond axis. Stretching vibrations require higher energy and occur at high frequency.

Stretching vibrations are of two types:
    i. Symmetric stretching
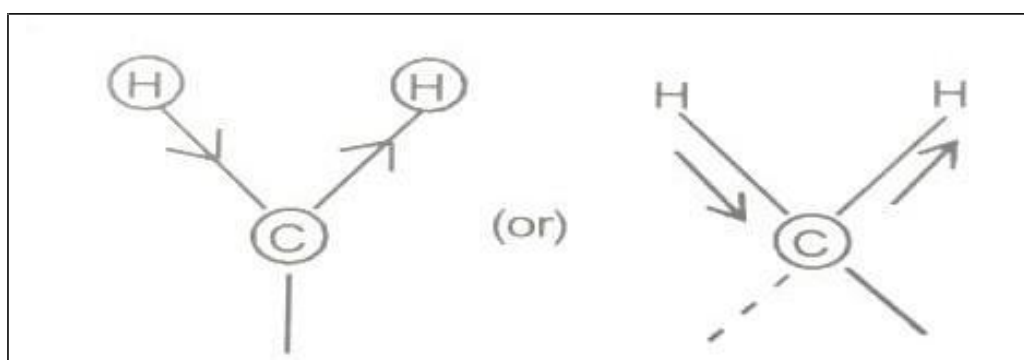   ii. Asymmetric stretching

i. Symmetric stretching

In this type both the atoms move in and out simultaneously
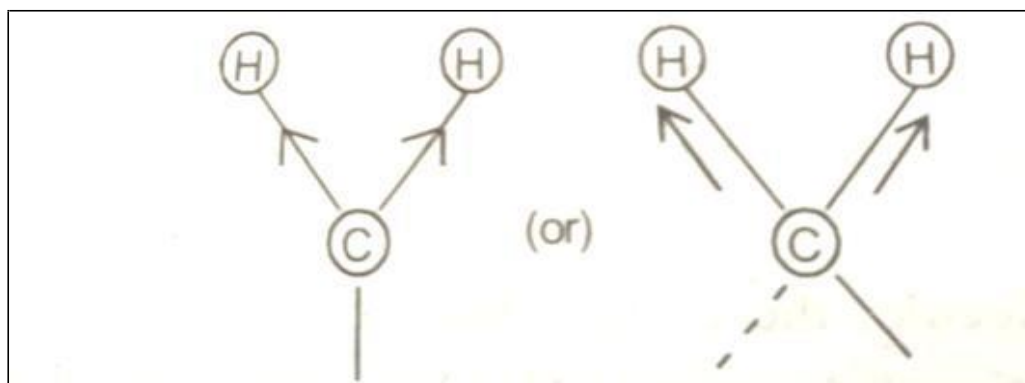
Symmetrical stretching of –CH$_2$ group

ii. Asymmetric stretching

In this type, one atom moves in and the other moves out

Asymmetric stretching of –CH₂ group

b. Bending vibrations

In this type, the distance between the atoms remains constant but the position of the atom changes relative to the original bond axis. Bending vibrations require lower energy and occur at lower frequency.

These vibrations are of two types:
    i) In-plane bending
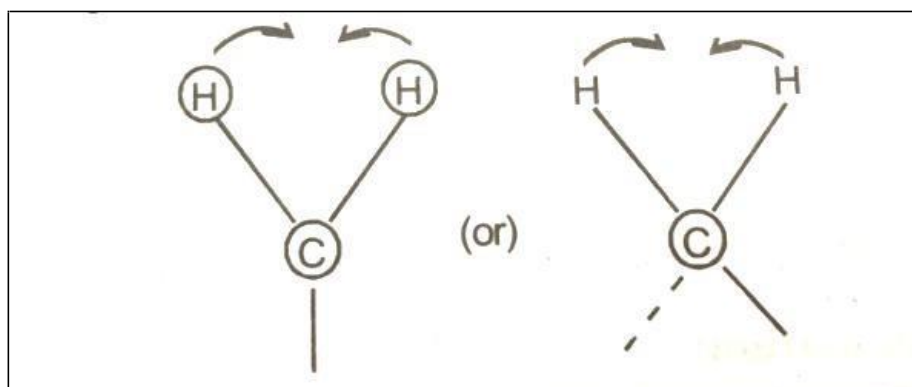   ii)   Out -of plane bending

i) In- plane bending

When the atoms bend, finally the atoms remain in the nodal plane of the system is called in-plane bending.

These vibrations are of two types:
    a.   Scissoring deformation
    b.   Rocking deformation

a. Scissoring deformation
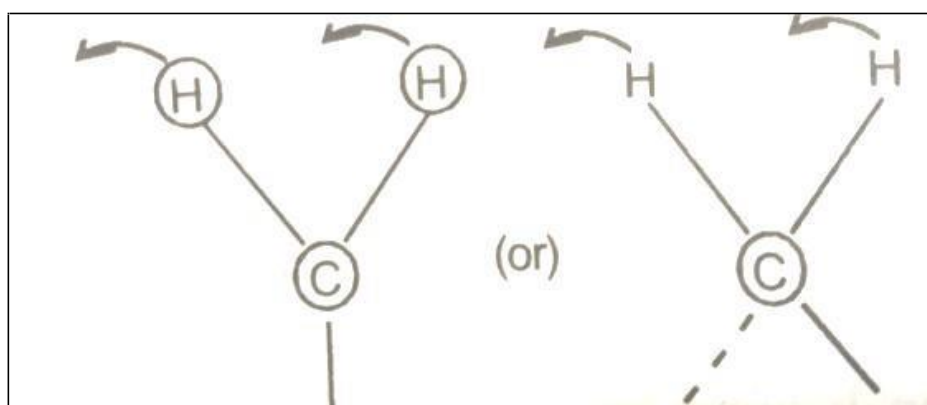
        In this type, both the atoms swing to the opposite side.

Scissoring of –CH₂ group

b. Rocking deformation

        In this type, both the atoms swing to the same side.

Rocking of –CH₂ group

ii) Out –of plane bending

        When the atoms bend, finally the atoms remain out of the nodal plane is called out-of plane bending.
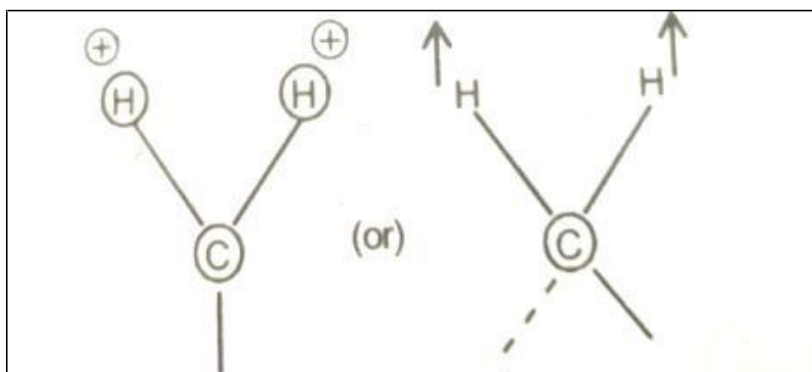
These vibrations are of two types:
- a. Wagging deformation
- b. Twisting deformation
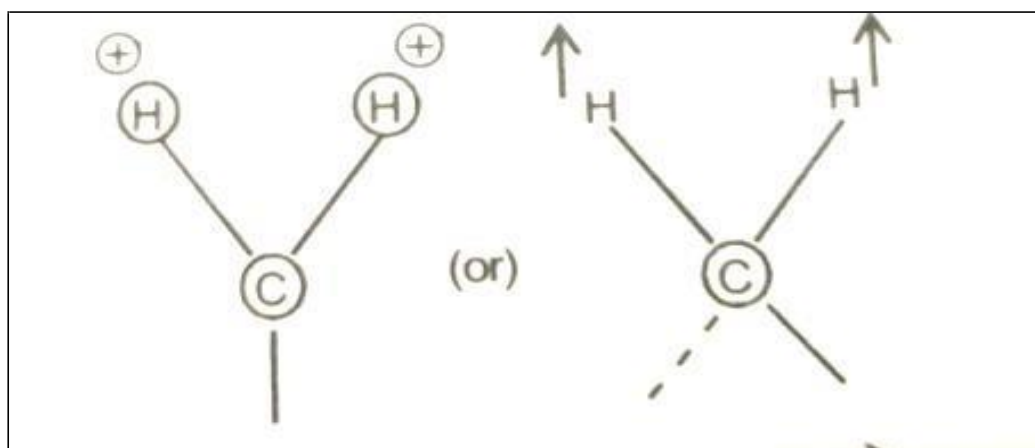
a. Wagging deformation

In this type, both the atoms swing up or down out of the plane of the papers.

Wagging of –CH₂ group

b. Twisting deformation

In this type, one atom swings up and the other swings down related to the plane of the papers.

Twisting of –CH₂ group

9. Finger print region

The IR spectrum are roughly divided into two parts

Characteristic frequencies		Finger print region	
4000	1500		900(cm⁻¹)

The region below 1550 cm⁻¹ is known as finger print region. The region is rich in much absorption due to bending vibrations and stretching vibrations (C-C, C-O and C-N bonds). It is useful to determine the identity of two compounds. Similarly, the identity of an unknown can also be revealed by comparing its IR spectrum with a set of spectra of known compounds under identical conditions.

The useful absorption in the finger print region:

CH_2 (deformation) $1470-1440 cm^{-1}$

Trans alkene(C=CH) $1000-950 cm^{-1}$

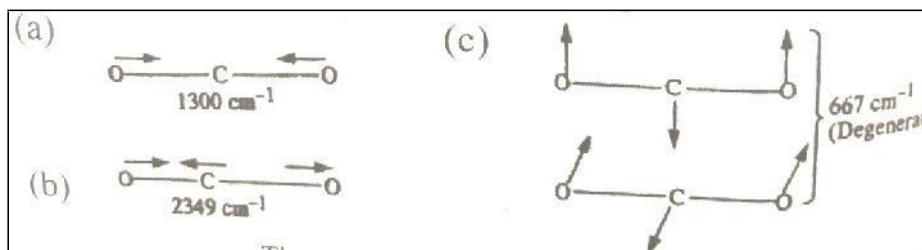## 10. Mode of vibrations of poly atomic molecules

1. **Normal vibration modes of CO_2 molecule**
   CO_2 is a linear molecule. Hence,
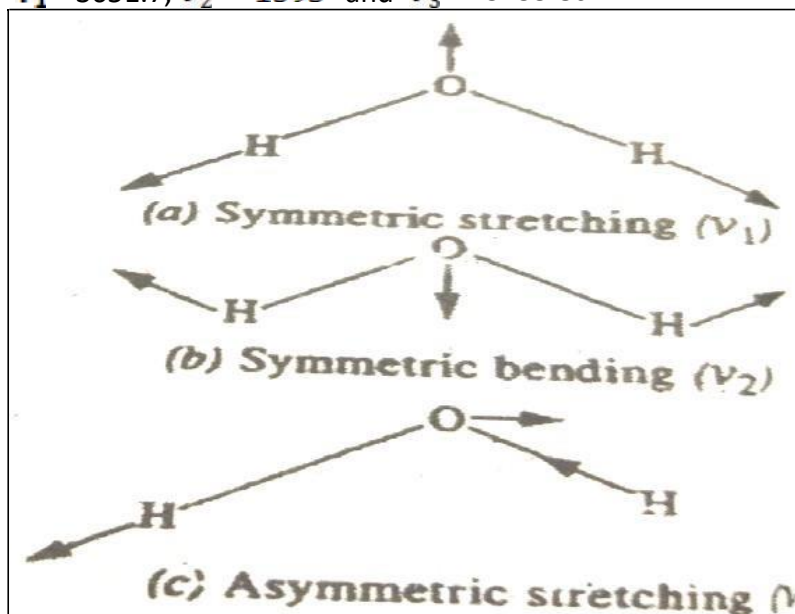   the normal modes of vibration of CO_2 is 3(3) -5 = 4

The normal modes of vibration of CO_2

   a. Symmetric stretching $\overline{v_1}$ = 1330cm^{-1} IR inactive

   b. Asymmetric stretching $\overline{v_3}$ = 2349cm^{-1} IR active

   c. Symmetric bending and Scissoring $\overline{v_2}$ cm^{-1} =667cm^{-1}
      Thus two bands are observed in IR spectra.

2. **Normal modes of vibration of H_2O molecule**
   H_2O is a non-linear molecule (V- shaped). Hence the normal modes of vibration is 3(3) -6 =3. Thus, three bands are appeared in IR spectra. These are
   $\overline{v_1}$ = 3651.7, $\overline{v_2}$ = 1595 and $\overline{v_3}$ = 3755.8cm^{-1}.

The normal modes of vibration of water molecule

11.Application of IR spectroscopy
i) Structural elucidation of organic molecules
   Every substance has produced characteristic IR absorption frequencies. Hence, we can easily identify any organic molecule by comparing its IR spectrum with that of the known compound spectra. Examples

Bond type	Frequency range(cm^{-1})
O-H	3650-3600
C-H	2900
N-H	3300

ii)IR spectra of carbonyl compounds

The carbonyl group is most important in IR spectrum because of its strong stretching band around $1700 cm^{-1}$. The actual position of the band depends upon the nature of groups attached to the carbonyl group. Th carbonyl group is present in variety of organic compounds like ketone, aldehydes, carboxylic acids, amides, esters etc.

Example: Ketones $1730\text{-}1645$ cm^{-1}

Aldehydes $1740\text{-}1690$ cm^{-1}

iii) Detection of hydrogen bonding in organic molecules

The free hydroxyl group of alcohols and phenols in the vapour phase appears as a **sharp band** at $3650\text{ -}3580$ cm^{-1}. But for the hydrogen bonded hydroxyl group lowers the absorption frequency and appears as a **broad band** at $3590\text{ -}2600$ cm^{-1}.

Application of IR spectra to distinguish inter and intramolecular hydrogen bonding

IR spectra may be used to distinguish inter and intramolecular hydrogen bonding by studying the effect of dilution.

Intermolecular H-bonding

Intermolecular hydrogen bonds are concentration dependent and it increases as the concentration of the solution increases. This appears as an additional broad band at $3500\text{-}3200$ cm^{-1} along with sharp free OH band at $3650\text{-}3580 cm^{-1}$.

Example:

The IR spectra of ethyl alcohol in CCl_4 (concentrated solution) gives two O-H absorption bands at $3620 cm^{-1}$ (sharp band due to free OH) and $3360 cm^{-1}$ (broad band due to H-bonded OH) .

On dilution, the intermolecular H-bonds are broken. Hence the broad band due to H-bonded OH at $3360 cm^{-1}$ decreases and finally disappears. Hence for dilute solution of ethyl alcohol, only one highly intensed absorption band at $3620 cm^{-1}$ due to free OH .
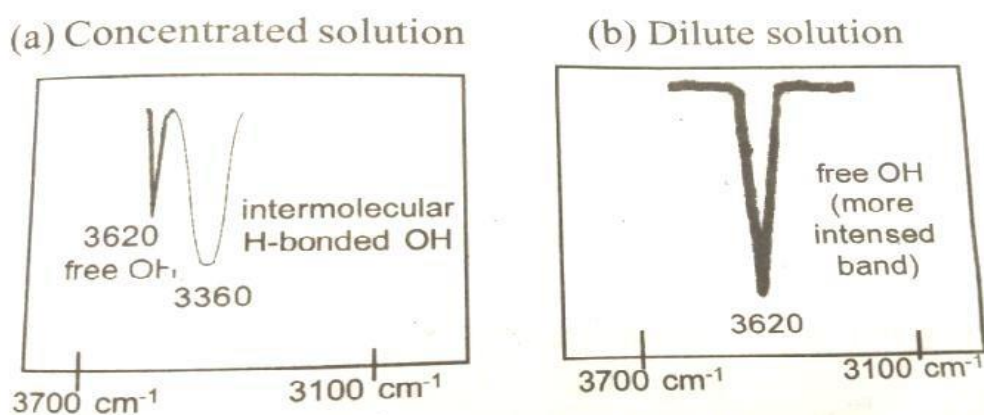
IR spectra of the O-H stretching region of ethyl alcohol in CCl_4

Intra molecular hydrogen bonding

Intra molecular hydrogen bonds are independent of concentration. On dilution, the absorption band remains unaffected.
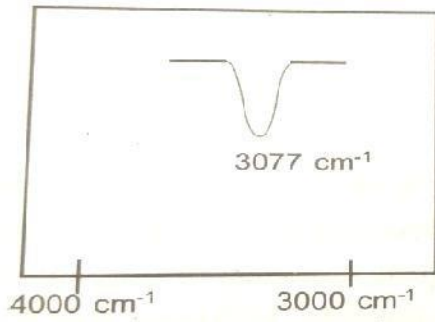
Example

The IR spectra of concentrated solution of methyl salicylate gives an absorption band at 3077 cm^{-1}. This band is due to intra molecular H-bonded OH. This appears as a shallow (low intense) broad band. On dilution, this absorption band remains unaffected.
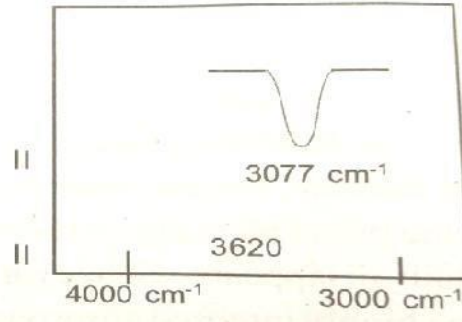
a.Concentrated solution(1.0M)   b. Dilute solution (0.031M)

IR absorption spectrum of the O-H stretching region of methyl salicylate