



**STUDY MATERIAL FOR B.SC CHEMISTRY
PHYSICAL CHEMISTRY
SEMESTER - V, ACADEMIC YEAR 2019-20**



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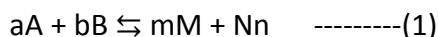
UNIT - I
THERMODYNAMICS - III

1. Van't Hoff reaction isotherm:

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

$$\Delta G^\circ = -2.303RT \log K_p$$

Let us consider a reversible reaction



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

Free energy of the reactants,

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

μ_A and μ_B = Chemical potential of species A and B

Similarly free energy of products,

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

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

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

$$\Delta G_{\text{reaction}} = 0$$

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

We know that,

$$\mu_i = \mu_i^\circ + RT \ln P_i \quad \text{-----(6)}$$

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

μ_i° = standard chemical potential

Therefore, equation (5) becomes

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

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

$$RT \left[\ln \frac{P_M^m \cdot P_N^n}{P_A^a \cdot P_B^b} \right] = - [G^\circ_{\text{products}} - G^\circ_{\text{reactants}}]$$

$$RT \ln K_p = - \Delta G^\circ$$

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

$$\text{ie } \Delta G^\circ = -RT \ln K_p \quad \text{-----(7)}$$

$$\Delta G^\circ = -2.303 \log K_p \quad \text{-----(8) Equation (8) is Van't Hoff isotherm}$$

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 K_p depends on the value of ΔG° . More the -ve value of ΔG° , more will be +ve value of K_p .
- iii. Using the reaction isotherm, we can work out the condition for maximum yield.
- iv. Since ΔG is related to ΔS and ΔH as $\Delta G = \Delta H - T\Delta S$. The value of ΔS (increase in entropy) makes K_p positive.

2. Van't Hoff isochore equation:

(Effect of temperature on chemical equilibria)

We know that

$$\Delta G^\circ = -RT \ln K_p \text{ -----(1)}$$

where K_p is the equilibrium constant at constant pressure.

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

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

Multiply by T,

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

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

Substitute in equation (3)

$$-T\Delta S^\circ = \Delta G^\circ - RT^2 \left[\frac{\partial (\ln K_p)}{\partial T} \right]_P \text{ (or) } \Delta G^\circ + T\Delta S^\circ = RT^2 \left[\frac{\partial (\ln K_p)}{\partial T} \right]_P$$

$$\text{(or) } \Delta H^\circ = RT^2 \left[\frac{\partial (\ln K_p)}{\partial T} \right]_P \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

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

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

Since ΔH does not vary with P, $\Delta H^\circ = \Delta H$

$$\left[\frac{d(\ln K_p)}{dT} \right] = \frac{\Delta H}{RT^2} \text{ -----(5)}$$

Integrated form of eqn (5)

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

On integrating both sides,

$$\int_{K_{P1}}^{K_{P2}} d(\ln K_p) = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

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

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

It is Van't Hoff's Isochore.



3. Significance of Clausius Clapeyron equation

Calculation of molar heat of vapourisation (H_v)

The molar heat of vapourisation, H_v 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 (K_b), molar depression constant (K_f). 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 $\left[\frac{\partial(\Delta G)}{\partial T}\right]$ approaches zero gradually as the temperature is lowered towards the absolute zero.

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

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

Substitute in (1)

$$\lim_{T \rightarrow 0} \Delta S = 0 \text{ and } \lim_{T \rightarrow 0} \Delta C_p = 0$$

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

Application:

- It is used to determine the transition temperature (T_f) of sulphur.

$$\Delta H^\circ = \Delta H - \frac{\beta}{2} T_f; \beta = \frac{\Delta C_p}{T}$$

- $\Delta G = -nFE$ to determine the emf of cells $\Delta G = \Delta H^\circ - T(\Delta C_p \ln T)$

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.

$$T \rightarrow 0, S = 0$$

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 S_{spec} (spectroscopic entropy ie the value obtained on the basis of spectroscopic data by means of statistical formula) is greater than S_{cal} 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.

$$S = 5.76 \text{ JK}^{-1} \text{ mol}^{-1}$$

NO (Nitric oxide)

It exists as a dimer N_2O_2 . Two orientations are possible

NO ON
 ON NO

Since there are $N/2$ dimer molecule per mole of Nitric oxide.

$$S = k \ln W$$

$$= 2.88 \text{ J K}^{-1} \text{ mo l}^{-1}$$

Ortho and para hydrogen:

In hydrogen molecule, the difference between S_{cal} and S_{spec} 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 S_{cal} values.

Ice:

In ice (H_2O), the entropy (S_{spec}) is higher than S_{cal} by 3.375 Joules. The is due to

- i. rotational motion of molecule in the solid state.
- ii. uncertainty 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

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 \text{-----(1)}$$

$$(G)_{T,P} = \mu_1 n_1 + \mu_2 n_2 \text{-----(2)}$$

Differentiate eqn (2), $(dG)_{T,P} = (\mu_1 dn_1 + n_1 d\mu_1) + (\mu_2 dn_2 + n_2 d\mu_2)$

$$(dG)_{T,P} = (\mu_1 dn_1 + \mu_2 dn_2) + (n_1 d\mu_1 + n_2 d\mu_2) \text{-----(3)}$$

Comparing equations (1) and (3),

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \text{-----(4)}$$

In general, $\sum n_i d\mu_i = 0 \text{-----(5)}$

Equation (5) is Gibbs- Duhem equation.

Application:



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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.

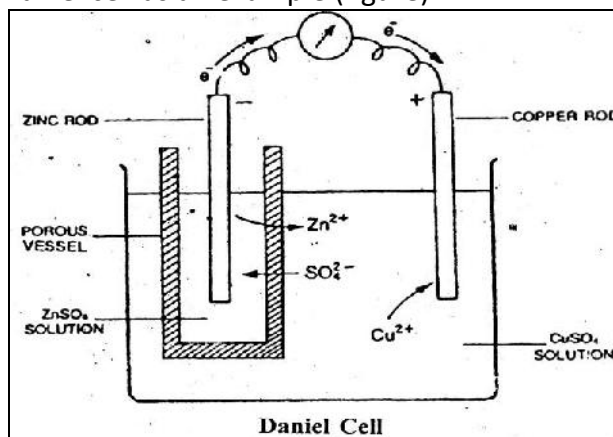
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UNIT - II
ELECTROCHEMISTRY

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)



It consists of a Zn – electrode dipped in ZnSO₄ solution and a Cu-electrode dipped in CuSO₄ 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 Zn²⁺ ions.



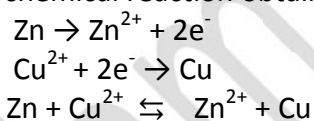
Thus Zn-electrode is called –ve electrode and sends electrons with the outer circuit.

Reduction reaction occurs at the Cu-electrode (i.e) Cu²⁺ ion from the solution undergoes reduction by taking two electrons to form Cu-metal and deposited on the Cu-electrode.



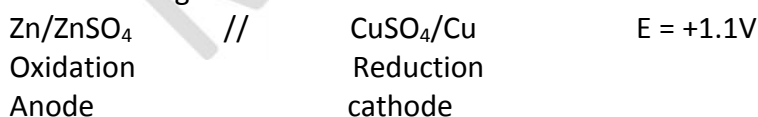
Cell reaction:

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



Cell representation:

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



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 the push 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 is expressed 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 25°C, the single electrode potential obtained is called standard electrode potential (E^0) and such electrode is called standard electrode.

Example:

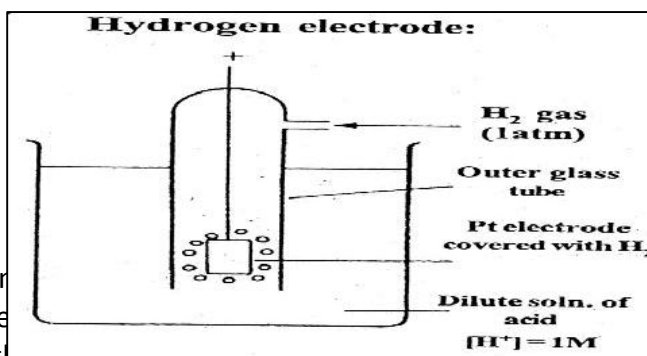
Standard Hydrogen Electrode

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

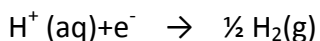
3. Reference Electrodes:

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.



When pure hydrogen part of it is covered (absorbed) absorbed hydrogen gas on the surface of the electrode and the electrode reaction is

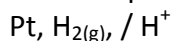


The electrode is reversible w.r.to hydrogen ion.

heric pressure, a hed between the acid solution. The



The electrode is represented as



At 25°C, when the pressure of H₂ 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 25°C.

Advantages:

- It can be used as a wide range of pH.
- It exhibits no salt error
- It is the fundamental electrode. Its potential is zero volt at 25°C.

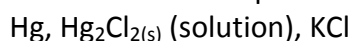
Disadvantages:

- Presence of impurities in H₂ gas may poison the electrode.
- To maintain the H₂ gas pressure at 1 atmosphere is difficult.
- It cannot be used for solution containing strong oxidizing agent.

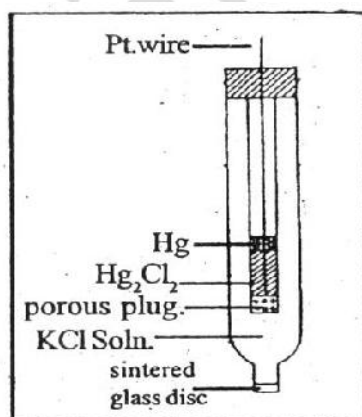
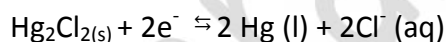
Calomel electrode:

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 (Hg₂Cl₂) 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



The electrode reaction is



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 electrochemical series.

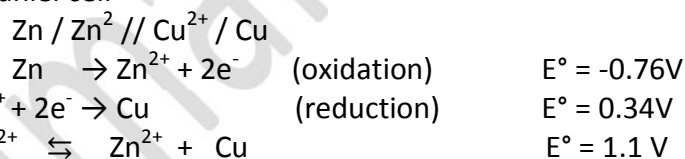
Electrode	E⁰ volts
Au ³⁺ , Au	+ 1.50
Hg ²⁺ , Hg ₂ ²⁺ , (Pt)	+ 0.92
Ag ⁺ , Ag	+ 0.80
Fe ³⁺ , Fe ²⁺ , (Pt)	+ 0.77
Cu ²⁺ , Cu	+ 0.34
2H ⁺ , H ₂ , (Pt)	0.00
Pb ²⁺ , Pb	- 0.13
Sn ²⁺ , Sn	- 0.15
Fe ²⁺ , Fe	- 0.44
Zn ²⁺ , Zn	- 0.70
Na ⁺ , Na	- 2.71

Applications or Significance:

1. A high positive value of E⁰ indicates that the electrode undergoes reduction (by accepting electrons). A high negative value of E⁰ indicates that the electrode undergoes oxidation (by donating electrons).

The emf of the cell reaction can be easily determined with the help of E⁰ values.

Example: In the Daniel cell



$$E_{\text{cell}} = \text{Redn. potential of RHS} - \text{Redn. potential of LHS}$$

$$E_{\text{cell}} = E^\circ_{\text{R}} - E^\circ_{\text{L}} = 0.34 - (-0.76) = +1.10\text{V}$$

2. The feasibility of the cell reaction can also be predicted with the help of E⁰ values. From E⁰ values, emf of the cell is calculated.

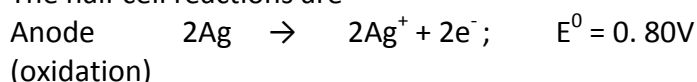
$$E_{\text{cell}} = E^\circ_{\text{R}} - E^\circ_{\text{L}}$$

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



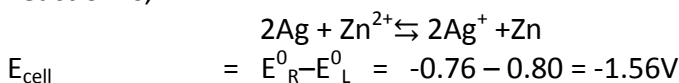
The half cell reactions are





0.76V
(Reduction)

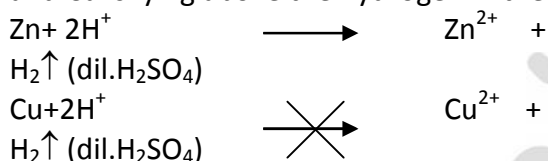
The Cell reaction is,



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

- 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.
- 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.



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,



If an external emf is increased infinitesimally, the cell reaction is reversed



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



Applying law of mass action,



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

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

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

According to Van't Hoff reaction isotherm,

$$\Delta G = \Delta G^\circ + RT \ln K \text{-----(2)}$$

Substitute the value of ΔG and ΔG° in eqn (2)

$$-nFE = -nFE^\circ + RT \ln K$$

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

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

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

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

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,

$$E = E^\circ - \frac{0.0591}{F} \log \frac{[C][D]}{[A][B]} \text{ at } 25^\circ\text{C}$$

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, $\text{Zn} / \text{Zn}^{2+} // \text{Cu}^{2+} / \text{Cu}$

The cell reaction is, $\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$

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

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

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

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

7. Potentiometric titrations

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

- Acid-base titrations
- Oxidation-reduction (Redox) titrations
- Precipitation titrations

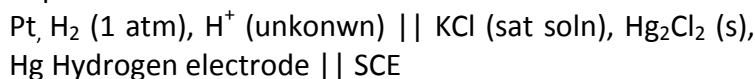
a. Acid-base titrations

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



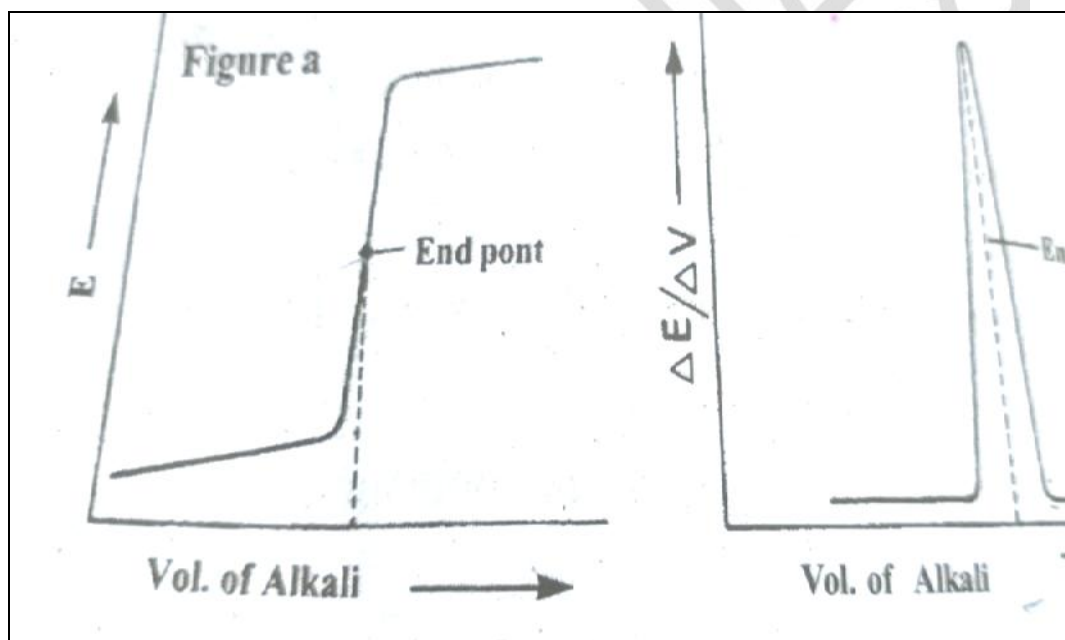
The EMF of the cell is measured potentiometrically. It is given by $E = E_R - E_L = E_{\text{calomel}} - E_{\text{hydrogen}}$
 $= 0.2422 + 0.0591 \text{ pH}$

Example: HCl × NaOH

When NaOH is added, the H^+ ion concentration goes on decreasing i.e. 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.

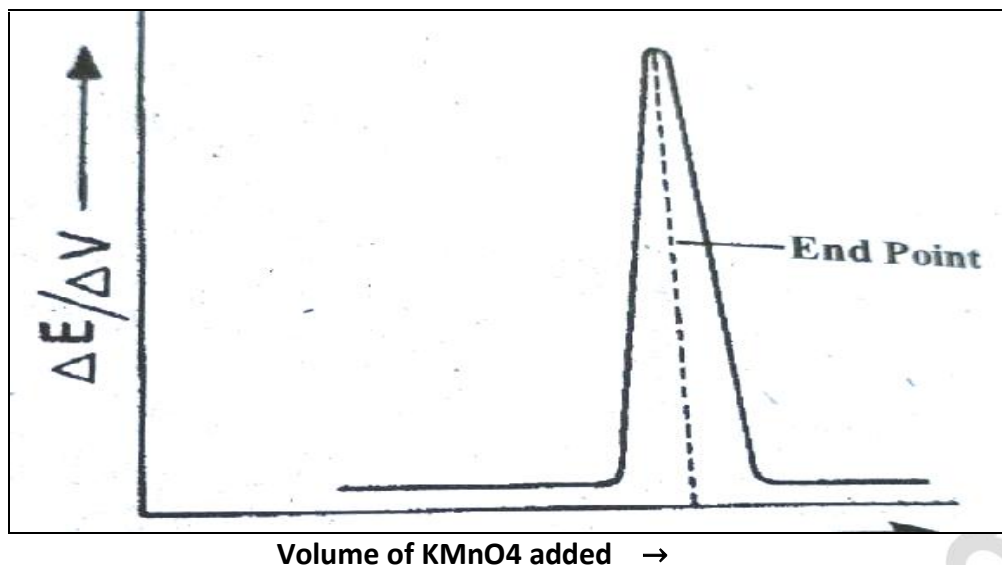


b. Redox Titrations

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

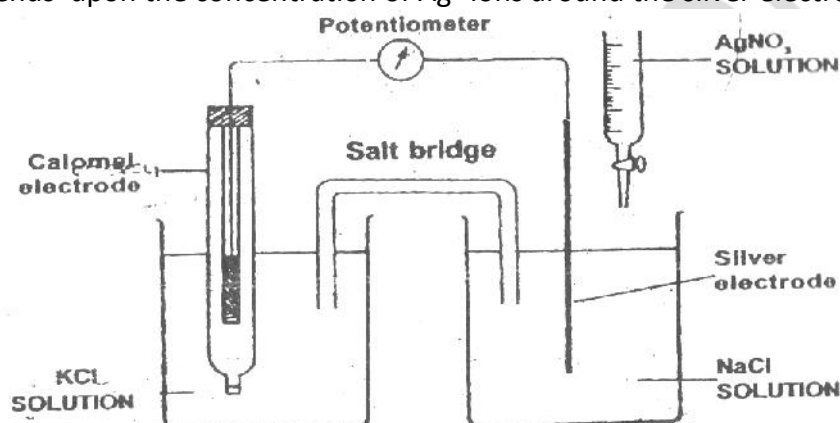


When KMnO_4 is added from the burette, the emf rises. Near the end point the emf rises sharply. The end point of this titration is determined by plotting $\Delta E/\Delta V$ against volume of KMnO_4 added.

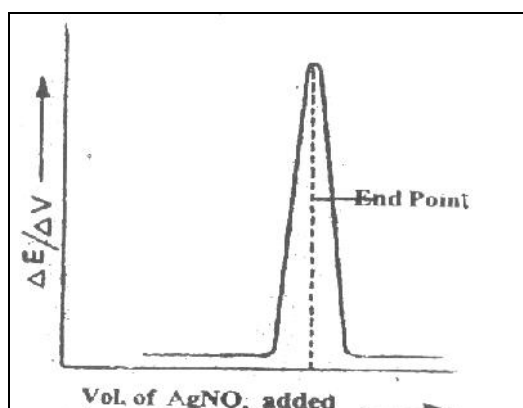


c. Precipitation titration

Consider the titration of AgNO_3 with NaCl solution. A silver electrode (indicator electrode) is dipped in the unknown sodium chloride. It is connected 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:



**STUDY MATERIAL FOR B.SC CHEMISTRY
PHYSICAL CHEMISTRY
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- 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.

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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 Langmuir 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 = 1.0cm^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 $(1-\theta)$

$$r_1 \propto P(1-\theta); \quad r_1 = k_1 P(1-\theta)$$

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

$$r_2 \propto \theta; \quad r_2 = k_2\theta$$

At equilibrium, $r_1 = r_2$

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

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

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



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

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

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

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.

$$\frac{x}{m} \propto \theta ; \frac{x}{m} = k \theta$$

Substituting the value of θ from equation (2)

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

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

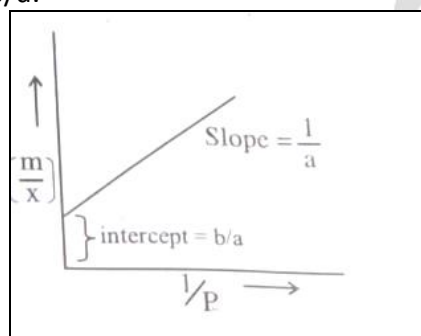
c) Validity of Langmuir isotherm

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

By rearranging,

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

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

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

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

2. When the gas pressure is very high

At very high Pressure $bp \gg 1$.

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

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.

$$\frac{x}{m} = kP^n \text{-----(1)}$$

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

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

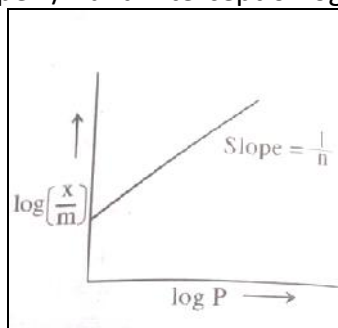
It is called Freundlich adsorption isotherm.



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 n^{th} layer is equal to the coverage of the $(n-1)^{\text{th}}$ 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.

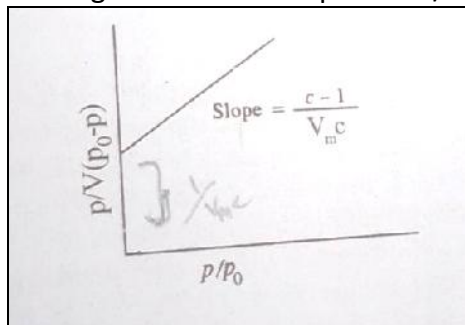
c = Constant depends on the nature of gas.

P_0 = Saturation Pressure



Validity:

The validity of BET can be tested by plotting $P/V(P_0 - P)$ against P/P_0 .
The plot obtained will be straight line with a slope of $c-1/V_m c$.



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 $\text{Pt/V}_2\text{O}_5$ 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 indicators 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.

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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 be 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:

$$\begin{aligned} E C_2 &= C_2 \\ C_2 \cdot \sigma_v(xz) &= \sigma_v'(yz) \\ C_2 \cdot \sigma_v'(yz) &= \sigma_v(xz) \\ C_2 \cdot C_2 &= E \text{ and so on.} \end{aligned}$$

ii)Identity:

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

iii)Inverse:

Since $C_2 \cdot C_2 = E$, 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

$$\begin{aligned} C_2 \sigma_v E \sigma_v' &= (C_2 \sigma_v) (E \sigma_v') \\ &= \sigma_v' \sigma_v = E \quad (\text{or}) \\ C_2 \sigma_v E \sigma_v' &= C_2 (\sigma_v E \sigma_v') = C_2 C_2 = E \end{aligned}$$

v)Commutative property:

It means $AB = BA$. i.e. $E C_2 = C_2$; $C_2 E = C_2$. 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, \dots, A^n form the elements of a cyclic group, here $A^n = E$, the identity element. All the cyclic groups are abelian.

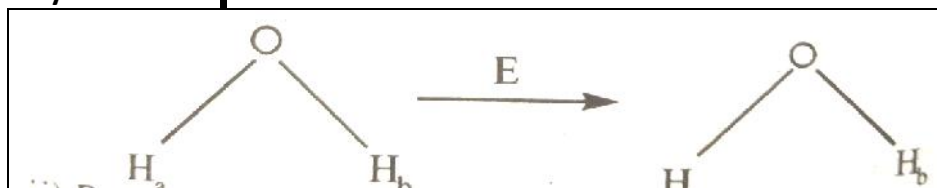
10.Group Multiplication table:

Multiplication table for H_2O molecule:

It is a V – shaped molecule

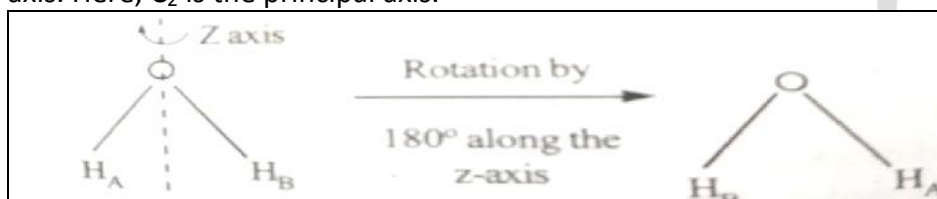


i) Identity element 'E'



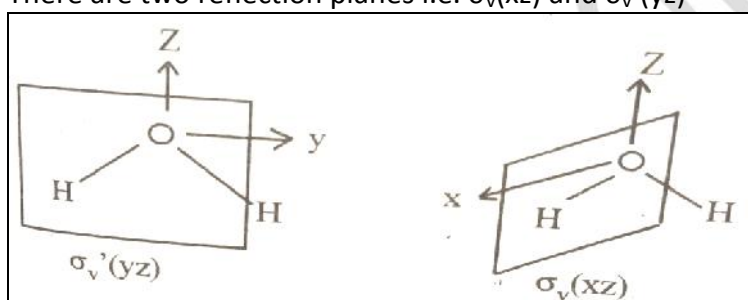
ii) Proper axis of rotation

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, $C_2 \cdot C_2 = E$; $C_2 \cdot \sigma_v = \sigma_v'$; $C_2 \cdot \sigma_v' = \sigma_v$



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
C_{2h}	E, C_2 , 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 (E_{tr})
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.

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

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 $1-100\text{cm}^{-1}$.

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 $200-4000\text{cm}^{-1}$.

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. ($12,500-25,000\text{ cm}^{-1}$).

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 $12,500 -25,000\text{cm}^{-1}$ for visible region, $25,000-66,500\text{cm}^{-1}$ for uv region and $66500 -2 \times 10^6\text{ cm}^{-1}$ for vacuum ultra violet region.

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

Type	Origin	Condition	Selection rule
Rotational spectra	<ul style="list-style-type: none"> Radiation of wavelength 10^{-2} to 10 cm 	Molecule should possess permanent dipole moment.	$\Delta J = \pm 1$ where J= rotational quantum number $\Delta J = +1$ – Absorption $\Delta J = -1$ - Emission
	<ul style="list-style-type: none"> 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.	
	<ul style="list-style-type: none"> 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	



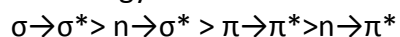
Electronic spectra	• 12500-2500cm ⁻¹ visible region.			<ul style="list-style-type: none"> Spin of the two states involved should be same for allowed transition. $\Delta S = 0$
	• 25000-66500cm ⁻¹ uv region			
	• Electronic transition			
	• UV or			
	Visible region			
Vibrational spectra	• Radiation of wavelength 10 ⁻³ to 10 ⁻⁵ cm	Case I <ul style="list-style-type: none"> Molecules like H₂, N₂, O₂ etc., have stretching motion and no bending motion. Dipole moment does not change. IR inactive 	$\Delta v = \pm 1$, Where vibrational quantum number $v = 0, 1, 2, \dots$ $\Delta v = +1$ – Absorption $\Delta v = -1$ - emission	
	• Due to vibrational transition			
	• Mid and near IR region			
				Case II <ul style="list-style-type: none"> Heteronuclear diatomic molecules like CO, NO etc and polyatomic molecules like CO₂, H₂O, CH₄ etc., possess change in dipole moment. IR active

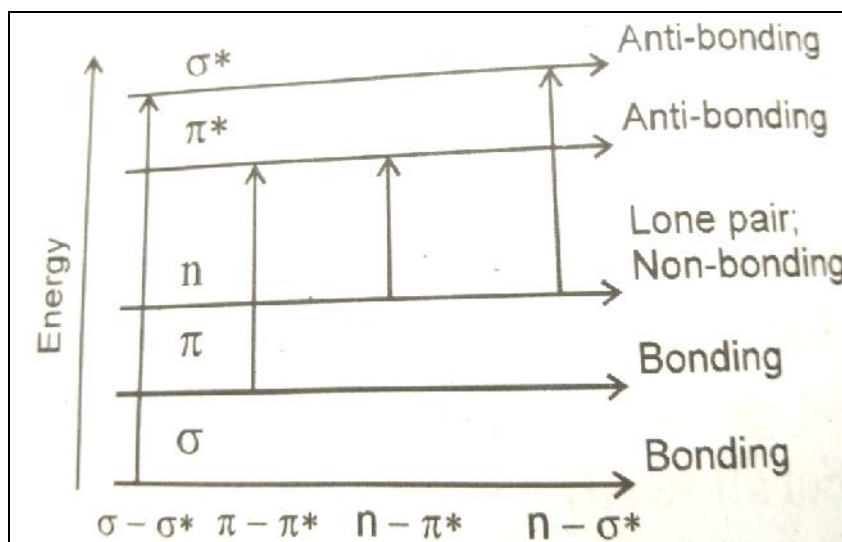
6. Electronic spectroscopy:

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 (σ^*, π^*) 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.





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

a) $\sigma \rightarrow \sigma^*$ transition

The transition of an electron occurs from a bonding sigma orbital of molecule to the higher energy antibonding sigma orbital is known as $\sigma \rightarrow \sigma^*$ transition. These 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) $\pi \rightarrow \pi^*$ transition

The transition of an electron occurs from π bonding orbital to π^* orbital is known as $\pi \rightarrow \pi^*$ 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) $n \rightarrow \sigma^*$ transition

The transition of an electron occurs from the non-bonding orbital of the ground state to the antibonding sigma orbital is known as $n \rightarrow \sigma^*$ 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) $n \rightarrow \pi^*$ 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).

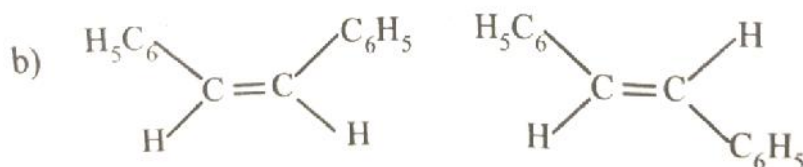
iii) Chemical kinetics

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.

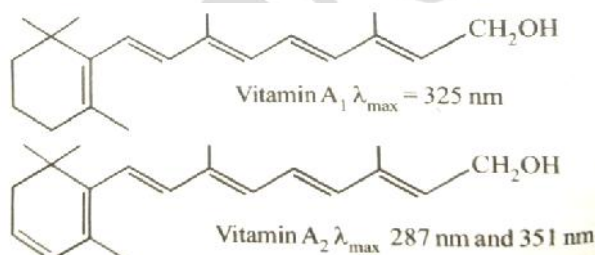
Example: a. cis-2-alkenes $\lambda_{\max} = 176\text{nm}$; trans-2-alkenes $\lambda_{\max} = 179\text{nm}$



b. cis-stilbene ($\lambda_{\max} = 280\text{nm}$); trans-stilbene ($\lambda_{\max} = 296\text{nm}$)

v) Elucidation of vitamin A and K

Electronic spectra are very much useful in elucidating the structures of Vitamin A₁ and A₂ and K₁ and K₂.



Vitamin A₁ absorbs at 325nm while Vitamin A₂ 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 $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ 1,3- pentadiene $\lambda_{\max} = 223\text{ nm}$

$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ 1,4-pentadiene $\lambda_{\max} = 182\text{ nm}$

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	$\text{CH}_2=\text{CH}_2$	165
1,3 butadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	217
1,3-pentadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$	223
1,3,5-hexatriene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	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.

- Stretching
- Bending

a. Stretching vibrations:

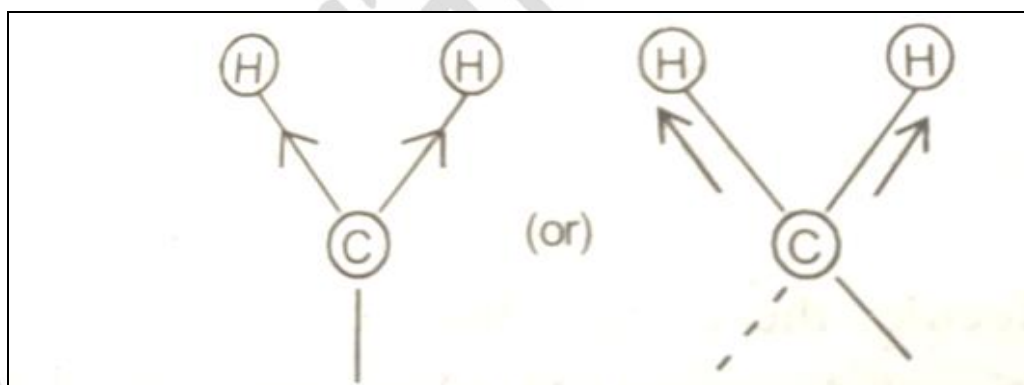
In this type, the distance between the two atoms (bond length) increases or decreases but the atoms remain in the same bond axis. Stretching vibrations require higher energy and occur at high frequency.

Stretching vibrations are of two types:

- Symmetric stretching
- Asymmetric stretching

i. Symmetric stretching

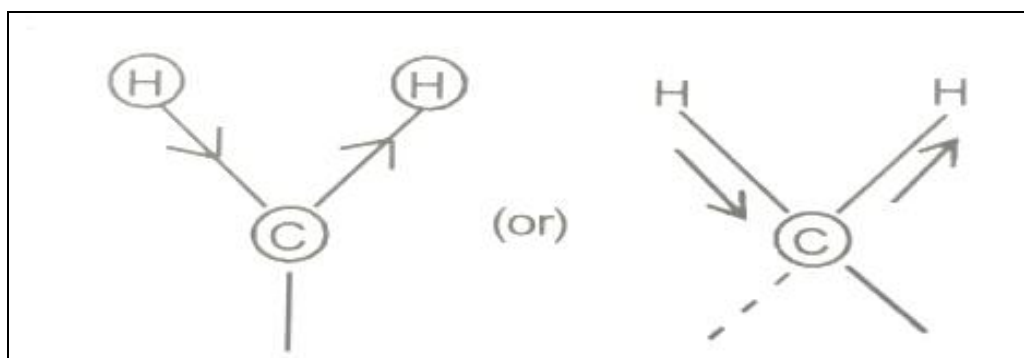
In this type both the atoms move in and out simultaneously



Symmetrical stretching of $-\text{CH}_2$ group

ii. Asymmetric stretching

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





Asymmetric stretching of $-CH_2$ 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

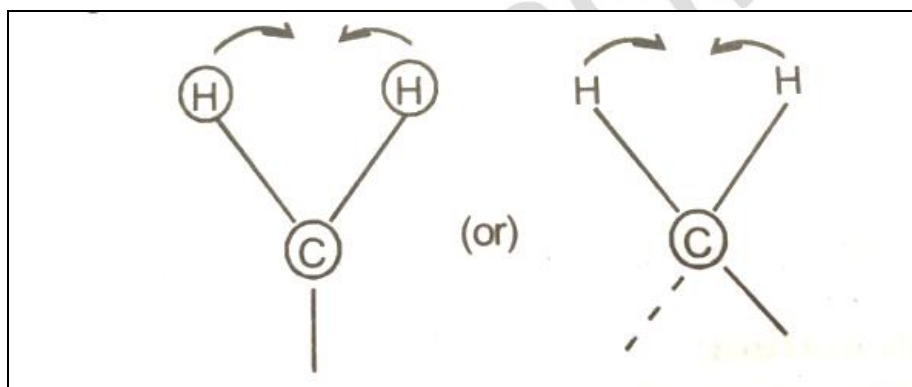
When the atoms bend, finally the atoms remain in the nodal plane of the system is called in-plane bending.

These vibrations are of two types:

- a. Scissoring deformation
- b. Rocking deformation

a. Scissoring deformation

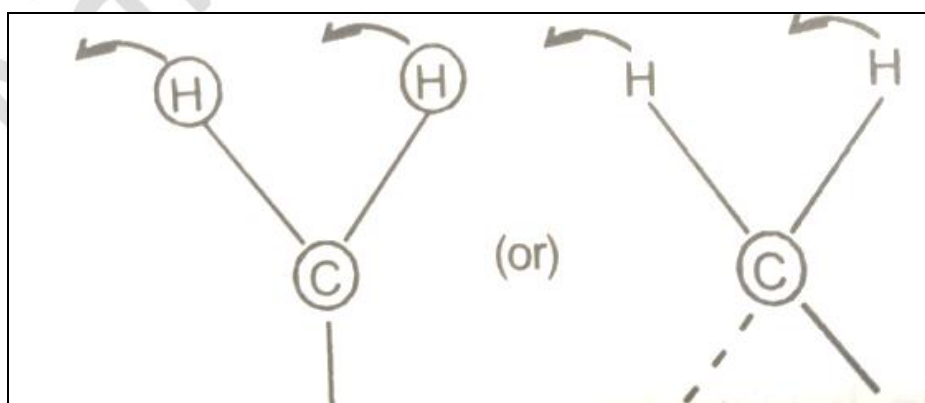
In this type, both the atoms swing to the opposite side.



Scissoring of $-CH_2$ group

b. Rocking deformation

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



Rocking of $-CH_2$ 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.

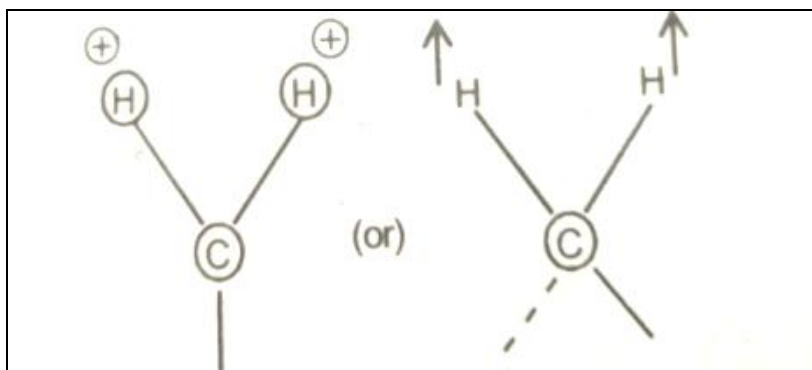


These vibrations are of two types:

- Wagging deformation
- Twisting deformation

a. Wagging deformation

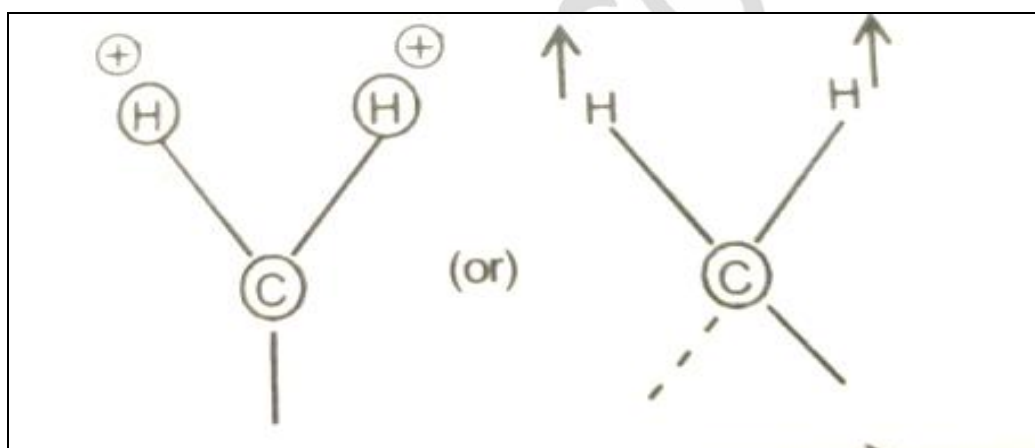
In this type, both the atoms swing up or down out of the plane of the papers.



Wagging of $-CH_2$ 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 $-CH_2$ 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:

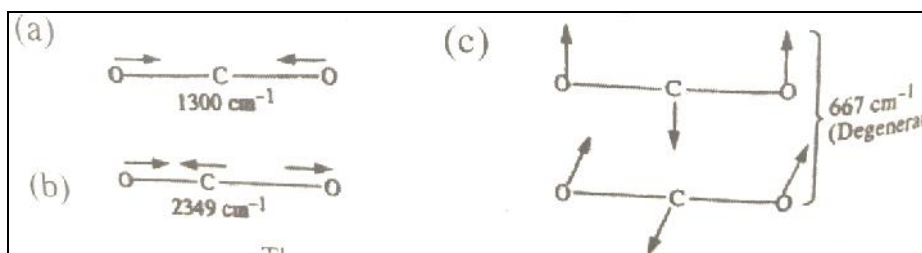
CH_2 (deformation)	$1470-1440\text{cm}^{-1}$
Trans alkene(C=CH)	$1000-950\text{cm}^{-1}$

10. Mode of vibrations of poly atomic molecules



1. Normal vibration modes of CO₂ molecule

CO₂ is a linear molecule. Hence,
the normal modes of vibration of CO₂ is $3(3) - 5 = 4$



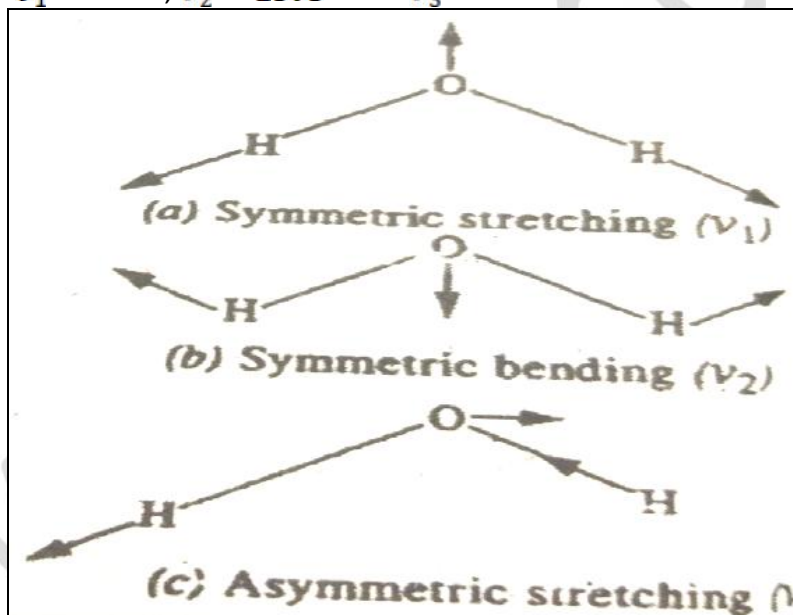
The normal modes of vibration of CO₂

- Symmetric stretching $\bar{\nu}_1 = 1330\text{cm}^{-1}$ IR inactive
- Asymmetric stretching $\bar{\nu}_3 = 2349\text{cm}^{-1}$ IR active
- Symmetric bending and Scissoring $\bar{\nu}_2 \text{ cm}^{-1} = 667\text{cm}^{-1}$
Thus two bands are observed in IR spectra.

2. Normal modes of vibration of H₂O molecule

H₂O 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

$$\bar{\nu}_1 = 3651.7, \bar{\nu}_2 = 1595 \text{ and } \bar{\nu}_3 = 3755.8\text{cm}^{-1}.$$



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 1700cm^{-1} . The actual position of the band depends upon the nature of groups attached to the carbonyl group. The carbonyl group is present in variety of organic compounds like ketone, aldehydes, carboxylic acids, amides, esters etc.

Example: Ketones $1730\text{-}1645\text{ cm}^{-1}$
Aldehydes $1740\text{-}1690\text{ cm}^{-1}$

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 $3650\text{-}3580\text{ cm}^{-1}$. But for the hydrogen bonded hydroxyl group lowers the absorption frequency and appears as a **broad band** at $3590\text{-}2600\text{ cm}^{-1}$.

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.

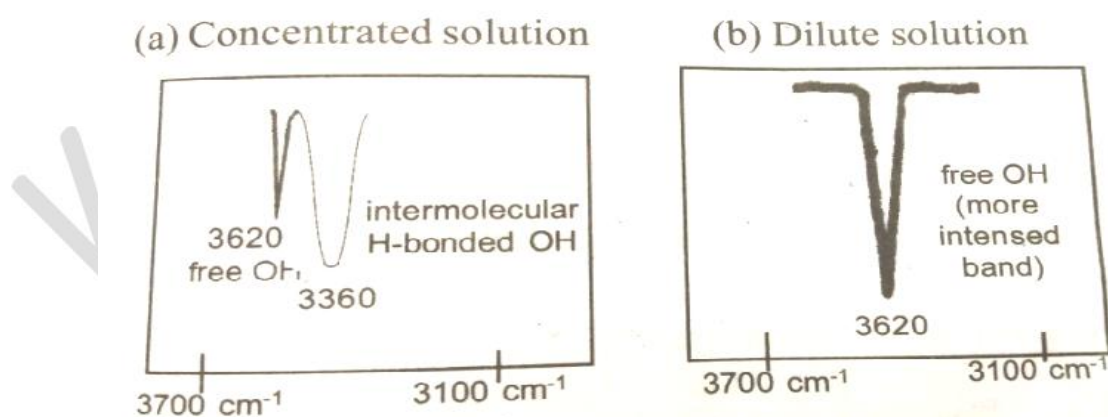
Intermolecular H-bonding

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

Example:

The IR spectra of ethyl alcohol in CCl_4 (concentrated solution) gives two O-H absorption bands at 3620cm^{-1} (sharp band due to free OH) and 3360cm^{-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 3360cm^{-1} decreases and finally disappears. Hence for dilute solution of ethyl alcohol, only one highly intensified absorption band at 3620cm^{-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



**STUDY MATERIAL FOR B.SC CHEMISTRY
PHYSICAL CHEMISTRY
SEMESTER - V, ACADEMIC YEAR 2019-20**

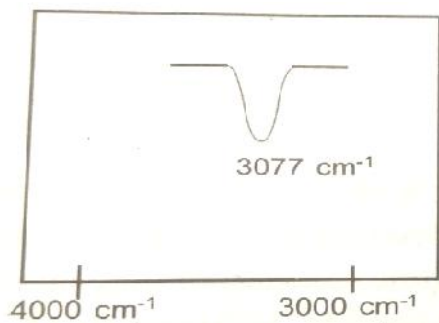


The IR spectra of concentrated solution of methyl salicylate gives an absorption band at 3077 cm^{-1} . This band is due to intra molecular H-bonded OH. This appears as a shallow (low intense) broad band. On dilution, this absorption band remains unaffected.

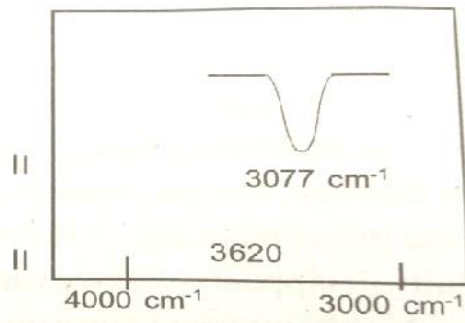
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a. Concentrated solution (1.0M)



b. Dilute solution (0.031M)



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

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