UNIT-I

Spectroscopy

NMR spectroscopy:- **Introduction**:- NuclearMagnetic Resonance Spectroscay

NMR spectroscopy discovered in 1946 by American Physicist F.Bloch and E-Mpurcell who should haved in 1952 physics Nobel prize. The NMR Spectrum exhibit the atom which is having net Nuclear Spin value (1+0)) The following rules are helpful predicting the Nuclear Spin

If A mass number = odd number Nucleous I = halt integrals " 3 ^ 1 * P = 1/2 , 11 B + 3/2 H = 1/2 0 = 5/7

If the mass number and atomic number are even number mass number is even and atomic number id A even, z = cdd , T = integral value, 63.3.... partial O partial H 1 =1 4pi*N_{7} odd NMR spectroscopy in a -copy in branch of obsorption Spectros which the radiowave frequency induced tramition between another level of atoms.

***Theory and Principle** :(when ever any one a magnetic nucleous is placed in a magnetic field magnetic No magnetic nucleous assum She stare magnetic of Splb of the 21+1 Orientations coirth respective in the direction of applied magnetic field)

* In the absence of magnetic field the Spin states of nuclei -erate spin States. when field the Levels degeneracy are present in doubly dege coe apply the magnetic is remove at and the energ can be split into two non-degerate energy States. X

Them quantum mechanics it is energy known that of interaction of nuclear magnetic mom external magnetic field (H), applied in -the (4) with an -the 2-direction is given by. Where MI = Energy Net Nuclear Spin IN B Nucleour 'g' factor = shor magnetor beta = (eh)/(4pi*MC) for a proton, M_{I} = H_{2}/2 E + 1 2 = mp 1/2 * g_{N}*beta*H - (3) E - 1/2 =+ 1 2 g N beta.

Chemical shift - **factors effecting chemical shitt:**

- Chemical Shitt is the most important factor in NMR Spectroscopy.

* Chemical shift may be defined as the difference between pression frequency of sample proton and reference protons)

* The position of signals in NMR spectroscopy car be explained on the basis chemical shitt value.

* chemical shift are depends upon the strength of the magnetic field (or) frequency of instrument. (Chemical shift sample - Dreference frequency of instrument (in Hz)

- Where sample = frequency of sample protons "Frequency = frequency of reference protons).
- In NMR spectroscopy the most widly used meta compound is tetra methyl silane (TMS) .
- The reasoη for used for TMS as reference.
- It has 12 equivalent protons. so, it gives a single short in ito NMR spectrum.

EX $CH3-CH2-OH$

- **Measurement of chemical shift**
  Chemical shift can be measured in two types of scales.
  1. Delta scale
  2. Tou scale

Factors affecting the chemical shift

Two types of factors effecting the chemical shift.

a. Intra molecular factors
- Inductive effect
- Vanderwalls deshelding
- An isotropic effect

b. Inter molecular bonding
- Hydrogen bonding
- Temperature
- Solvent

highly volatile substance so, it can be remo

sample easily.

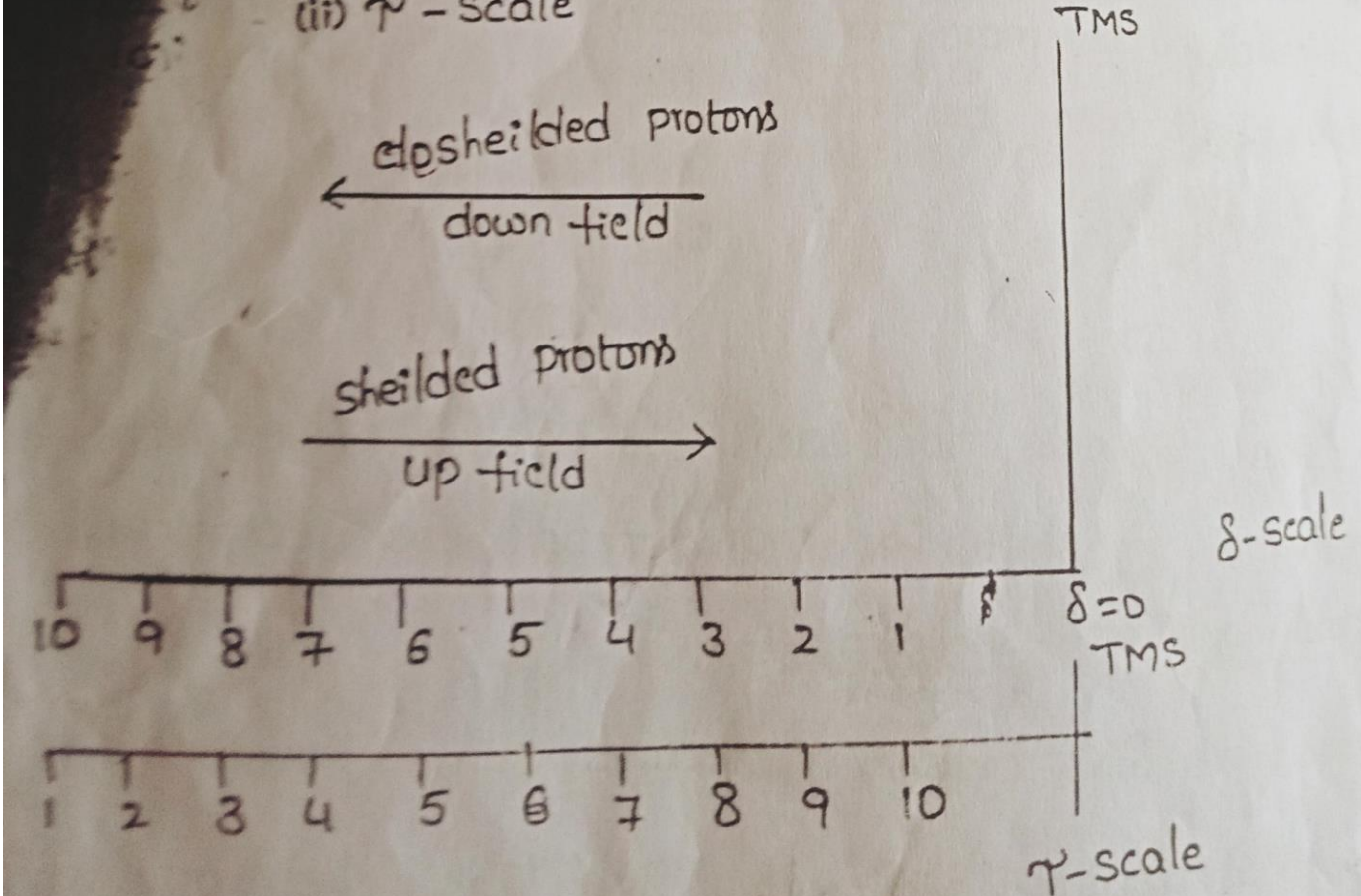
chemically inert compound.

ment of chemical shift :—

chemical shift can be measured in two types of

(i) δ- scale

(ii) τ - scale



inter

In NMR Spectroscopy the two scales are inter related by the following

(a) (i) **Inductive effect**:- A proton is said to be deshelding it is attached with an electro negative atoms or group deshelding is more for proton then it's chemical shift value will also be more.

CH3-CH2-I. CH3-CH2-F

ii. **Vanderwalls deshelding**. In bulky molecules some protons may be occupied sterically hendred position. The electron cloud and the bulky group will tend to repul the electron cloud eason chemical shift.

iii. **Ani isotropic effect**. **Non** uniform space distribution in a molecules is called Ani isotropic.when electron molecules is placed magnetic field.

Iv.**Hydrogen bonding**. Increase in the strength of the hydrogen bonding chemical shift value is also increases.

V.**Temperature.** Increase in temperature of the hetero atom proton compound the chemical shift value is also increases.

Vi.**Solvent If the** polarity **of the** solvent then **c.s also hetero atom** proton **is also** increases.

A Proton is said to attached with be desheiding it it is an electro-negative atom (or) group(24 compound the cherm desheilding is more for proton then its chemical shitt value will also be more.

(ii) vandurwalls De-Sheliding:-

bulky molecules some protons may occupy sterically hendered position. The clectron cloud & the bulky group -unding will tend to repul the election cloud Sun then the the proton. Hence, such) proton will be resona at down field with high chemical shitt value. If the generated Magnetic field is distribcde.

(iii)-Anisotropic Effect: non uniformly Ps called Anisotropic effect.

This is gbserved in alkena & alkyna Deshielding formly at different regions, then it Non uniform Space distribution in a molecule in Spin Spin interacti called -Anisotropic When TT-electron molecule 18 placed external magnetic field, T electron cloud produces .

(**Hydrogen Bonding**:Increase inthe strength of the hydrogen bonding chemical shift value also increases.

(v) **Temperature**:

Increase in temperature of the hetero atom proton compound the chemical shift value also increases.

(vi) **Solvent**:

It In the polarity of the Solvent then c.s also↑ Polar Solvents chemical shitt values of more hetero atom protons is also increases due to dipole-dipele interaction.

Acidic character:-

With increase in acidic character of proton chemical Shift values are also increases.

Spin spin coupling in NMR spectroscopy:

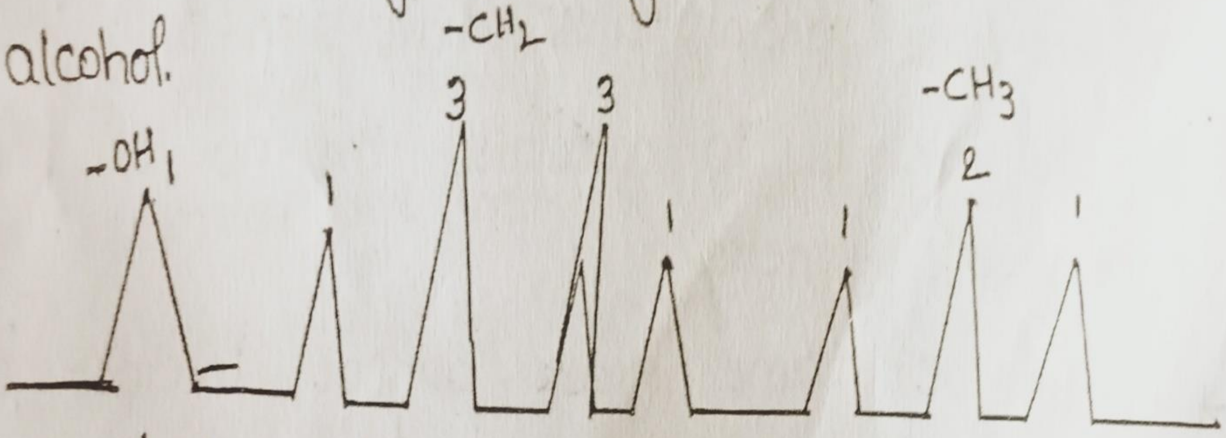
- The interaction blw the spins of Neighbouring nuclei in a molecule cause the splitting of lines in the NMR Spectrum. This is known as Spin-Spin coupling)

- The Area under the broad NMR signal and the total area under the splitting signals remains same. -

- The splitting of lines arises as a result of nuclear Spin Spin interaction.

- The first compound invistigated under NMR Study ethyl alcohol. The high invistigated under NMR Spectrum of ethyl alcohol.

ethyl alcohol.



high resolution NMR spectrum of C_2H_5OH

high resolution NMR spectrum of C2H5OH

The Spin-spin coupling -ted below. in ethyl alcohol as illustrated

CH3-CH2-OH

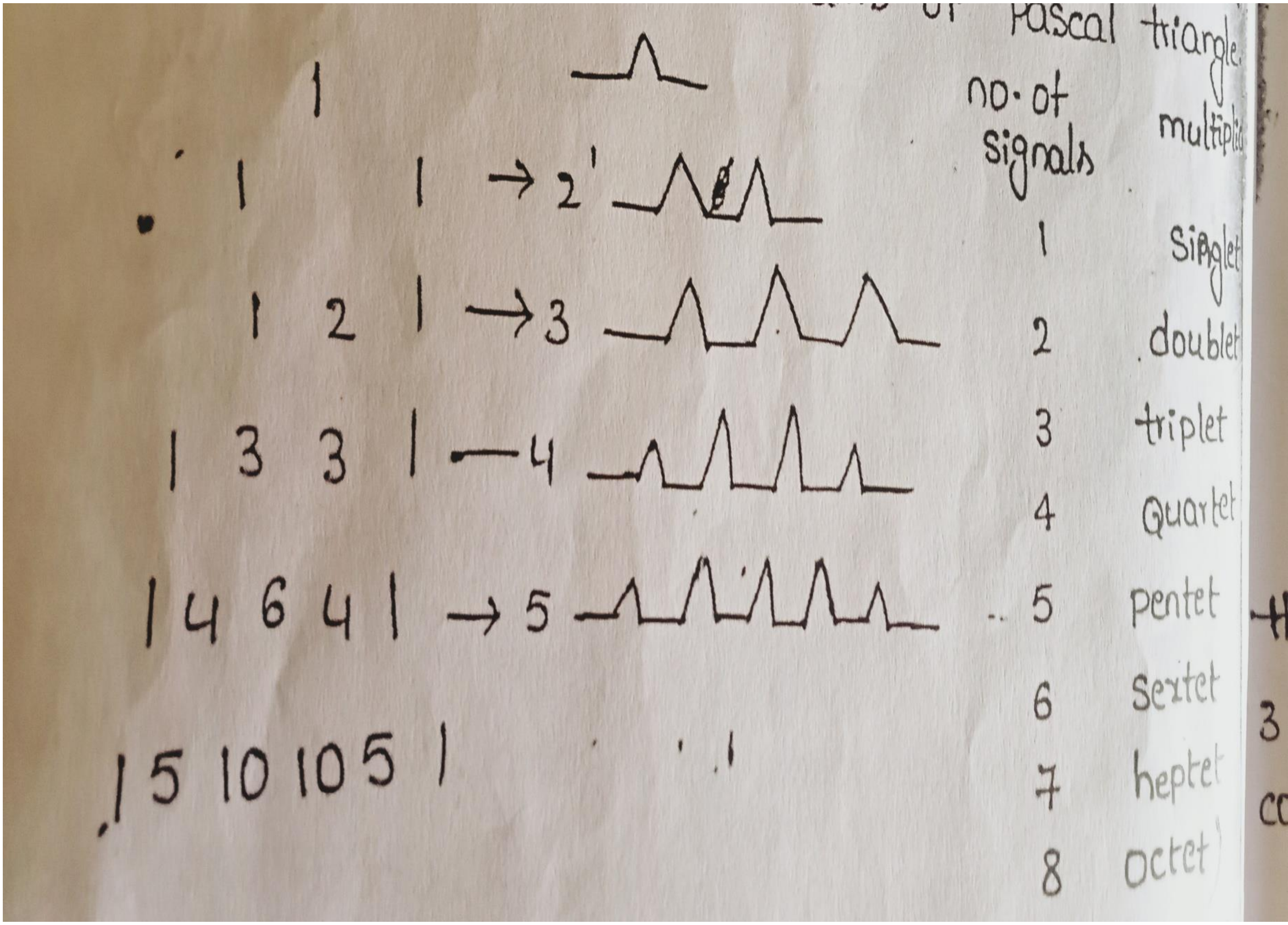
3 Possible local fields - Orientations of CH□ protons produce 3 dite at CH3 Protons. Thus splitting of CH□absorpt ion peak into a triplet with relative intensity ratio

1:2:1.

4 possible orientations of methyl protons prat 4 different local fields at CH□ protons. Thus the splits of CH protons into a "Quartet".

The OH protons in NMR spectroscopy does no play spin-spin interaction because it is away from methylene and methyl proton.

The intensity of signals in NMR spectroscopy explained on the basis of Pascal triangle.



Pascal triangle.

1

1 1 → 2

1 2 1 → 3

1 3 3 1 — 4

1 4 6 4 1 → 5

1 5 10 10 5 1

no. of signals	multipli
1	Singlet
2	doublet
3	triplet
4	Quartet
5	pentet
6	sextet
7	heptet
8	octet

There are in the are general rules above Spin-Spin interactions helpful in calculated the no. of lines NMR spectra.

protons of same group do not interact among themselves to Cause Observable splitting.

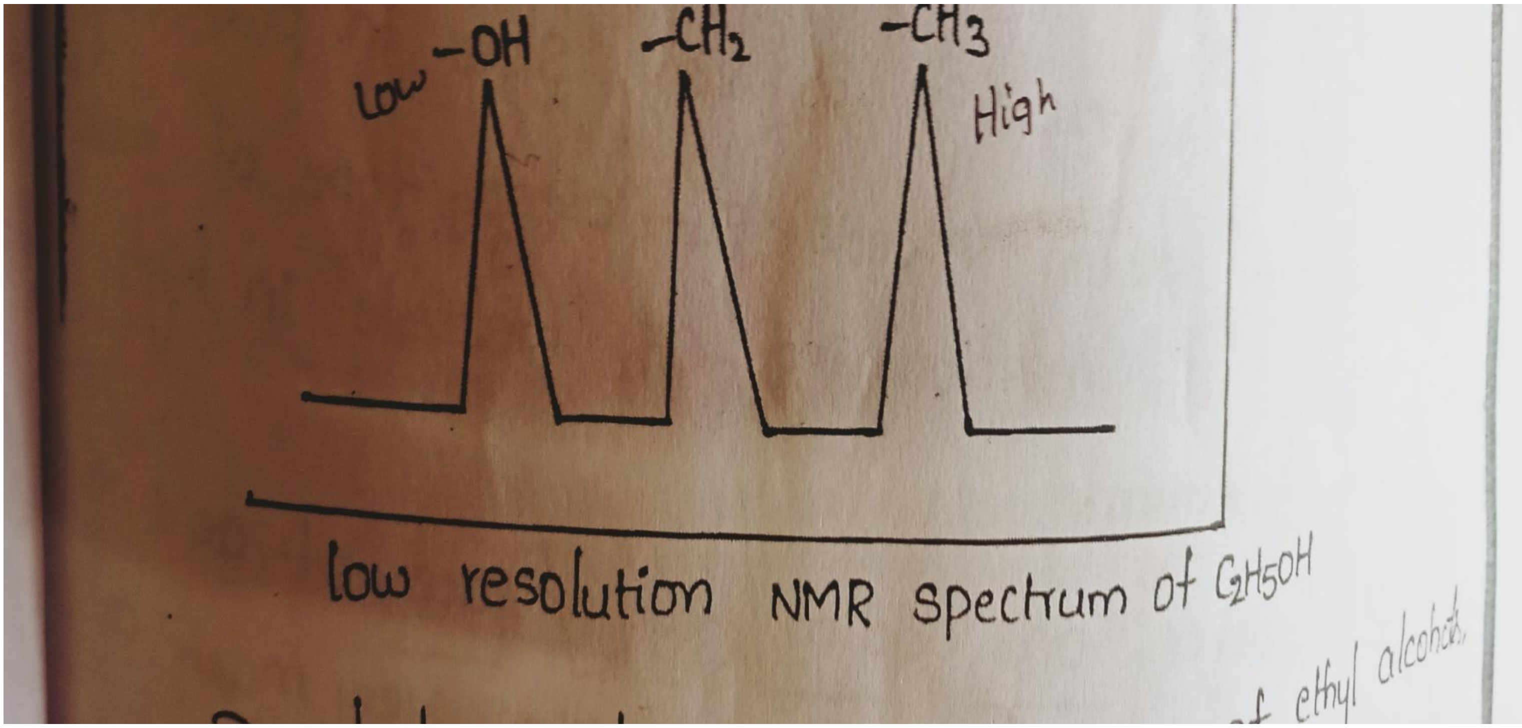
* The multiplicity of the peak of a group of equivalent protons is determined by neighbouring protons.

In general It "n" equivalent in protons connected to neighbouring carbonatom. The resonance peak is split into (nti) peaks.

Applications of NMR spectroscopy

Structural eluciadation of ethyl alcohol (CH□CHOH) (ethanol.

The low resolution NMR spectrum of ethyl alcoh of comits of speaks corresponding to OH-protons, methyl protons, Methylene protons. In these 3 peaks, Methyl protons resonate at high field. OH protons resonate at low field and methylene protons resonate at in blw there two fields.



low resolution NMR spectrum of C2H5OH

In high resolution NMR spectrum of ethyl alcohch. the absorption peak of methyl protons coill split into 3 peaks with relative intensity 1:2:1 due to spin-Spin coupling.

The absorption peak of methylene protons split into 4 peaks with relative intensity 1:3:3:1. In a very high resolution spectrum the mettylene protons will split into out with relative intermities 1:1:3:3:3:3:1:3.3.1.

ESR Spectroscopy

Electron spin resonance

Introduction:-

Electron Spin resonance spectroscopy is a be of absorption. Spectroscopy frequency is absorbed by in which the microwa the sample solution.

* This technique was introduced by "zovoiskir" in 1944.

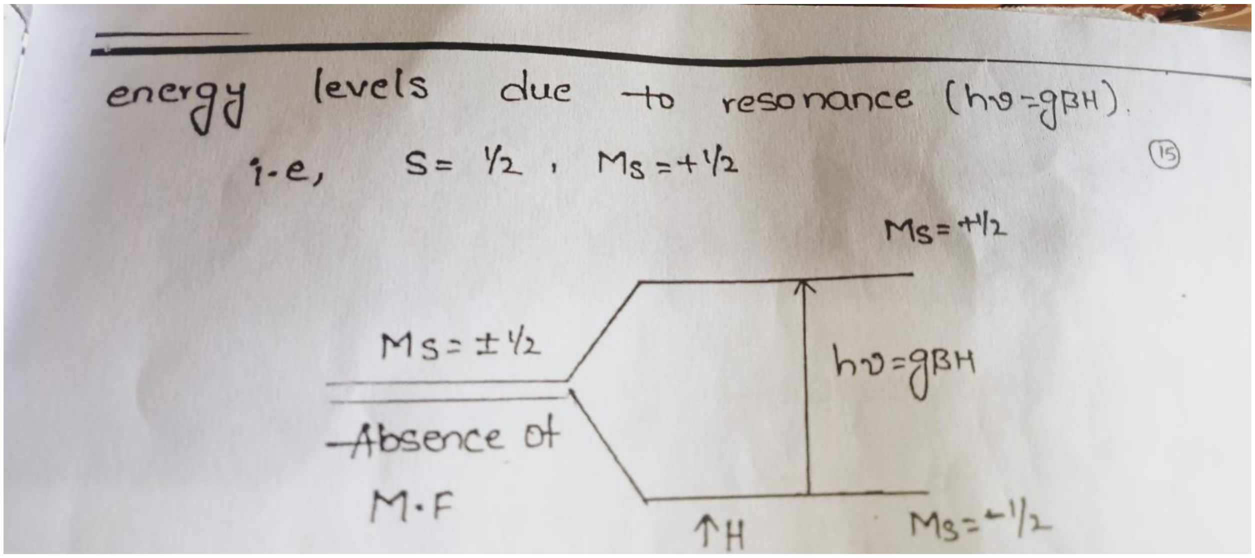
* The ESRS exhibits the compounds which is har the number of unpaired election.

+ from ESR Spectra information we can furnishes (toget) 10 about Structure of molecule. polarity, phase transformations and chemical reaction.

* **Theory and principle**:

When is ESR spectrum is recorded for the having the number of unpaired cle present in doubly degen apply the external magr degeneracy be split is remov into (or) energy state is passed through which the energy levels Spin states. When we field to the sample the and the energy Non - degenerate *The microwave levek can Spin State - frequency Sample solution, the tramitions occurs below.

energy levels due to resonance (hv=gpH)



energy levels due to resonance ($h\nu = g\beta H$).

i-e, $S = \frac{1}{2}$, $M_S = +\frac{1}{2}$

*__gfactor__:

The position of signals in ESR be explained on the basis of g-factor. fror. resonance condition. Spectroscopy.

The Value of is not constant for free electron g=2.0023 for Dp PH=92-0036 for transition metal complex 9-2-000.

The value of 'g is of 2 types

1. Isotropic value

2. Anisotropic 'g' value

1. **Isotropic g value:-**

Isotropic & value is the value which * DPPH depends upon the orientation of molecule in the But it for example gx=gy,gz a for cubic crystal.

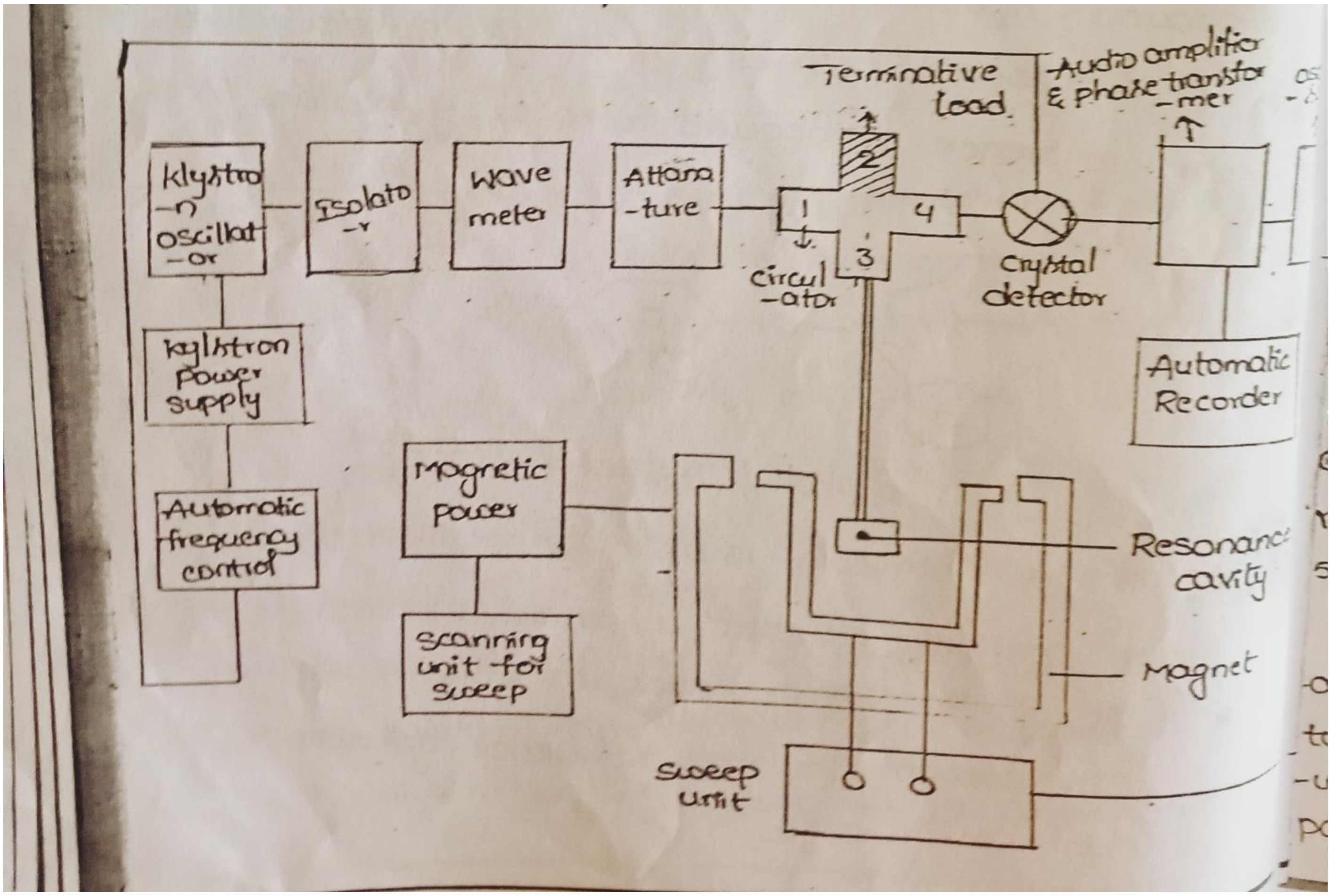
DP PH

* The ESR spectrum will show two signals for reterence compound and unknown compound.

* from this we can calculate the field seperate to (ΔH)- SO, value of 'g' is g=gs.

* **Instumentation of ESR Spectroscopy:-**

The are ESR Spectroscopy different types of Sped used. The most important spectrometer -meters is shown as follows.



The decription of various components of ESR spectrome ter is as follows.

1. **Source**:- The various components of source are

(a) **klysron**.

The most of ESR spectrometirs the source is klystron oscillator which is operating in micromave radiation A klystron oscillator is a vaccum tube which can produce microwave oscillations. A klystion which cans prod is generally operated at 9500 mc/sec.

b.Isolater.

Isolator is strip of ferrite material which minimzations the vibration in microwave frequency prodewek Produced by a klystion Oscillator.

C.**Wave meter:**

Wave meter is put in between isolator and attanature. known trequency of micro wave are passed trough it.

d) **Attanature**:-

It is present in blw Wavemeter and Eirculator cwhich adjust the level of me microwave radiation

5) **Circulator**:-

The microucave radiations produced by klystion oscill ator are passed through isolator, wavermeter and attana ture and finally entered into the circulator. The micro -wave radiation enter into the circulator is finally passed through the Sample

The decription of various components of ESR spectrome ter is as follows.

1. Source:- The various components of source are

(a) klystion: -

The most of ESR spectrometirs the source is klystron oscillator which is operating in micromave radiation A klystion oscillator is a vaccum tube which can produce microwave oscillations. A klystion which cans prod is generally operated at 9500 mc/sec.

Isolator is strip of ferrite material which minimi zes the vibration in microwave frequency prodewek Produced by a klystion Oscillator.

Wave meter:

Wave meter is put in between isolator and attanature. known trequency of micro wave are passed trough it.

4) Attanature:-

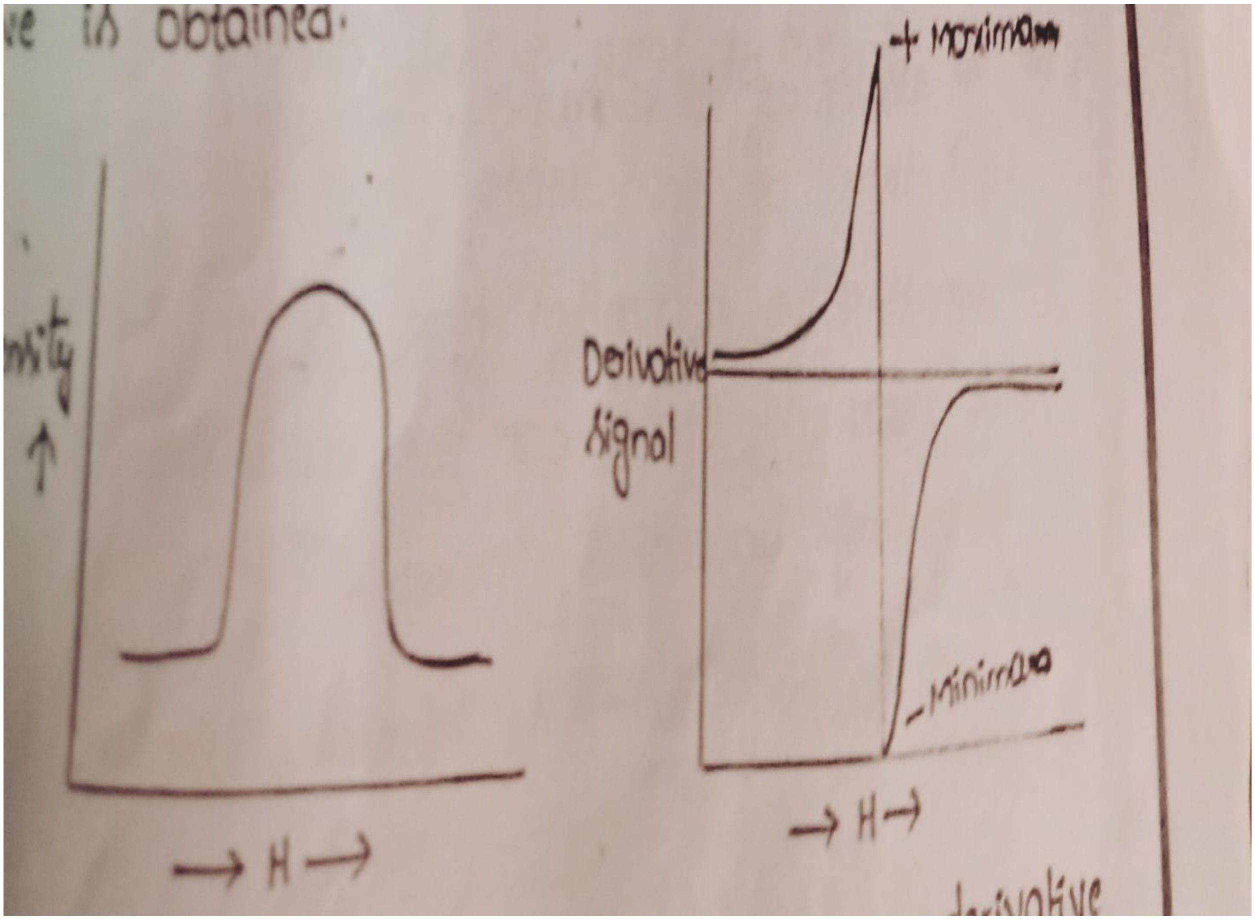
It is present in blw Wavemeter and Eirculator cwhich adjust the level of me microwave radiation-

5) Circulator:-

The microucave radiations produced by klystion oscill ator are passed through isolator, wavermeter and attana ture and finally entered into the circulator. The micro -wave radiation enter into the circulator is finally passed through the Sample.

* **Line with and line shapes** in **cafe spectroscopy**

Line shapes:



ESR Spectrum is obtained by plotting intensity against strength of magnetic field. A single absorption curve is obtained.

The ESR Spectrum is represented as a derivative mode.

The derivative curve comits of one maxima ard one minima

Each negative slope in clerivative curve represents, a Peak in the absorption spectrum.

Therefore the number of peaker in the absorption Curve can be determined from. The no of minima (or) maxima in the derivative Curve.

* The total area under the curve 16 directly proportional to the no. of unpaired electrons present in the sample.

*TO calculate the no. of unpaired in the unknown Sample comparision is made cwith a reference compound which is having the known no. of unpaired electron.

* The most widely spectroscopy is DPPH. uned reference compound

DPPH TS a chemically stable compound it hol Splitting factor. 9=2.0036 and it contain 15 unpaired electrons/gram.

Line Width:

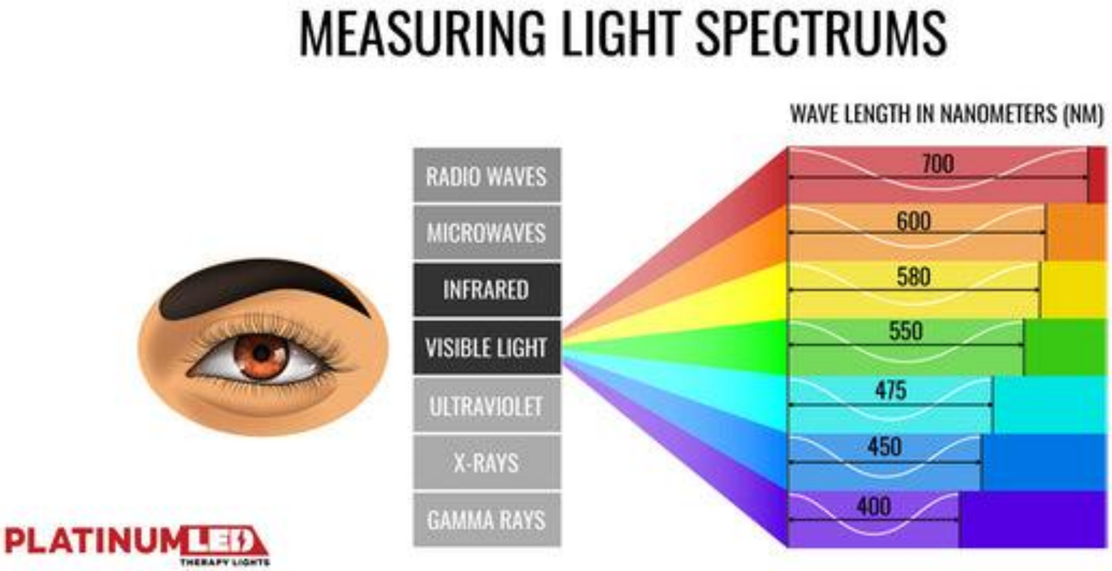
* The width of ese signal depends up the red the bro -on time of spin state under study for mor Samples the relaxation time is 16 ^ 7 sec. The high -on time of state can be calculated by using The major Heisenberg uncertainity Principle

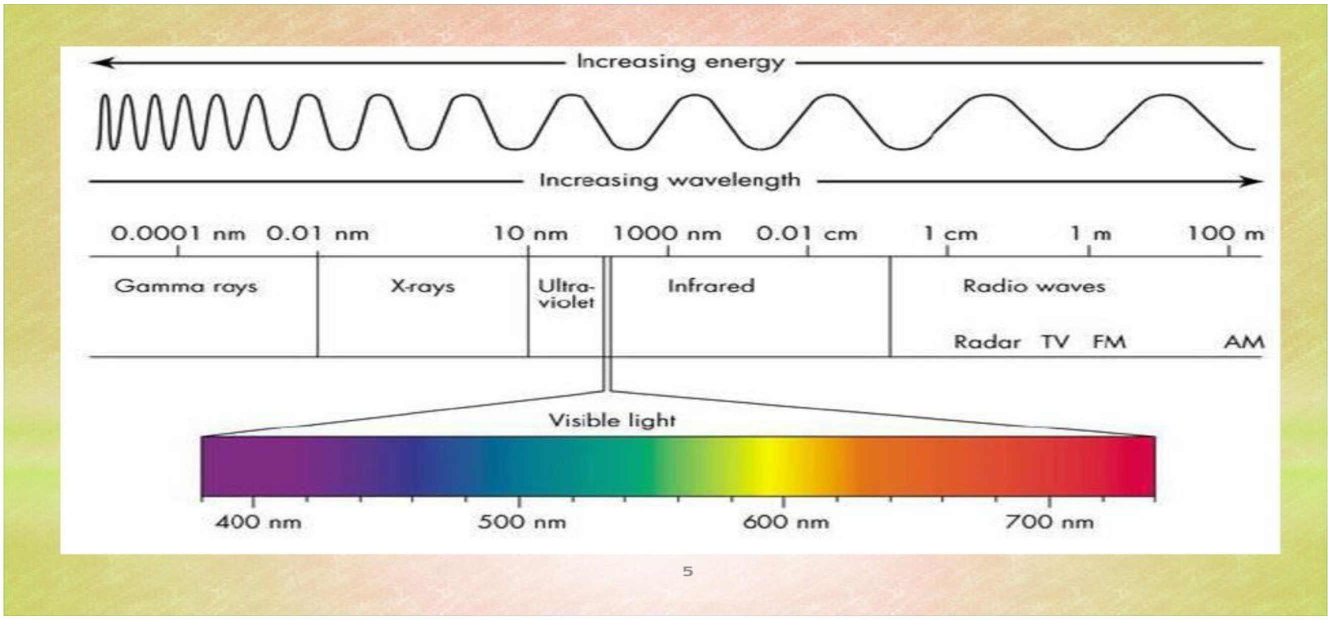
According to this principle Delta*epsilon*Delta*t = b/(Delta*pi*t) Delta*c = 1/(Delta*t) * h/(4pi) WKT e=ho Δε= hov from& h*Delta*D = 1/(Delta*t) * h/(a*pi) Delta*v = 1/(Delta*t) * (1/(2pi)) Delta*t = 1/(Delta*rs) * 1/(2pi)

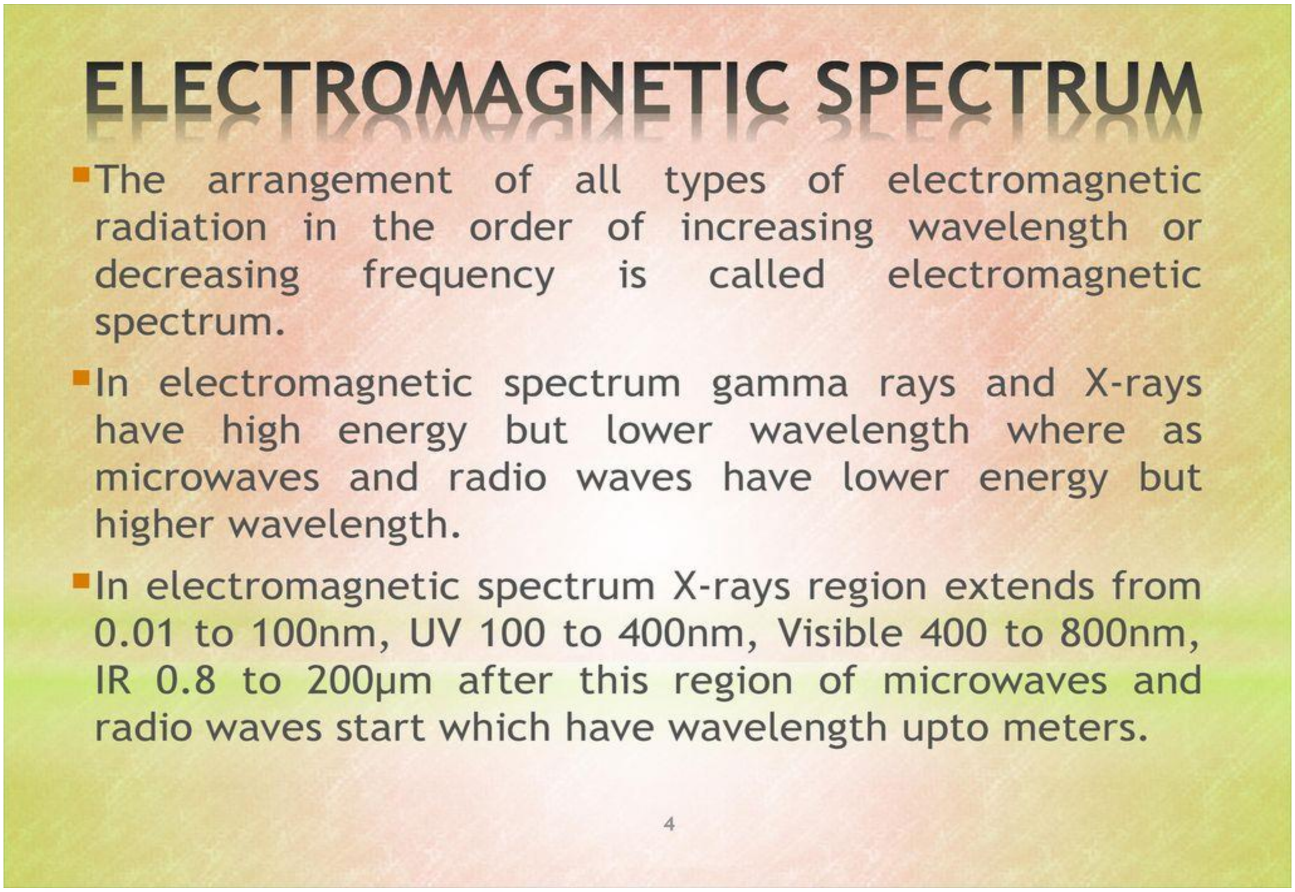
from this equation. we can caloubits the (anz+1) multiple -on. of spin State which is depends upon the If the electr of spin state.

PHOTO CHEMISTRY

- Photo chemistry is the branch of chemistry concerned with the chemical effects of light.
- Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wave length from 200 – 400 nm), visible light (wave length from 400 – 750 nm) or infrared radiation (wave length from 750 – 2500 nm).







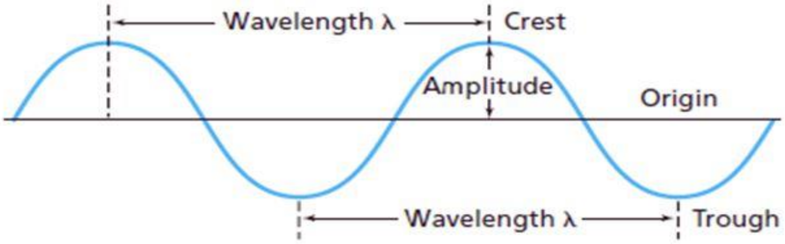
ELECTROMAGNETIC SPECTRUM

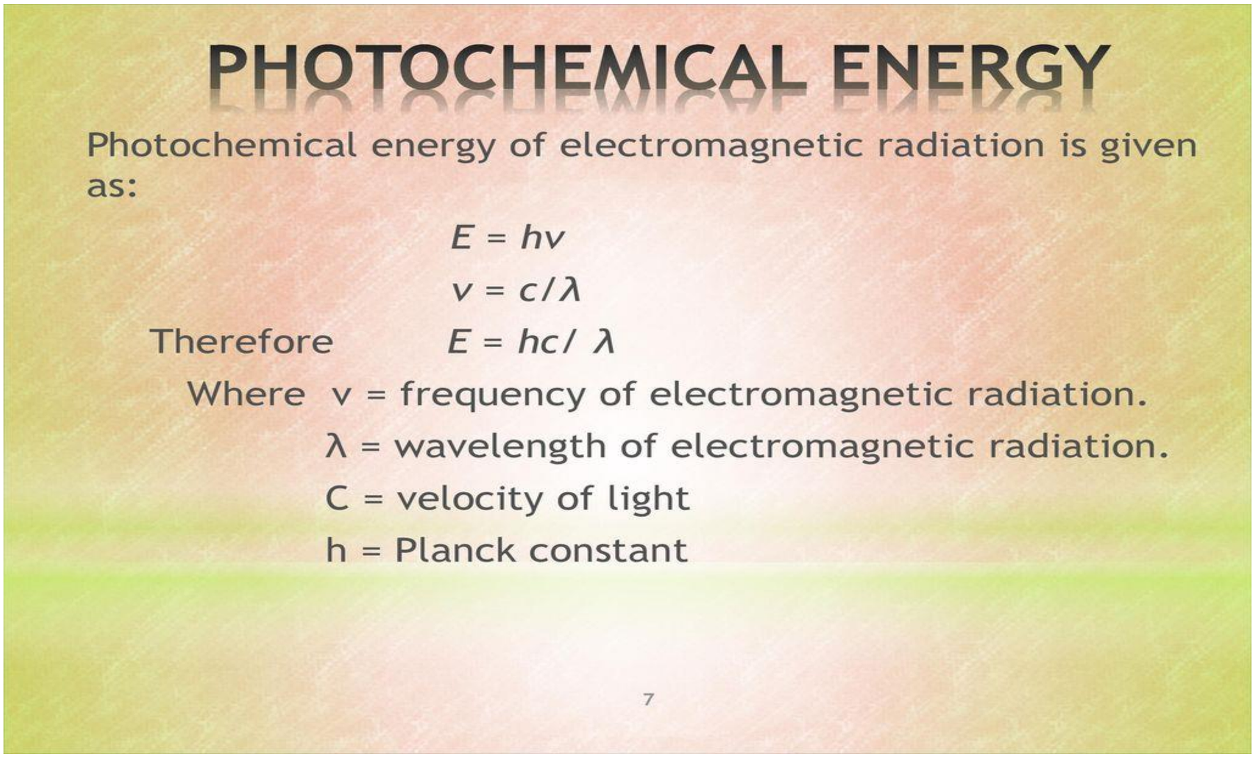
- The arrangement of all types of electromagnetic radiation in the order of increasing wavelength or decreasing frequency is called electromagnetic spectrum.
- In electromagnetic spectrum gamma rays and X-rays have high energy but lower wavelength where as microwaves and radio waves have lower energy but higher wavelength.
- In electromagnetic spectrum X-rays region extends from 0.01 to 100nm, UV 100 to 400nm, Visible 400 to 800nm, IR 0.8 to 200μm after this region of microwaves and radio waves start which have wavelength upto meters.

Electromagnetic Radiation

- Defined as energy that exhibits wavelike behavior.
- Waves are characterized by:
  - **Wavelength (λ)**: The distance between successive crest or troughs. Measured in m, cm, nm.
  - **Frequency (υ)**: The number of waves that pass a given point per second. Measured in 1/s (s^{-1}) or Hertz (Hz).
  - **Amplitude**: The waves height from the origin to the crest or the trough.
  - **C = speed of light, is a constant** (always known, never changes) = **3.00×10^8 m/s**

$c = \lambda \times \upsilon$





PHOTOCHEMICAL ENERGY

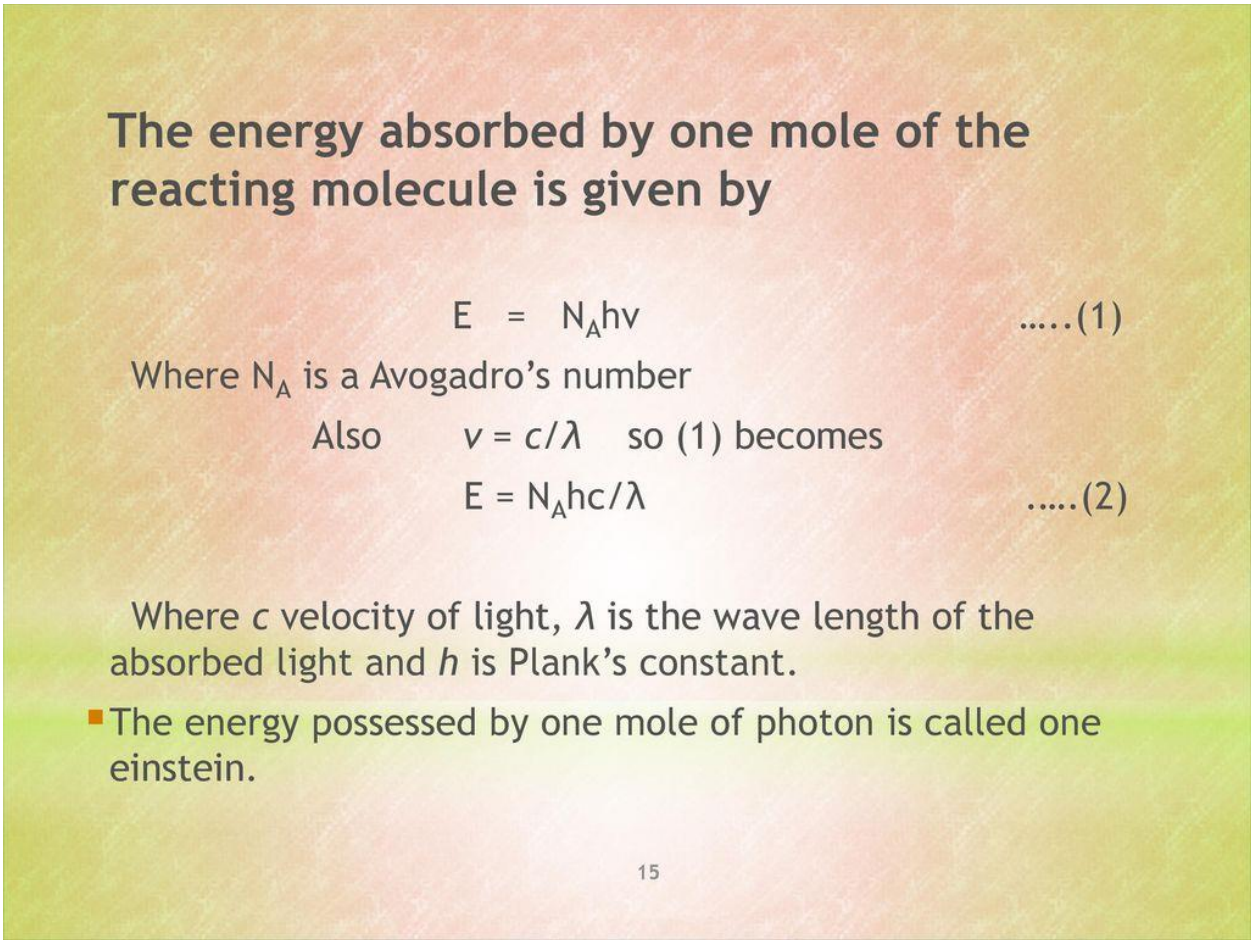
Photochemical energy of electromagnetic radiation is given as:

$$E = h\nu$$

$$\nu = c/\lambda$$

Therefore $E = hc/\lambda$

Where v = frequency of electromagnetic radiation.
λ = wavelength of electromagnetic radiation.
C = velocity of light
h = Planck constant



The energy absorbed by one mole of the reacting molecule is given by

$$E = N_A h\nu \qquad .....(1)$$

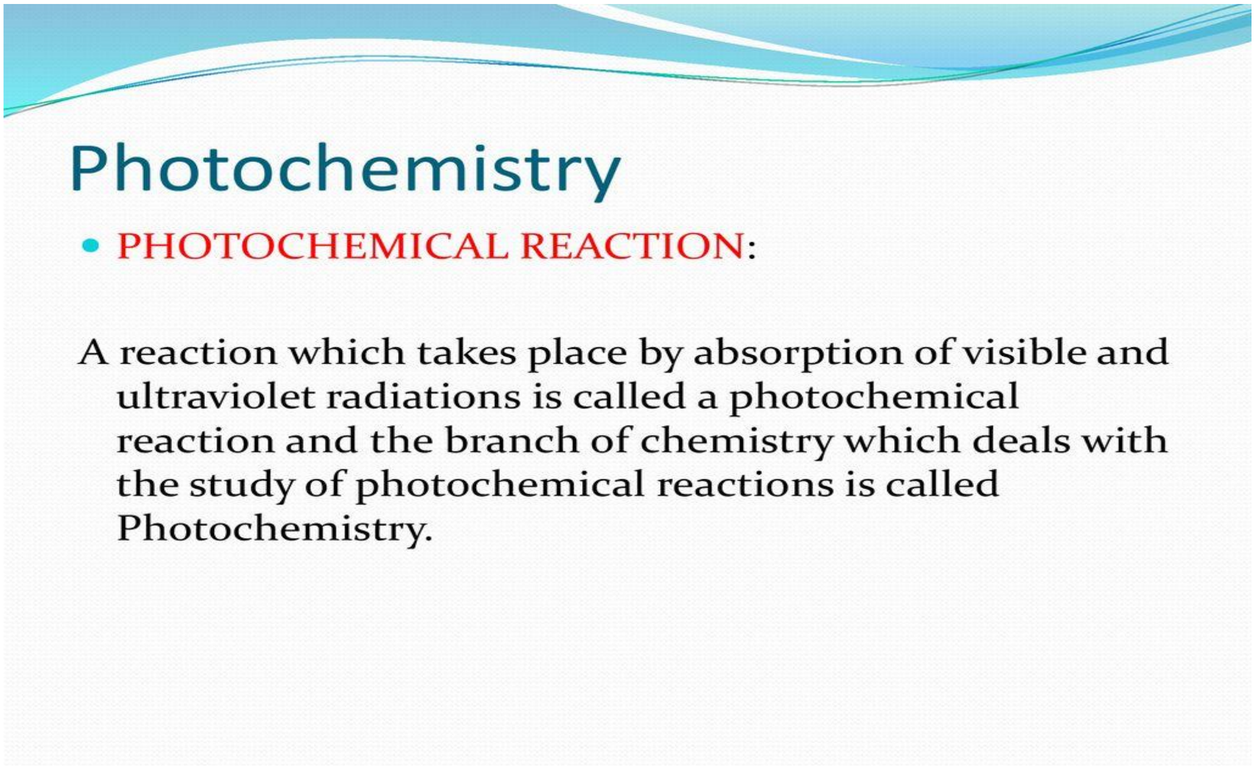
Where N_A is a Avogadro's number

Also $\nu = c/\lambda$ so (1) becomes

$$E = N_A hc/\lambda \qquad .....(2)$$

Where *c* velocity of light, *λ* is the wave length of the absorbed light and *h* is Plank's constant.

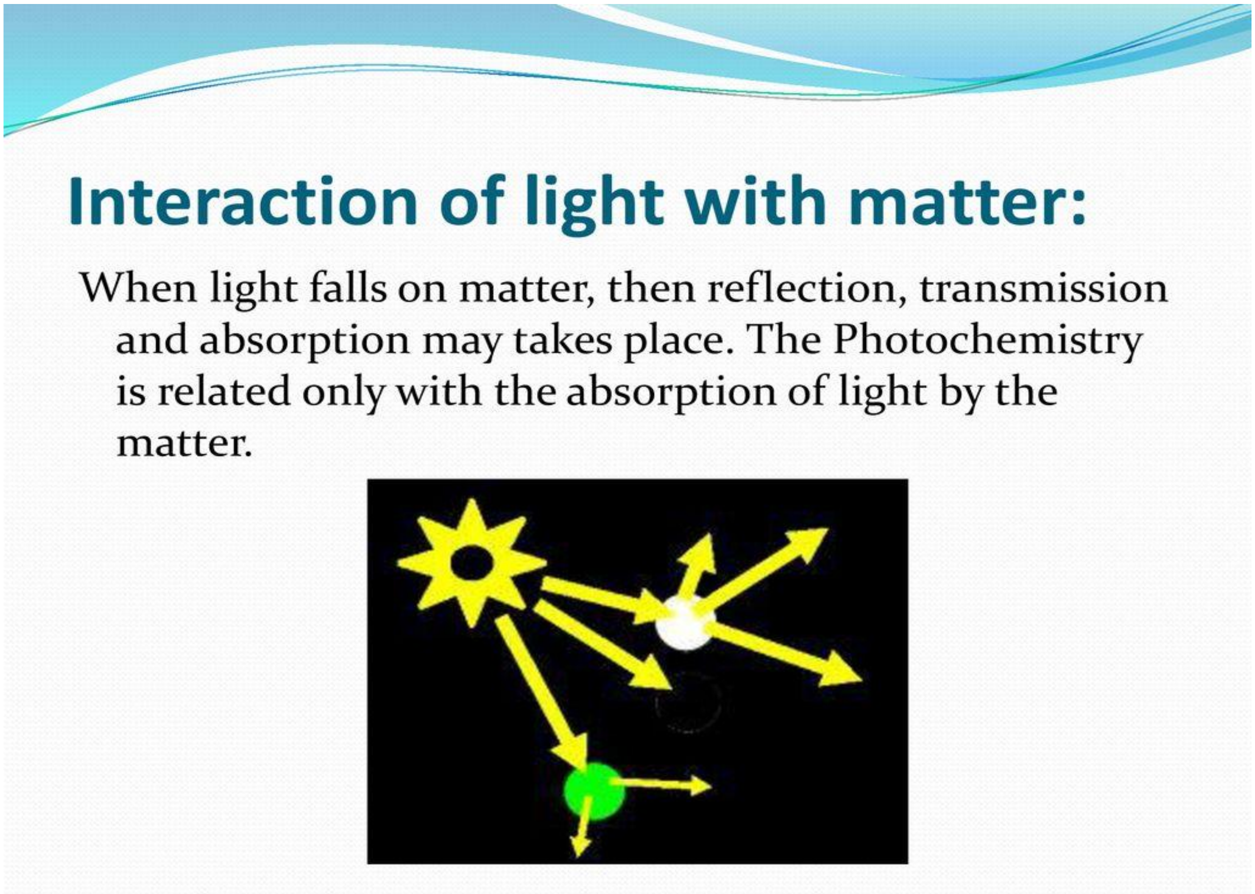
- The energy possessed by one mole of photon is called one einstein.



Photochemistry

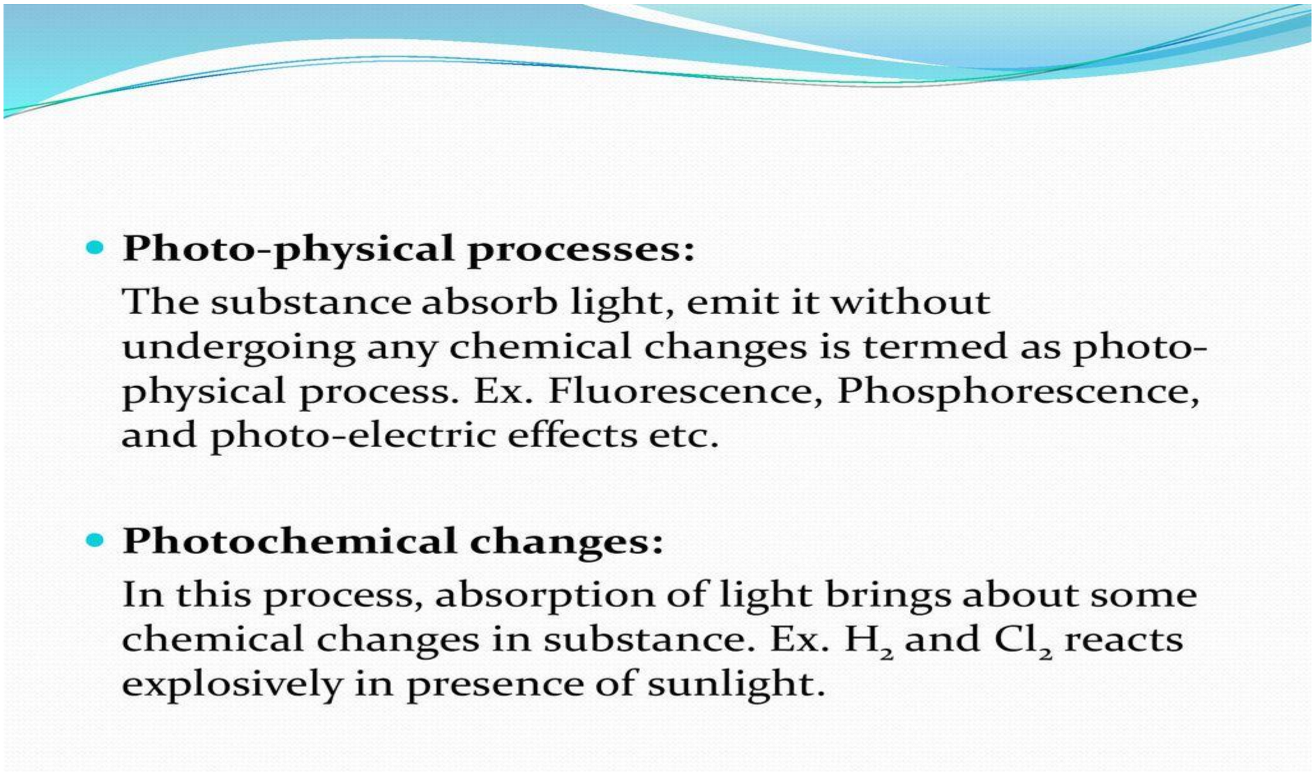
- PHOTOCHEMICAL REACTION:

A reaction which takes place by absorption of visible and ultraviolet radiations is called a photochemical reaction and the branch of chemistry which deals with the study of photochemical reactions is called Photochemistry.



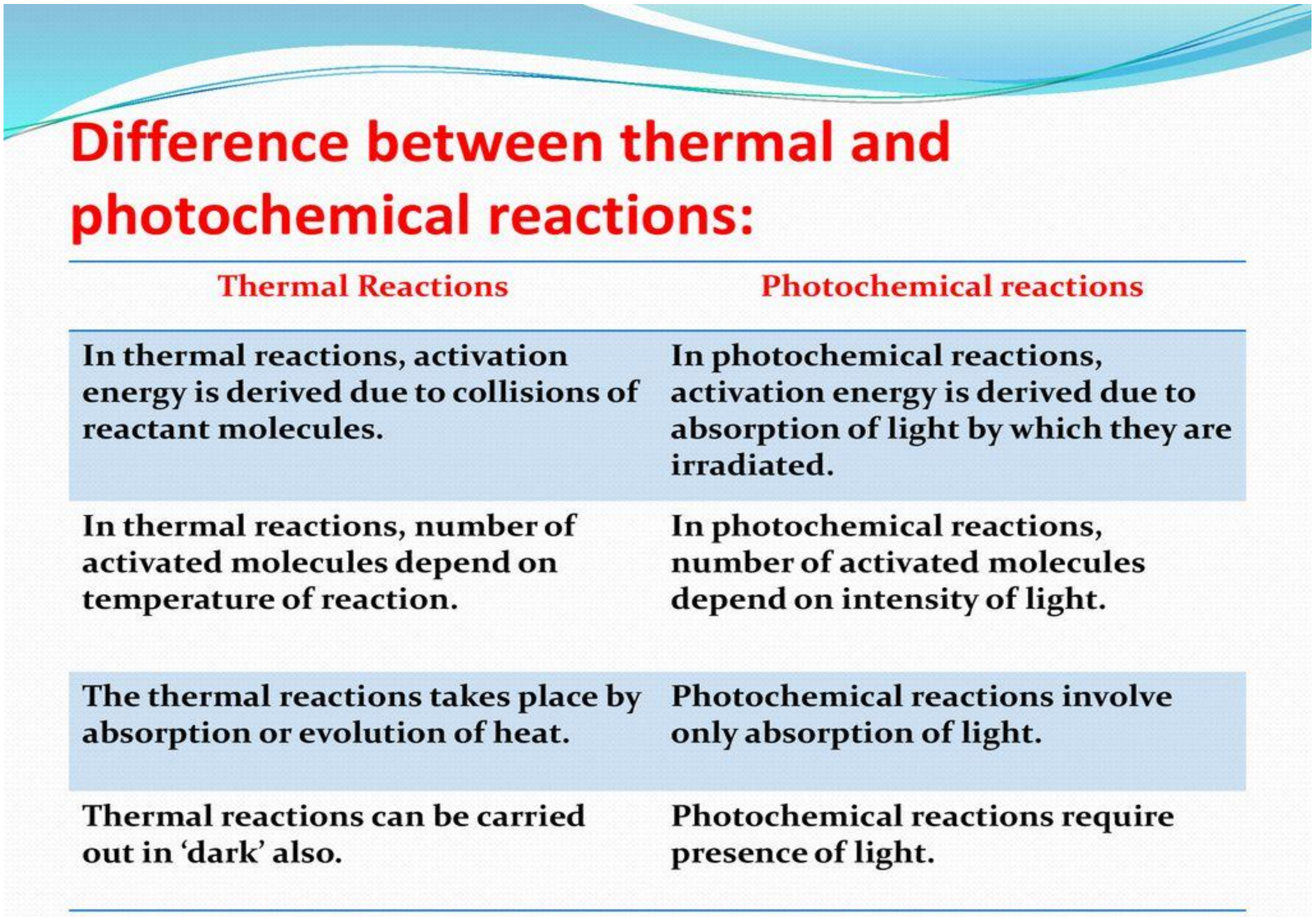
Interaction of light with matter:

When light falls on matter, then reflection, transmission and absorption may takes place. The Photochemistry is related only with the absorption of light by the matter.



- **Photo-physical processes:**
  The substance absorb light, emit it without undergoing any chemical changes is termed as photo-physical process. Ex. Fluorescence, Phosphorescence, and photo-electric effects etc.

- **Photochemical changes:**
  In this process, absorption of light brings about some chemical changes in substance. Ex. H_2 and Cl_2 reacts explosively in presence of sunlight.

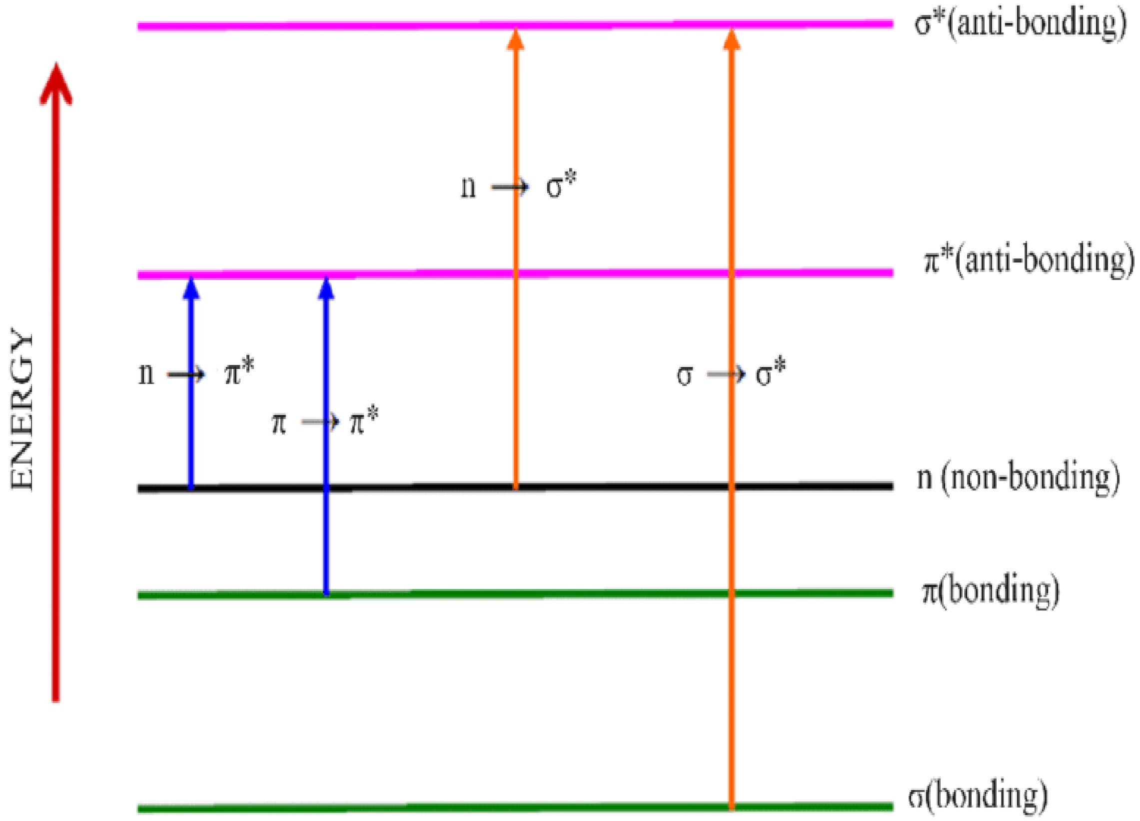


Difference between thermal and photochemical reactions:

Thermal Reactions	Photochemical reactions
In thermal reactions, activation energy is derived due to collisions of reactant molecules.	In photochemical reactions, activation energy is derived due to absorption of light by which they are irradiated.
In thermal reactions, number of activated molecules depend on temperature of reaction.	In photochemical reactions, number of activated molecules depend on intensity of light.
The thermal reactions takes place by absorption or evolution of heat.	Photochemical reactions involve only absorption of light.
Thermal reactions can be carried out in 'dark' also.	Photochemical reactions require presence of light.

1. Explain about Types of Electronic transitions?

- When a molecule absorbs UV (or) Visible light then the molecule undergo different types of electronic transitions.
- Ground state organic compound contains three molecular orbital's "σ", "π" and "n" orbital's.
- Both "σ" and "π" molecular orbital's are formed from overlapping between two atomic orbitals.
- Each "σ" and "π" molecular orbital's contains an anti - bonding σ (σ^*) and anti - bonding π (π^*) molecular orbital's.
- An orbital containing non – bonding (n) electron, it does not give anti – bonding molecular orbital. Because the two atomic orbital's are not overlap.
- There are four types of electronic transitions
    1. $\sigma - \sigma^*$
    2. $n - \sigma^*$
    3. $\pi - \pi^*$
    4. $n - \pi^*$



- **1. $\sigma - \sigma^*$ transition:** when an electron gets promoted from bonding "σ" orbital to an anti – bonding "σ" orbital (σ^*) is called $\sigma - \sigma^*$ transition.

  Example: alkanes.

- **2. $n - \sigma^*$ transition:** when an electron gets promoted from non – bonding orbital (n) to an anti – bonding "σ" orbital (σ^*) is called $n - \sigma^*$ transition.

  Example: alcohols, amines, ethers etc.

- **3. $\pi - \pi^*$ transition:** when an electron gets promoted from bonding "π" orbital to an anti – bonding "π" orbital (π^*) is called $\pi - \pi^*$ transition.

  Example: aromatic compounds, alkenes.

- **4. $n - \pi^*$ transition:** when an electron gets promoted from non – bonding orbital (n) to an anti bonding "π" orbital (π^*) is called $n - \pi^*$ transition.

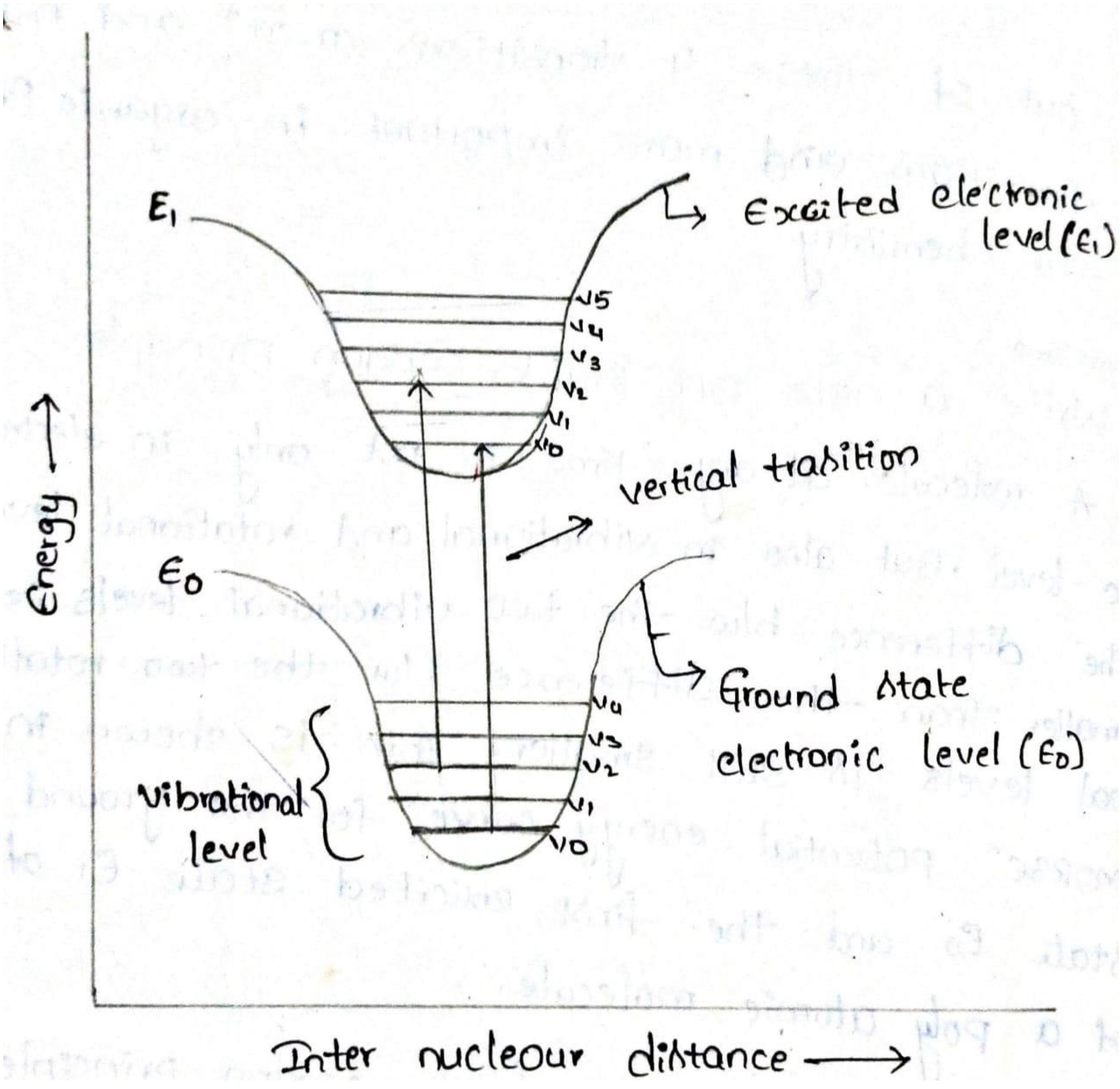
  Example: carbonyl compounds.

- The energy order of these transitions is $\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$.
- Out of these four transitions $\pi - \pi^*$ and $n - \pi^*$ transitions are more important in organic photochemistry.

2. Write a note on Frank – Condon principle?

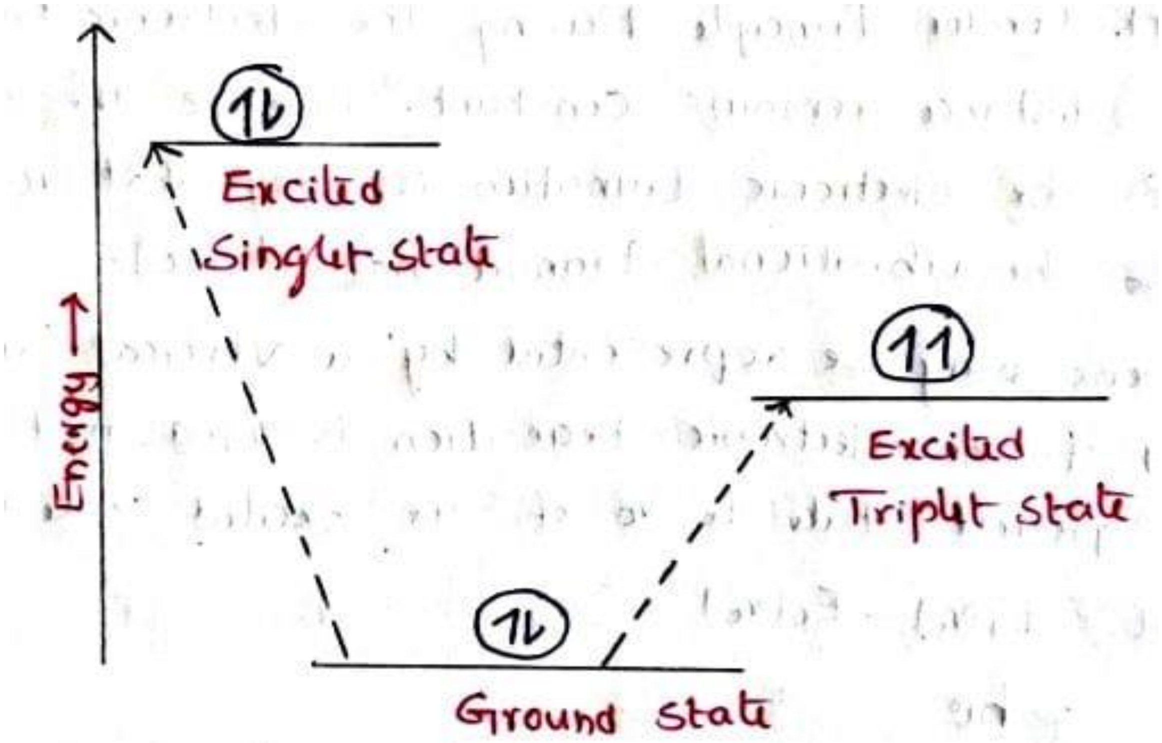
- A molecule at any time is not only in electronic level. But also in vibrational and rotational levels. The difference between two vibrational levels is smaller than the difference between two rotational levels is still smaller. This is shown in "MORSE" potential energy curve for the ground state (E_0) and the first excited state (E_1) of a poly atomic molecule.
- According to Frank – Condon principle **"During electronic transitions inter nuclear distance remains constant".** Because the time required for the electronic transition is very short (10^{-6} sec) compared to the vibrational transition (10^{-13} sec).
- The transitions may be represented by a vertical line. The energy of the electron transition is measured from V_0 of the ground state to V_0 of the excited state.

- $\Delta E = E_1 (V_0) - E_0 (V_0)$
- $\Delta E = h\vartheta$



3. Explain singlet and triplet states of electronically excited molecules?

- According to planks Quantum theory the photon having energy in the form of small packets.
- When a molecule is irradiated with photon then the molecule undergoes transition from lower energy orbital to higher energy orbital. This is known as "Electronic Excitation".



- If molecule can promote from lower energy level to higher energy level **<u>"Without changing its electron spin"</u>** then that excited state is called singlet state.
- Spin multiplicity = 2S + 1 here $s = \frac{-1}{2} + \frac{1}{2} = 0$

  = 2 (0) + 1

  = 1
- The spin multiplicity "1" means it is singlet state. Here two electrons having opposite spins. So one $\frac{-1}{2}$ and another one is $+\frac{1}{2}$. Net spin is "0".
- On singlet state electrons are paired with opposite spins.
- If molecule can promote from lower energy level to higher energy level **<u>"With changing its electron spin"</u>** then that excited state is called triplet state.

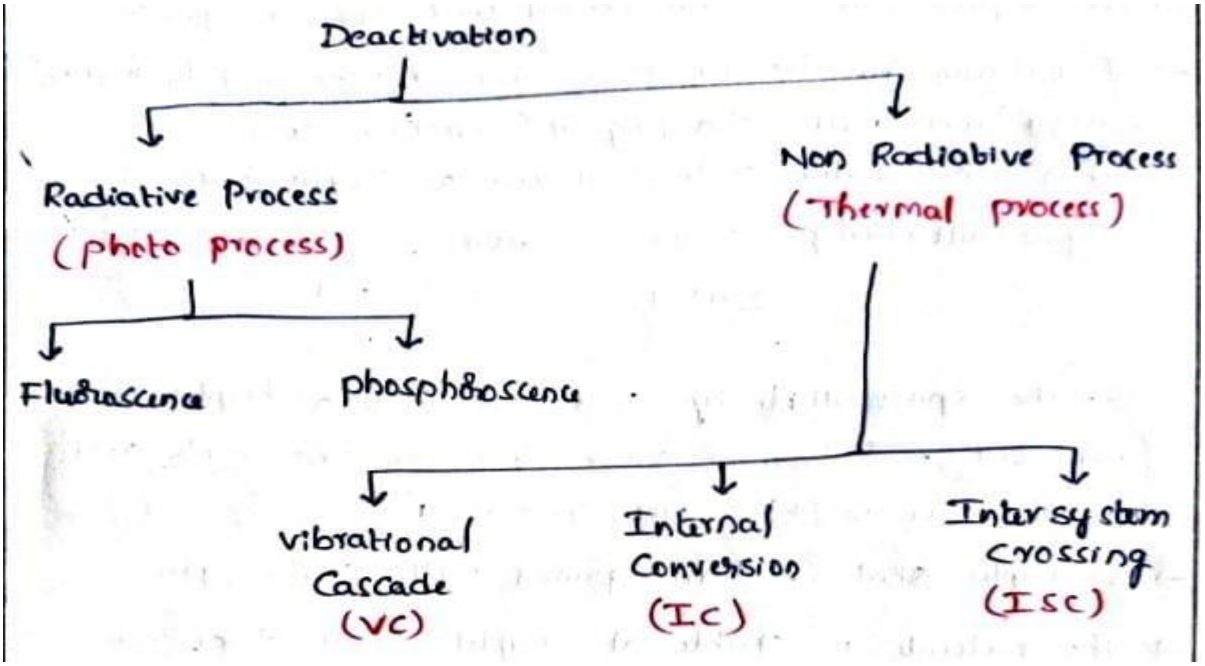
- Spin multiplicity = 2S + 1 here $s = \frac{1}{2} + \frac{1}{2} = 1$

  = 2 (1) + 1

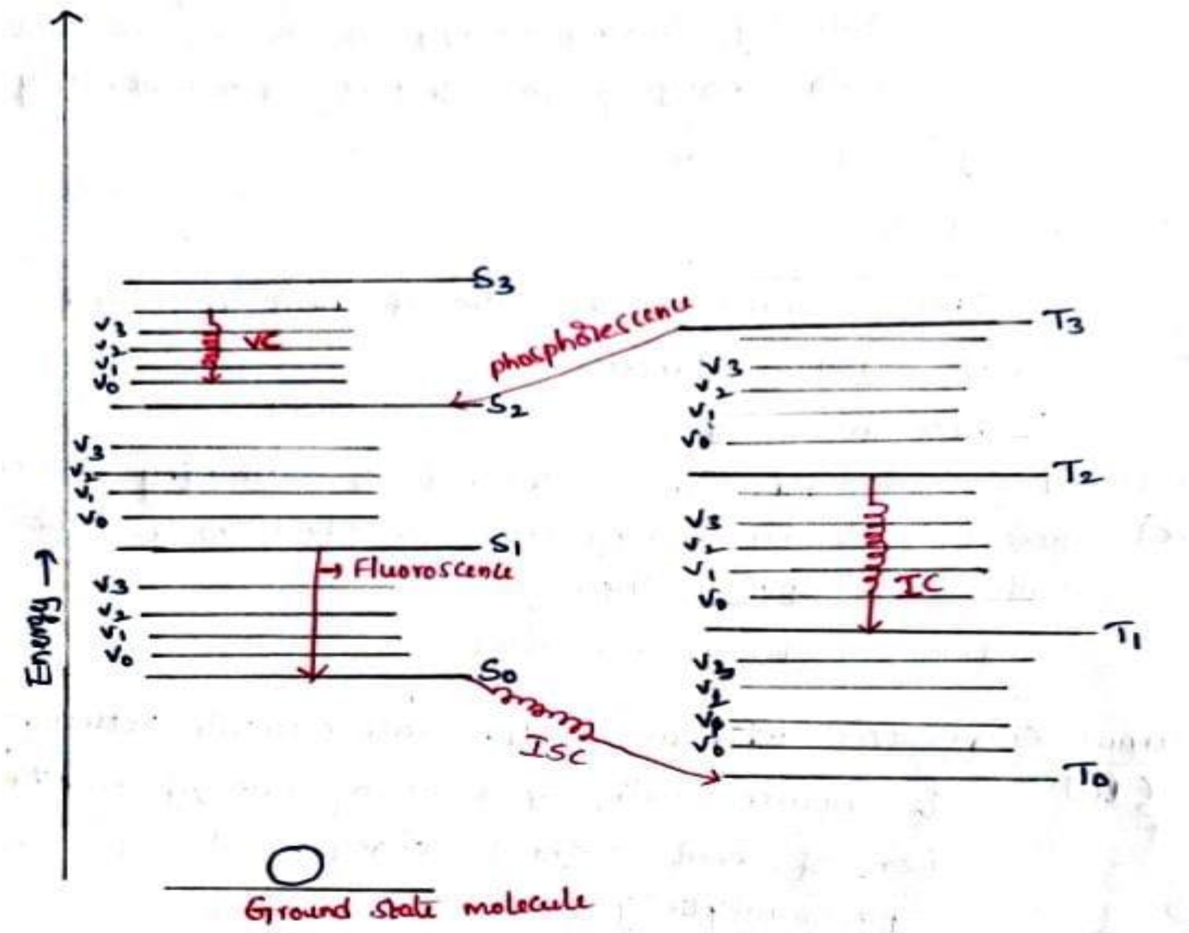
  = 3
- The spin multiplicity "3" means it is triplet state. Here two electrons having same spins. So one $+\frac{1}{2}$ and another one is $+\frac{1}{2}$. Net spin is "1".
- On triplet state electrons are paired with same spins.
- The molecule is stable at triplet state than singlet state because triplet state having lower energy than singlet state.

4. Explain "Jablonski Diagram" briefly?

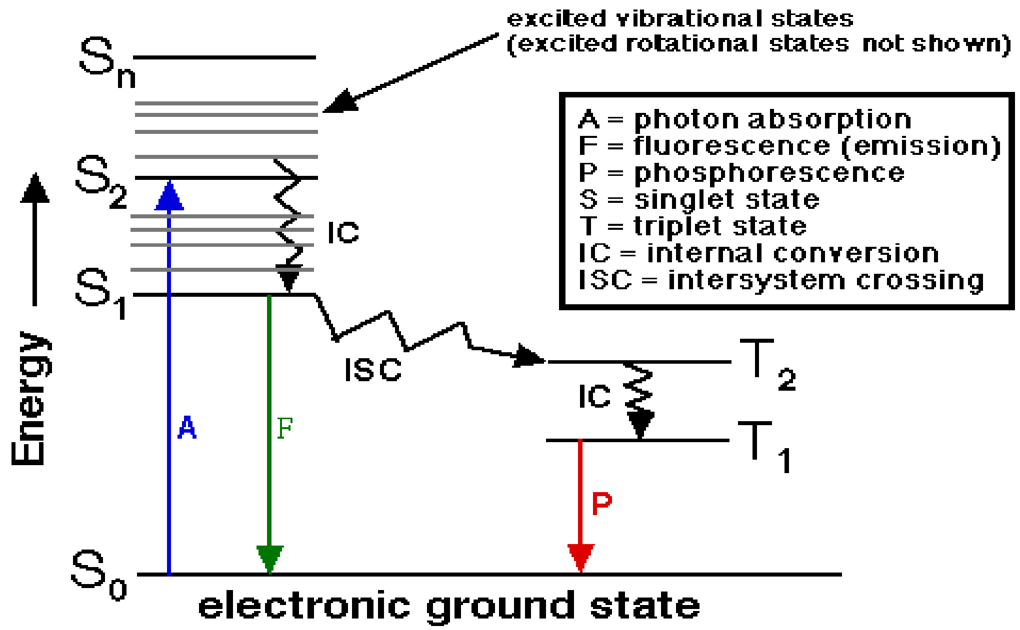
- If the energy releases in the form of light is represented by "straight arrow' is known as "Radiative Process".
- If the energy releases in the form of heat is represented by "spring like arrow" is known as "Non Radiative Process".
- The molecule is not stable in higher energy level. So readily deactivated through radiative and non radiative processes. Then the molecule comes to lower energy level for stability of the molecule.



- All these properties are shown in "jablonski diagram".
- It is a graphical representation of electronic energy levels with multiplicities.



Jablonski Diagram



- **Radiative Process:** An Energy release in the form of light is called Radiative process. These are two types
    1. Fluorescence
    2. Phosphorescence
- **Fluorescence:** when an excited molecule return to ground state by releasing energy in the form of light **"without changing its electron spin multiplicity".**

  Example: $S_1 \rightarrow S_0$ (or) $T_1 \rightarrow T_0$
- **Phosphorescence:** when an excited molecule return to ground state by releasing energy in the form of light **"with changing its electron spin multiplicity".**

  Example: $T_1 \rightarrow S_0$ (or) $T_3 \rightarrow S_2$
- **Non Radiative Process:** An energy release in the form of heat is called Non radiative process. These are three types
    1. Vibrational cascade
    2. Internal conversion
    3. Inter system crossing
- **Vibrational Cascade:** when an excited molecule return to ground state by releasing energy in the form of heat with same spin multiplicity.

  Eg: $S_2(v_3) \rightsquigarrow S_2(v_0)$
- **Internal Conversion:** when an excited molecule return to ground state by releasing energy in the form of heat without changing its electron spin multiplicity.

  Eg: $T_2 \rightsquigarrow T_1$ (or) $S_2 \rightsquigarrow S_1$
- **Inter system crossing:** when an excited molecule return to ground state by releasing energy in the form of heat with changing its electron spin multiplicity.

  Eg: $S_0 \rightsquigarrow T_0$

5. What is Quantum yield and explain the experimental determination of Quantum yield?

- The Quantum yield (or) efficiency of photochemical reaction explained in terms of Quantum yield.
- Quantum yield is denoted by "ϕ".
- It is defined as the ratio of the number of molecules reacted to the number of quanta absorbed i.e.,

$$\emptyset = \frac{\text{Number of molecules reacted}}{\text{Number of Quanta absorbed}}$$

(OR)

$$\emptyset = \frac{\text{Number of molecules reacted}}{\text{Number of Einstein absorbed}}$$

(OR)

$$\emptyset = \frac{\text{Number of reactants decomposed per unit time}}{\text{Number of Einstein absorbed}}$$

(OR)

$$\emptyset = \frac{\text{Number of products formed per unit time}}{\text{Number of Einstein absorbed}}$$

(OR)

$$\emptyset = \frac{\text{Rate of chemical reaction}}{\text{Intensity of incident light}}$$

- Quantum yield is classified into three types
    1. Normal Quantum yield
    2. High Quantum yield
    3. Low Quantum yield
- **1. Normal Quantum yield:** In some photochemical reactions Quantum yield is unity (1). This is called Normal Quantum yield.
  Example: $SO_2 + Cl_2 \rightarrow SO_2Cl_2$ $\phi = 1$
- **2. High Quantum yield:** In some photochemical reactions Quantum yield is greater than unity (1). This is called High Quantum yield.
  Example: $H_2 + Cl_2 + h\vartheta \rightarrow 2HCl$ $\phi = 10^4 – 10^6$

Mechanism:

1. Primary Process:

Initiation Step: It is a light medium reaction.

$Cl_2 + h\vartheta \rightarrow (Cl_2)^* \rightarrow Cl^* + Cl^*$

2. Secondary Process:

Propagation Step: It is a dark medium reaction and highly exothermic.

(a) $Cl^* + H - H \rightarrow HCl + H^*$

(b) $H^* + Cl - Cl \rightarrow HCl + Cl^*$

Termination Step: $Cl^* + Cl^* \rightarrow Cl_2 + h\vartheta$

Other Examples: 1. $2HI + h\vartheta \leftrightarrow H_2 + I_2$ $\phi = 2$

2. $CO + Cl_2 + h\vartheta \rightarrow COCl_2$ $\phi = 10^2 - 10^4$

- **3. Low Quantum yield:** In some photochemical reactions Quantum yield is less than unity (1). This is called Low Quantum yield.

Example: $H_2 + Br_2 + h\vartheta \rightarrow 2HBr$ $\phi = 0.1 - 0.01$

Mechanism:

1. Primary Process:

Initiation Step: It is a light medium reaction.

$Br_2 + h\vartheta \rightarrow (Br_2)^* \rightarrow Br^* + Br^*$

2. Secondary Process:

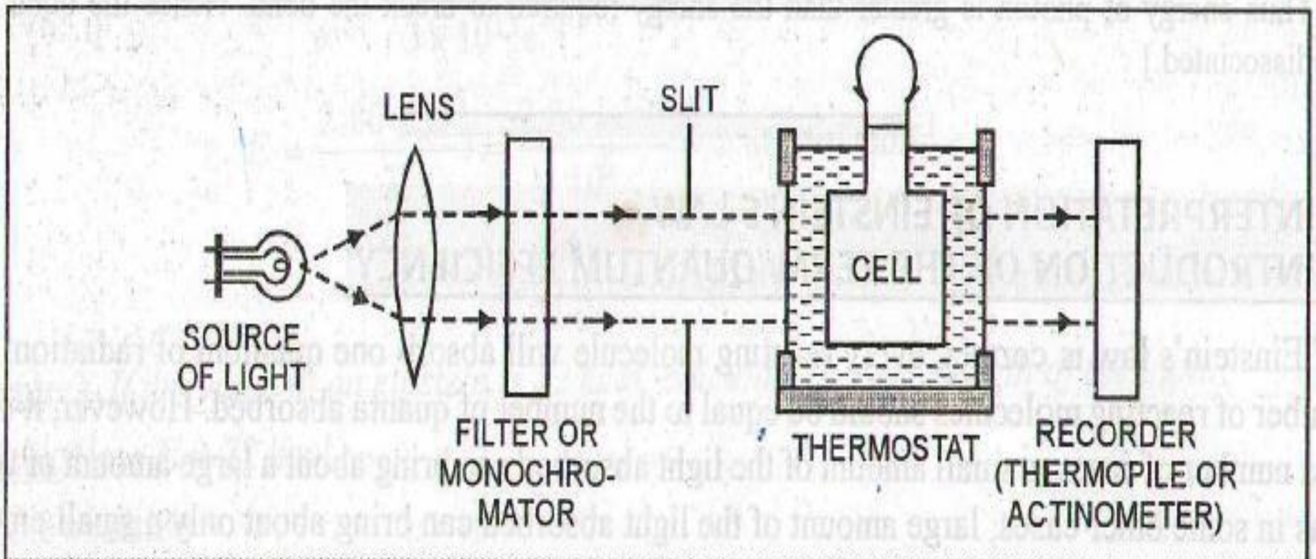
Propagation Step: It is a dark medium reaction and Endothermic.

(a) $Br^* + H - H \rightarrow HBr + H^*$

(b) $H^* + Br - Br \rightarrow HBr + Br^*$

Termination Step: $Br^* + Br^* \rightarrow Br_2 + h\vartheta$

Experimental Determination of Quantum yield:



FIGURE

Apparatus for the determination of quantum yield of a photochemical reaction.

Experimental setup consists of the following parts

1. Light source
2. Lens, slit
3. Monochromator
4. Reaction chamber
5. Detector

1. Light source: The light source to be used for absorption spectrum of the compound under study.

The light sources are 1. Tungsten lamp most commonly used
2. Xenon arc lamp
3. Mercury lamp

2. Lens, slit: The lens slits and Nicol prism are used the light source behavior is changed to a mono chromatic.

3. Monochromator:

- Monochromator works as a filter for light source.
- When light from the source passed through the lens and allowed to pass through filter, it will absorb all of undesired wavelengths and transmit light of definite wavelength which is needed for the reaction.
- Monochromators are generally made up of gelatin (gum) or colored glass.

4. Reaction chamber:

- Light from monochromator enters into reaction chamber which contains reaction mixture.
- The reaction cell which is made up of glass (or) quartz.

5. Detector: Detector is used for the determination of intensity of light from a reaction chamber.

Procedure:

1. The monochromatic light is first passed through the empty reaction chamber from the light source and the intensity of light (I_0) is measured by detector.
2. Now the reactants are taken in a reaction chamber and the same light is passed through reaction chamber and the intensity of transmitted light (I) is measured by detector.
3. The difference in the two intensities gives the intensity of absorbed reaction.

$$I_{abs} = I_0 - I$$

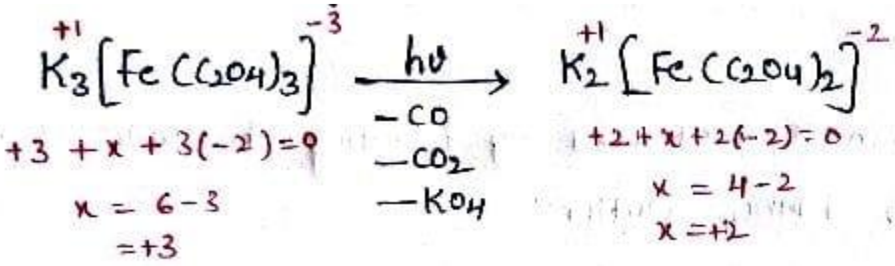
$$\emptyset = \frac{\text{Rate of reaction}}{\text{I abs}}$$

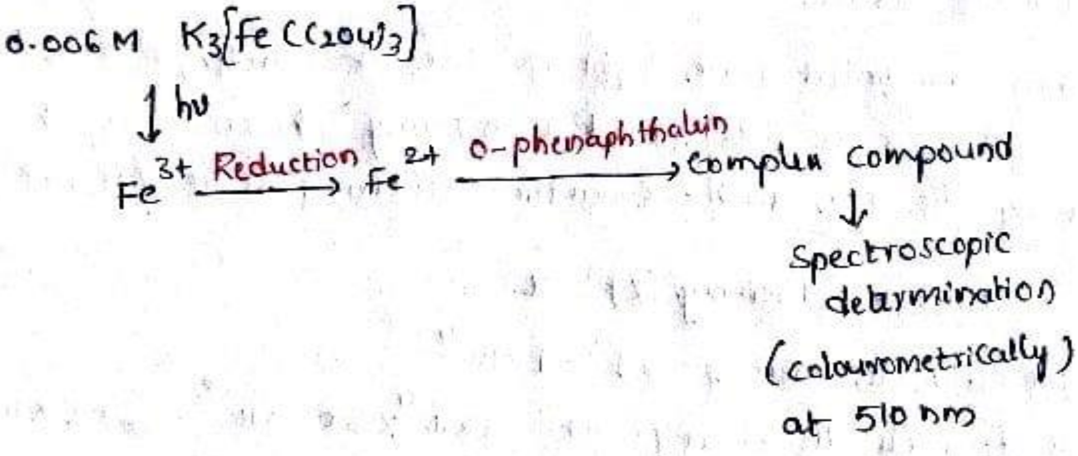
6. Explain about Actinometry?

(OR)

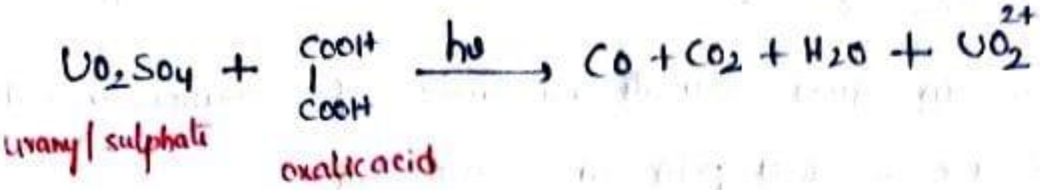
Write about Ferrioxalate and Uranyl oxalate Actinometers?

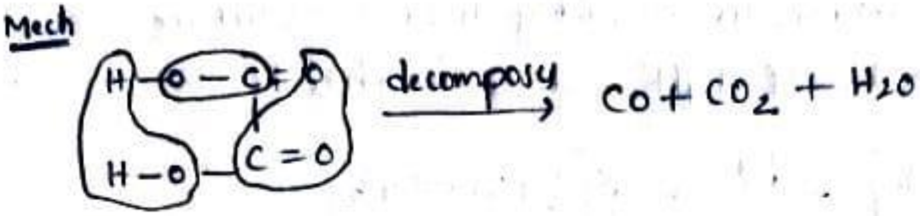
- The accurate measurement of the Quantum yield depends mainly on the accuracy of the actinometer.
- Actinometer measures radiation intensity (I_0, I and $I_0 - I = I_a$).
- Intensity of radiation for Quantum yield is measured by chemical actinometer. This process is called actinometry.
- A chemical actinometer gives accurate values of I_0, I and I_a.
- A chemical actinometer should have the following features
    1. Thermal stability
    2. Availability
    3. Uniform response over a large wavelength range
- The normal range for solution phase photochemistry is from 250 – 450 nm.
- Chemical actinometer is best suitable for solution phase photochemistry.
- In the range from 250 – 450 nm most commonly used actinometers are
    1. Ferri oxalate actinometer
    2. Uranyl oxalate actinometer
- Actinometer is nothing but one type of detector.
- **1. Ferri oxalate Actinometer:**
- This actinometer gives accurate measurements of radiation intensity.
- In this we use 0.006M Potassium ferri oxalate.
- The ferri oxalate actinometer is widely used to determine the intensity of light source in photochemical reactions.
- In this we use wavelength range from 250 – 450 nm and $\phi = 1.2 - 1.7$.





- **2. Uranyl oxalate actinometer:**
- This is one of the most commonly used actinometer.
- It consists of 0.05M oxalic acid and 0.01M uranyl sulphate solution in water.
- When uranyl oxalate exposed to light the reaction takes place oxalic acid converting into CO_2 and H_2O.
- Here uranyl oxalate acts as a photo sensitizer (absorbs the light and then passes it on to oxalic acid)



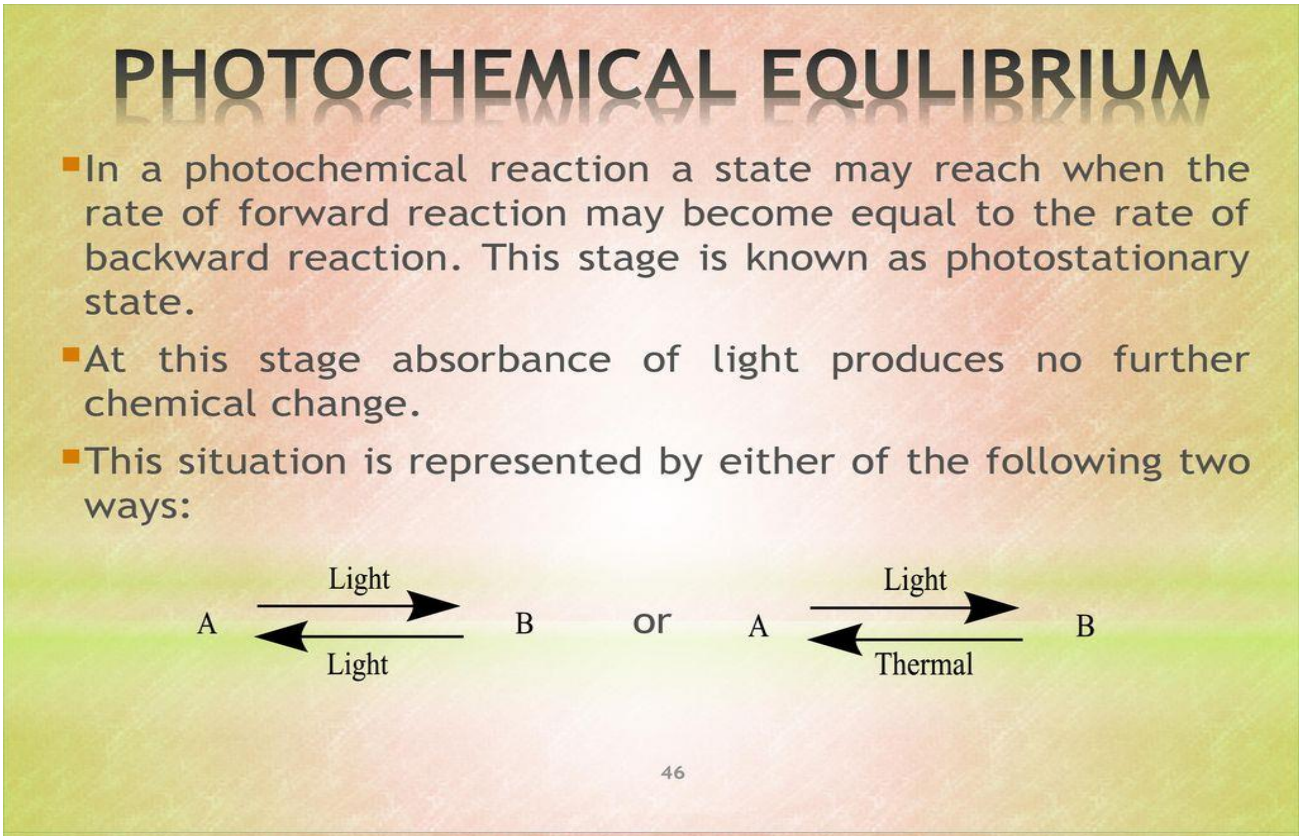


- The extent of reaction is measured by titrating oxalic acid solution with $KMnO_4$ solution.

7. Write a note on Photochemical Equilibrium?

(OR)

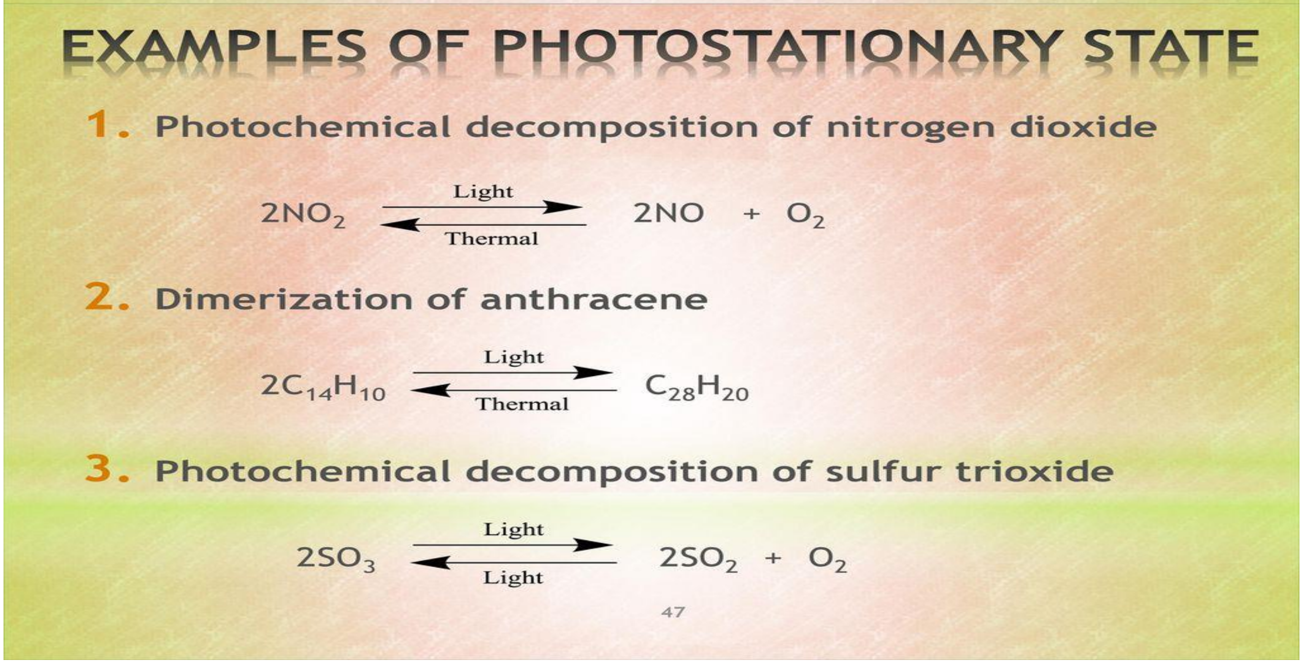
Write a note on Photo Stationary State?



PHOTOCHEMICAL EQULIBRIUM

- In a photochemical reaction a state may reach when the rate of forward reaction may become equal to the rate of backward reaction. This stage is known as photostationary state.
- At this stage absorbance of light produces no further chemical change.
- This situation is represented by either of the following two ways:

$$A \underset{\text{Light}}{\overset{\text{Light}}{\rightleftharpoons}} B \quad \text{or} \quad A \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} B$$



EXAMPLES OF PHOTOSTATIONARY STATE

1. Photochemical decomposition of nitrogen dioxide

$$2NO_2 \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} 2NO + O_2$$

2. Dimerization of anthracene

$$2C_{14}H_{10} \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} C_{28}H_{20}$$

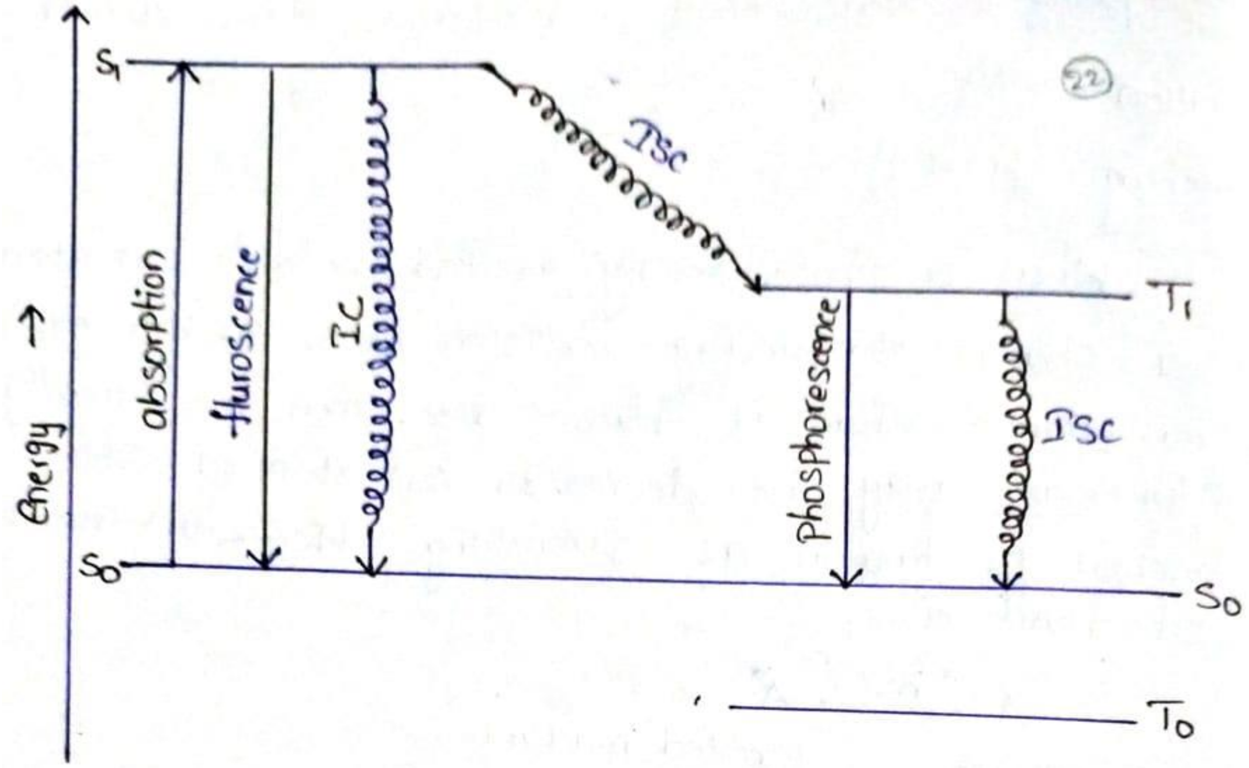
3. Photochemical decomposition of sulfur trioxide

$$2SO_3 \underset{\text{Light}}{\overset{\text{Light}}{\rightleftharpoons}} 2SO_2 + O_2$$

Chemical Kinetics of Photo Chemical Reactions

8. Derive Quantum Yield of Fluorescence and Phosphorescence?

- When a molecule absorbs a photon then it will excited to higher energy level. The molecule is in higher energy level is not stable and goes to ground state through Radiative (or) Non radiative process.



1. $S_0 \xrightarrow{h\nu} S_1$ $\quad \text{Rat}_1 = I_a$

2. $S_1 \xrightarrow{k_f} S_0 + h\nu$

3. $S_1 \xrightarrow{k_{IC}} S_0 + \text{heat}$

4. $T_1 \xrightarrow{k'_{ISC}} S_0 + \text{heat}$

5. $T_1 \xrightarrow{k_p} S_0 + h\nu$

6. $S_1 \xrightarrow{k_{ISC}} T_1 + \text{heat}$

Quantum Yield of Fluorescence

The ratio of rate of fluorescence to rate of first step is known as Quantum yield of fluorescence.

$\Phi_f = \frac{\text{Rate of Fluorescence}}{\text{Rate of 1st step}}$ --------- (1)

Rate of fluorescence = $K_f\ [S_1]$ -------- (2)

Apply steady state approximation to $[S_1]$

Rate of formation = Rate of decomposition

$I_a = K_f\ [S_1] + K_{IC}\ [S_1] + K_{ISC}\ [S_1]$

$I_a = [S_1]\ \{K_f + K_{IC} + K_{ISC}\}$

$[S_1] = \frac{Ia}{Kf+K\ +K}$ ------- (3)

Substitute eq(3) in eq(2), we get

Rate of fluorescence = $\frac{Kf\ Ia}{Kf+K\ \ +K}$ ------- (4)

Rate of 1st step = I_a ----------- (5)

Substitute eq(4),(5) in eq(1), we get

$\Phi_f = \frac{Kf\ \ Ia}{[Kf+K\ \ +K\ \ \ ]Ia}$

$\Phi_f = \frac{Kf}{Kf+K\ \ +K}$

Quantum Yield of Phosphorescence

The ratio rate of phosphorescence to rate of 1st step is known as Quantum yield of Phosphorescence.

$\Phi_P = \frac{\text{Rate of Phosphorescence}}{\text{Rate of 1st step}}$ -------- (1)

Rate of Phosphorescence = $K_P\ [T_1]$ ------ (2)

Apply steady state approximation to $[T_1]$

Rate of formation = Rate of decomposition

$K_{ISC} [S_1] = K_P [T_1] + K^1_{ISC} [T_1]$

$K_{ISC} [S_1] = [T_1] \{K_P + K^1_{ISC}\}$

$[T_1] = \frac{K}{K + K} [S_1]$ $\qquad\qquad \because [S_1] = \frac{Ia}{Kf + K + K}$

$[T_1] = \frac{K}{K + K} \frac{Ia}{Kf + K + K}$ ---------- (3)

Substitute eq(3) in eq(2), we get

Rate of Phosphorescence = $K_P \frac{K}{K + K} \frac{Ia}{Kf + K + K}$ ------ (4)

Rate of 1st step = I_a ----------- (5)

Substitute eq(4),(5) in eq(1), we get

$$\Phi_P = \frac{K \; K \quad Ia}{(K + K \quad)(K + K \; + K \quad) \; Ia}$$

$$\Phi_P = \frac{K}{K \; +} \frac{K}{K + K \; + K}$$

9. What is Quenching effect and derive Stern – volmer equation?

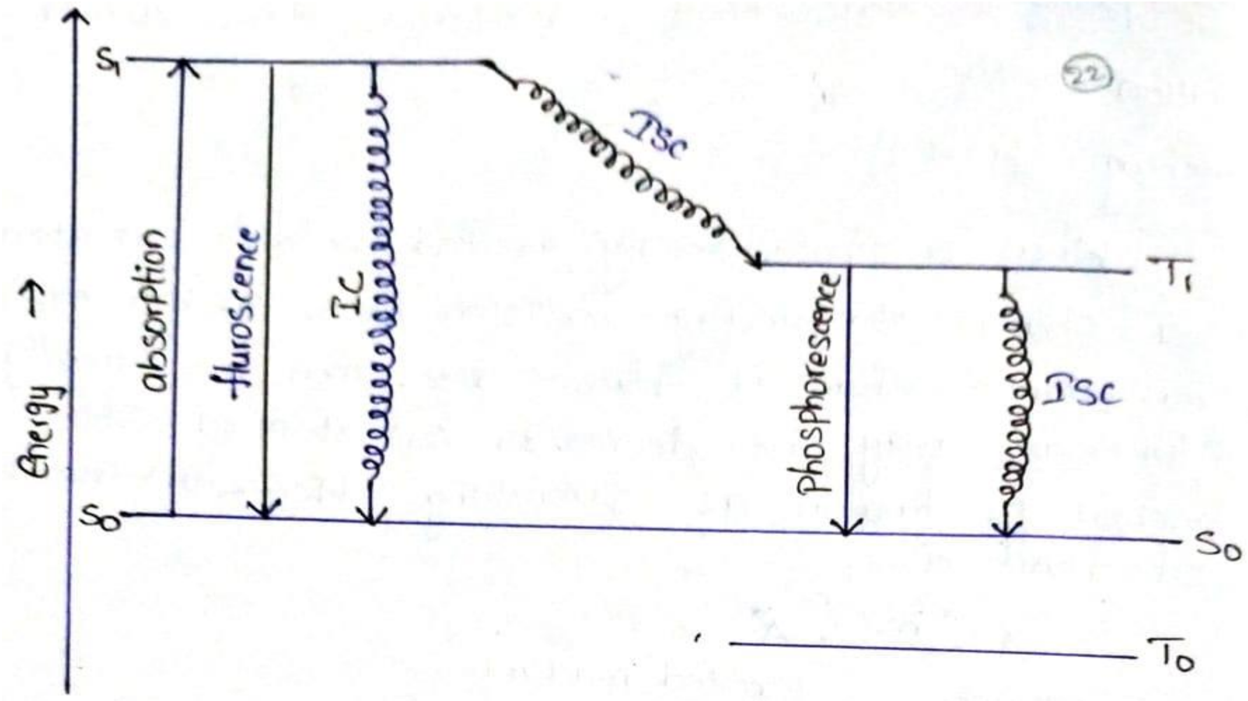
Quenching effect: when a photochemically excited molecule (or) atom has a chance to collision with another molecule (or) atom before it fluorescence then the intensity of fluorescence may be decreased (or) stopped. This phenomenon is known as Quenching effect (or) Quenching of fluorescence.

$A + h\vartheta \rightarrow A^*$

$A^* + Q \rightarrow A + Q^*$

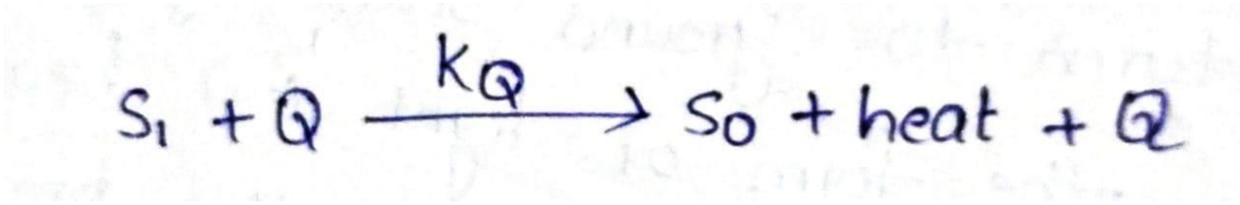
Derivation of Stern – Volmer equation:

- It is the explanation of Quenching of fluorescence in photochemical reactions.
- Let us consider a molecule in a ground state will absorb light energy and goes to excited state.
- Now, the molecule is not stable in excited state. So it returns to ground state by releasing energy in the form of light (or) heat through radiative (or) Non radiative process.
- This process is shown below



1. $S_0 \xrightarrow{h\nu} S_1$ Rate = I_a
2. $S_1 \xrightarrow{k_f} S_0 + h\nu$
3. $S_1 \xrightarrow{k_{IC}} S_0$ + heat
4. $T_1 \xrightarrow{k'_{ISC}} S_0$ + heat
5. $T_1 \xrightarrow{k_p} S_0 + h\nu$
6. $S_1 \xrightarrow{k_{ISC}} T_1$ + heat

- A Quenching substance is added to the reaction, the energy is released in the form of heat. So it is Non radiative process.



- Apply steady state approximation to S_1.
- Rate of formation of S_1 = Rate of decomposition of S_1
- $I_a = K_f [S_1] + K_{IC} [S_1] + K_{ISC} [S_1] + K_Q [S_1] [Q]$
- $I_a = [S_1] \{K_f + K_{IC} + K_{ISC} + K_Q [Q]\}$
- $[S_1] = \frac{Ia}{K + K + K \quad + K \ [Q]}$
- Now Rate of fluorescence = $K_f [S_1]$

$$= K_f \frac{Ia}{K + K + K \quad + K \ [Q]} \text{ ----------- (1)}$$

- Quantum yield of fluorescence in presence of Quencher

$$\Phi_f = \frac{Rate\ of\ fluorescence}{Ia} \text{ -------- (2)}$$

Substitute eq(1) in eq(2), we get

$$\Phi_f = \frac{K \ Ia}{K + K + K \ + K \ [Q] Ia}$$

$$\Phi_f = \frac{K}{K + K + K \ + K \ [Q]} \text{ --------- (A)}$$

- Quantum yield of fluorescence in the absence of Quencher
- I.e. [Q] = 0 ---- (3)
- Substitute eq(3) in eq(1), we get
- Now Rate of fluorescence = $K_f [S_1]$

$$= K_f \frac{Ia}{K + K + K} \text{ ------ (4)}$$

- $\Phi_f^0 = \frac{Rate\ of\ fluorescence}{Ia}$ ------- (5)
- Substitute eq(4) in eq(5), we get

$$\Phi_f^0 = \frac{K \ Ia}{[K + K + K \ ] Ia}$$

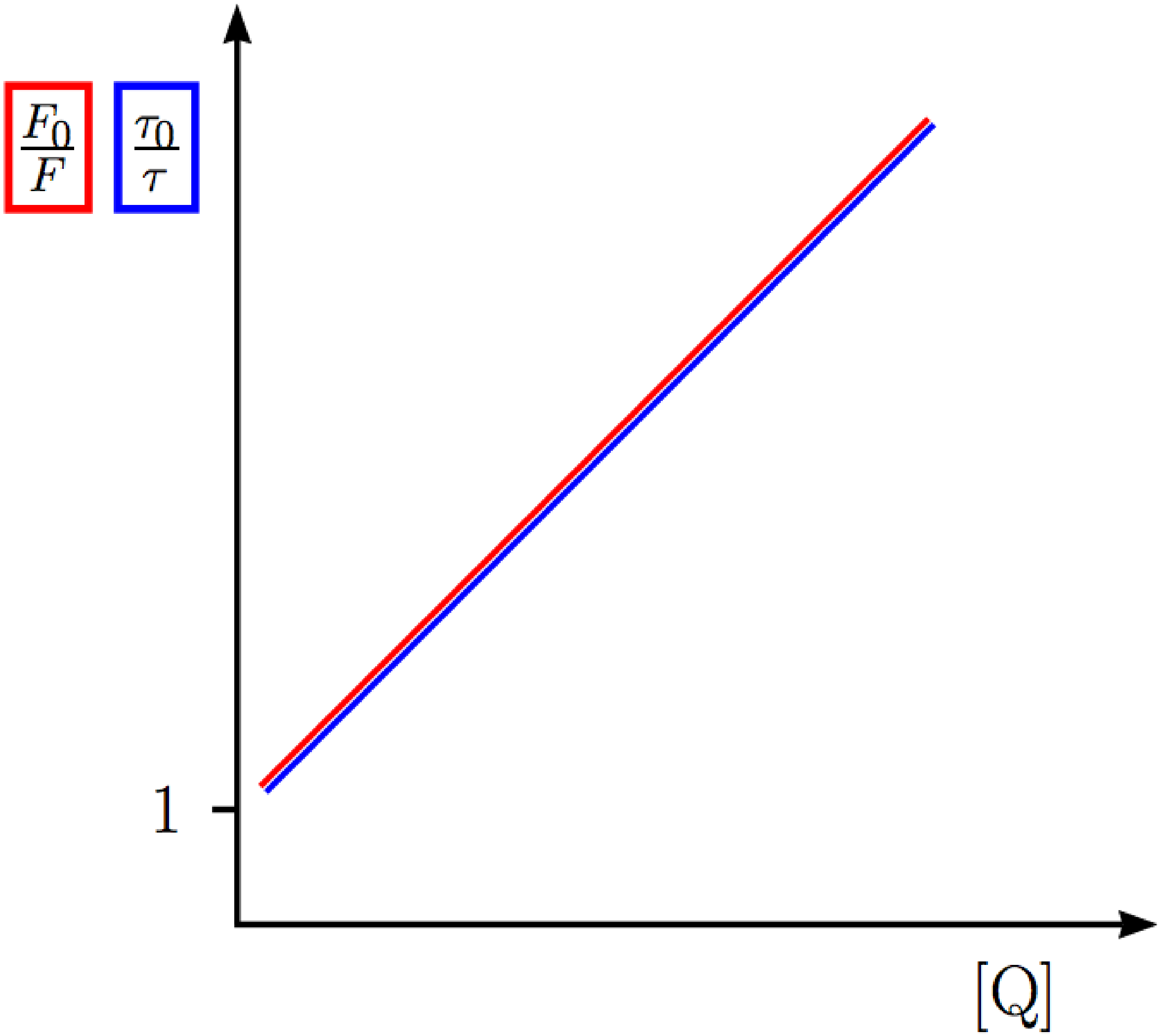
$$\Phi_f^0 = \frac{K}{[K + K + K \ ]} \text{ --------- (B)}$$

- $\frac{B}{A} = \frac{\emptyset f}{\emptyset f} = \frac{K}{[K + K \ + K \ ]} \ X \ \frac{K + K \ + K \ \ + K \ [Q]}{K}$

$$= \frac{K \ + K \ \ + K}{K \ + K \ \ + K} + \frac{K \ [Q]}{K \ + K \ \ + K}$$

$\frac{\emptyset f}{\emptyset f} = 1 + K_{SV} [Q]$

- This is called Stern – Volmer equation.
- A graph is drawn between $\frac{\emptyset f}{\emptyset f}$ v/s [Q] gives a straight line with slop K_{SV} and intercept 1.
- $\frac{\emptyset f}{\emptyset f} = 1 + K_{SV} [Q]$
- Y = c + m x



10. What is delayed fluorescence and explain the types of delayed fluorescence

Delayed fluorescence: the spectral characteristics of delayed fluorescence are different from spectral characteristics of fluorescence. But some delayed emission exactly coincides with the phosphorescence from the lowest singlet state. The only difference in their lifetimes such process is known as delayed fluorescence.

Delayed fluorescence is two types

1. E – type delayed fluorescence
2. P – type delayed fluorescence

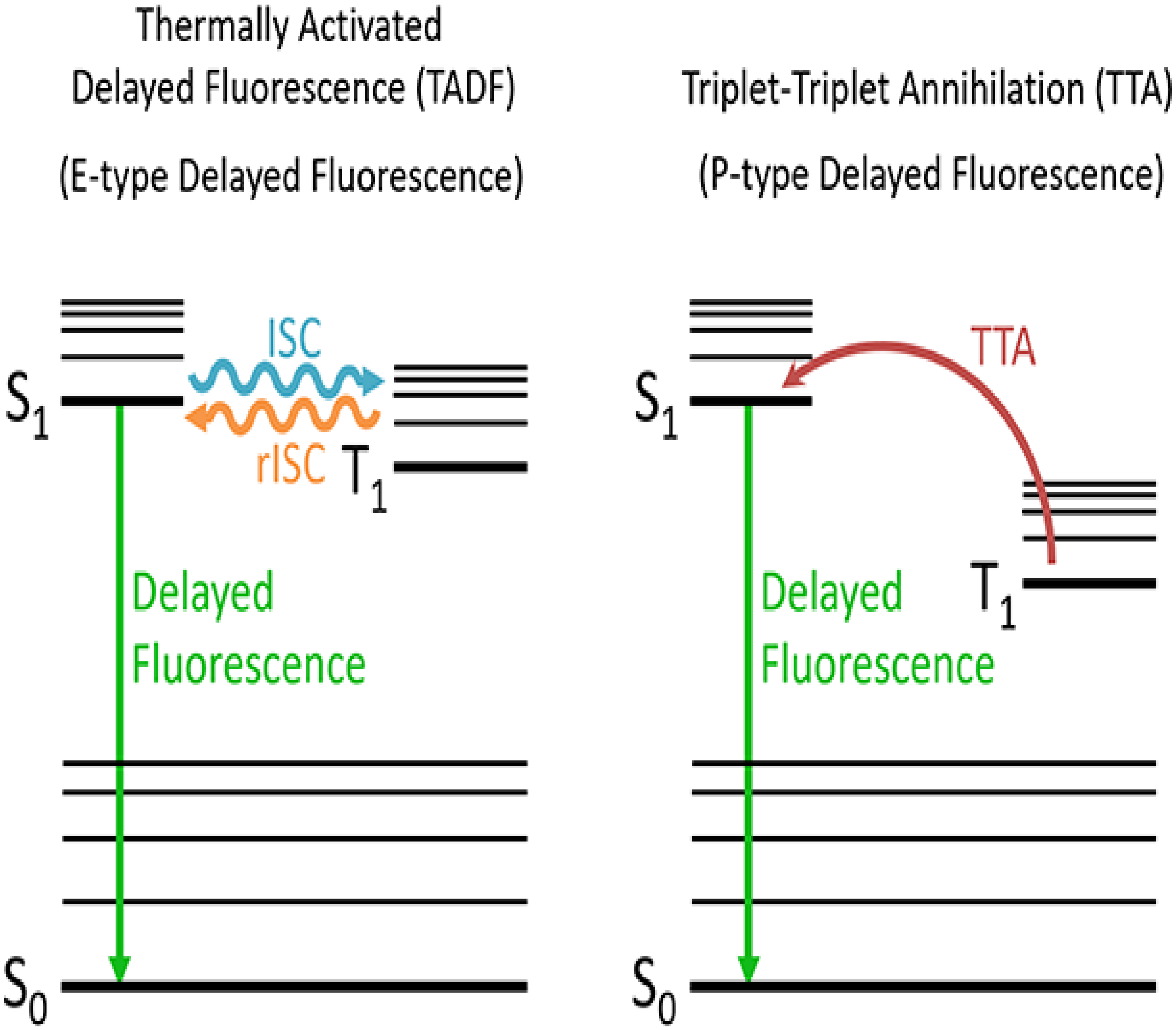
1. E – delayed fluorescence:

- This is also known as TADF (thermally activated delayed fluorescence).
- This type of fluorescence can be observed where the singlet – triplet energy is small.
- This is first observed in deoxygenated solutions of cosine in glycerol (or) alcohol.
- This is also known as α - phosphorescence.
- Energy gap is small between S_1 & T_1.
- This is observed at room temperature.

2. P – type delayed fluorescence:

- This is also known as TTA (triplet – triplet annihilation).
- This type of fluorescence can be observed where the singlet – triplet energy gap is high.
- This is first observed in solutions of aromatic hydrocarbons like Pyrenees and phenanthrene.
- Energy gap is high between S_1 & T_1.
- In aromatic hydrocarbons the singlet – triplet energy is large, due to this reason thermal activation from triplet – singlet state at room temperature is not possible.
- "Parker and Hatchard" first formulated a mechanism.

- According to this mechanism
  Intensity of emission of delayed fluorescence was directly proportional to the square of the intensity of incident radiation.
  $I_{P.D} \alpha I_a^2$
  Mechanism:
  1. $S_0 + h\vartheta \rightarrow S_1$
  2. $S_1 \rightarrow T_1$
  3. $T + T \rightarrow S_1 + S_0$
  4. $S_1 \rightarrow S_0 + h\vartheta_f$



11. Explain the types of photochemical reactions?

(OR)

Explain a) Photo dissociation reactions

b) Photo dimerisation reactions

There are different types of photochemical reactions some them are discussed below.

a) Photo dissociation reactions:

- When a molecule dissociates from excited state is called photolysis.
- Photo dissociation occurs in presence of light, radicals are produced in this type of reactions.
- Ex(1) : Gas phase photolysis
  In gaseous mixture of H_2 and Cl_2
  Mechanism:
  1. Primary Process:
  Initiation Step: It is a light medium reaction.
  $Cl_2 + h\vartheta \rightarrow (Cl_2)^* \rightarrow Cl^* + Cl^*$
  2. Secondary Process:
  Propagation Step: It is a dark medium reaction and highly exothermic.
  (a) $Cl^* + H - H \rightarrow HCl + H^*$

  (b) $H^* + Cl - Cl \rightarrow HCl + Cl^*$

  Termination Step: $Cl^* + Cl^* \rightarrow Cl_2 + h\vartheta$

- Ex(2): Photochemical reaction between H_2 and Br_2

  Mechanism:

  1. Primary Process:
  Initiation Step: It is a light medium reaction.
  $Br_2 + h\vartheta \rightarrow (Br_2)^* \rightarrow Br^* + Br^*$
  2. Secondary Process:
  Propagation Step: It is a dark medium reaction and Endothermic.

(a) Br* + H – H → HBr + H*

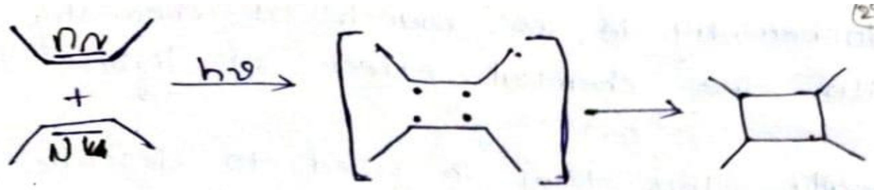
(b) H* + Br – Br → HBr + Br*

Termination Step: Br* + Br* → Br_2 + hϑ

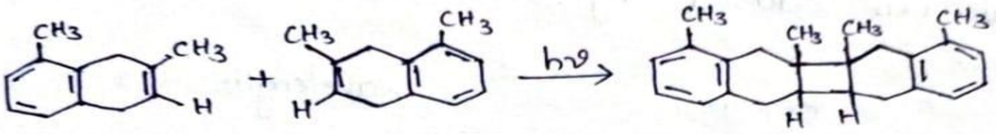
b) Photo dimerisation reactions:

- The dimerisation of alkenes under photochemical condition is a (2+2) cyclo addition reaction and forms various cyclobutane derivatives.

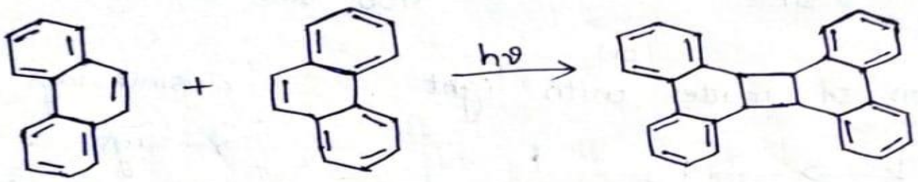
eg①



eg②

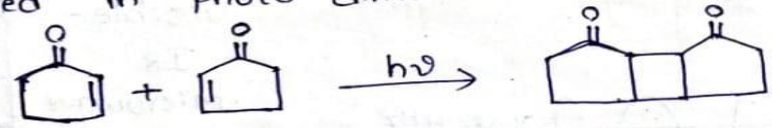


eg③

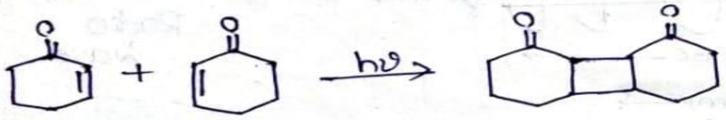


Cyclic α, β – unsaturated carbonyl compounds are easily involved in photo dimerisation reactions

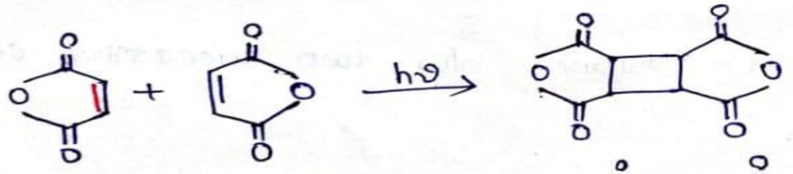
eg①



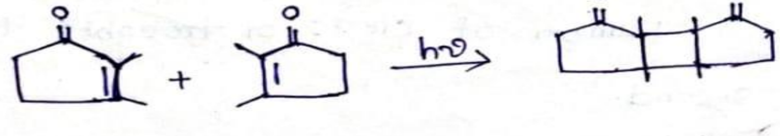
eg②



eg③



eg④



UNIT-III

Electrochemistry-I

Electrochemistry is a branch of science which deals withs transformation of chemical energy into electrical energy and electrical energy Into chemical energy. The basis for this electrochensical processes is the transformation of electrons from one system to anottier during the course of the process. Electrolytes and Non Electrolytes

1) Electrolytes :

Substance which conduct electricity either in molten state (or) in aqueous state is known as Electrolytis. They Conduct Current due to movement of tons.

Acids, Bases, aqueous solutions of metallic salts. Electrolytes are two typy

a) strong Electrolylts

b) Weak Electrolytes

a) Strong Electrolytes: Electrolytes which ionises completely at moderati dilutions and shows high Conclictivity are called strong Electrolytas.

Eg: Mineral acids like Hel, Hasoy, HNO3 Bases Uke NaOH, KOH. tequeous salt solutions like Nacl, kcl

b) Weak Electrolytes:- Electrolytes which ionises partially at moderate dilutions and show low Conductivity are Called Weak Electrolytes.

Eg: organic acids like CH3COOH., Bajy like NHион, масон oxalic acid .

Non Electrolytes :

substance which do not conduct Electricity either in molten state (01) in aqueous statt are Called Non Electrolysis.

Eg:- Glucose solution, urea solution, Benzene.

What is Electrolysis?

Electrolysis is definded as the process of decomposition of an electrolyte elther in molten state (or) in aqueous state by the passage of electricity

ectrode potential:

The tendency of an electrode to Lace (or) yain elections when it is in contact with it's own ions in solution is Called Electrode potential (or) single Electrode potential. It is denoted by 'E' and expressed in volts.

****

Explain about Electrolyte Concentration Cell without transference?

→ These are the alls in which the two Electrodes are of the "Same material which are dipped in two solutions of Same electrolytes with different concentrations.

→ In these type of calls there is no direct transfer of Ekctrolyte from one solution to other solution. The transfer occurs due to the result of chemical reaction.

• Electrical Energy is produced due to transfer of matter. A ConGanbation Cell without bransference Can be obtained by two simple alls connected in opposite direction.

There are 2 possible Cases are there.

1. End Electrode revase to cation
2. End Electrode reverse to Anion

End Electrode severse to Cation:-let us consider a Cell with Same Electrolytes of different Concentration.

Eg : cu/cuso4// cuso4/cu

At Anode : $\cancel{cu} \rightarrow cu^{+2}$ (a1) + $\cancel{2e}^{-}$

At cathode: cu^{+2} $\cancel{+2e}^{-} \longrightarrow \cancel{cu}$

Net current : $cu^{+2} \rightarrow cu^{+2}$

According to Nernest equation the emf of the Cell is .

E cell = E0 cell – RT/nf ln (p)/ (R)

= o – RT/2F ln (a1)/(a2)

End Electrode reverse to Anion:

Eg : Pt,Cl2/HCL//H^+CL^-/CL2,PT

****

What is Redex potential and Explain the Effect of Complexation Redex potentials salt of Fe(III)/Fe(II) and ferrocyanide/foniczaniteCouples?

oxidation is a process of removal of electrons from the species- Reckuction is a preas of addition of electrons from the spacily Nova Reden reaction may be definded as bethanidation and reduction baker plaasimultanearly in a reaction.

then the electrode clipped in a Solution Containing Totox Traction, then it shows the potanical value which is known

Efect of Complexation on Redox potentials :

The effect of fedes potentials on Compleation is xplained on the basis of potentiometric bitraron of Gulphate (Mohrs salt) k2cr2o7.

When we proland in tration, we add KartofColution Mater salt the restenpoternital is gradually increased by the on of Kally solution, at the end point, the redeSucksenky Increases at tugh value. The it due is meirapatarinal of FeIl)/FeIl) Couple in a mixture.

End Electrode reverse to Anion :

Eg : Pt,Cl2/HCL//H^+CL^-/CL2,PT

At Anode : $cl^- \rightarrow \frac{1}{2} cl2_{(g)} + 1e^-$

At cathode : $\frac{1}{2} cl2_{(g)} \rightarrow cl^-_{(a2)}$

Net current :$cl^-_{(a1)} \rightarrow cl^-_{(a2)}$

****

Explain Debye-Hackel theory of Electrolytic Solution?

The first successful attempts to explain the variation of Equivalent conductance of strong electrolytes with illution was made by Debye and Huckel in 1923.

Accading to this theory strong Electrolytes underga 100% Ionisation. for strong Electrolyte conductance Increases with dilution.

for weak Electrolytes ConductancaIncreafy with dilution.

Alc to Debye-Huckel theory Ions are assumed as hard spheres.

Fα Q1Q2/γ2

F = Electro Static attractive force

Q1 ,Q2 = charge of Ions.1, 2 respectively.

γ = Distance blw the Ions.

→ Each ion is surrounded by a number of oppositely charged ions, such an atmosphere is known as ionic atomsphere.

Under the influence of electric field, the Central ion and It's Ion atmosphere move in opposite direction Thus the presence of ionic atmosphere of opposite charge on the central 100 affects the speed of the ton in an electric field.

****

Write a note on Fuel Cells?

"Fud Gulls are Electrochemical / Galvanic alls Consisting of two Electrodes and an electrolyte.

"Fuel Calles are Galvanic ally in which chemical Energy of fuel is directly Converted to Electrical Energy. The Conventional process to produce Electrical energy is as followss

But in fuel Cell, it directly converts chemical Energy to Electrical The efficiency of energy Conversion in furl cell is mởe than 702

The flow through the extomalcreuit to the Cathock At Cathode, ondant gets reduced.

The produce Electrcity while passing through the external corallt. but Sekis $22H_2O$

dvantages of fuel cell.

Hydrogen-oxygen fuel Celly produce drinking water of Potable Quality.

****

Unit-4

Electrochemistry -II

Introduction:

Electrical double layer:

(OR)

Electrode - Electrolyte interface:

when a metal electrode is in contact with an aqueous solution of an electrolyte, the electrode aquires a tve change and the Solution interface becomes slightly -ve charge. The electrostatic interaction keeps the byer of -ve charge to the visidity of the charge on electrode. This pair of charged layer is called electrical double layer.

1) Structure of electrical double layer

(OR)

Theories of electrical double layer

There are many methods to explain the structure of electrical double layer. They are

1) Helmholtz - perrin parallel-plate model

2) Gowy-Chapman diffuse charge model

3) Stern model

1) Helmholtz-Perrin parallel-plate model :

In order to understand the structure of double layer, The helmholtz - perrinPriose propose a mathematical method based on experimental findings

→In this method, Helmholtz-perrin Suggested that the charge on metal takes -ve charge with reference to electrolyte Solution so the double layer Consist of two sheets of charge, one on electrode and other on Solution

→Hence we use the term symbol double layer ashich behaves like a parallel plate Condensor

since the charge density on the two sheet are equal in magnitude but Oppositely Signed

→The Potential Graph blw these two sheets is linear.charge density on metal electrode-outer helmholtz plane

To explain this structure of electrical double layer, coe can use electrostatic theory of Capacitors for double layer.

→According to this theory we know that the potential difference (v) across a Condensor of unit area is

V =d/€0 €r (qm) ---------------------- (1)

where d-distance b/w two plates

€r = dielectric constant of material. b/w two plates

€o = permitivity of free space

qm = charge density on metal electrode

we take differentfalion on both sides, we get

dv = d/ €0 €r dqm -------------------(2)

According to Lipmann equation the value of

dv = d/ €0 €r ∫qm dqm ------------------- (3)

This equation shows the structure of electrical double layer which is symmetrical w.r.to Vmax.

from the a bove discussion we conclude that the Helmholtz - pesurin model is Suite satisfactory for some metal eledrodes However the experimental results are not -agree with the theoritical results. This meary the model is does not explain the exact Structure of electrical double layer.

2) Gouy-Chapmann diffuse charge model :

- This model is based on Parallel plate model. Helmholtz-perrin parallel plate model.
- According to Gouy-chapmann charge diffuse model, the ions are liberating from double layer into the solution.
- In this model the excess chargé density on outer helmholtz plane is not equivalent to the excess change density on metal electrode

- A few ions are randomly diffuse into the solution. from outer helmholtz plane So the excess change density on outer helmholtz plane is decreases-
- This model is depends upon the ion-ion interactions in solutions

Dψx = (8Kt Co/€r€o).(Ze ψx/2Kt) ------------------------- (1)

→In this model the ions are considered as point charges.

→The density of diffuse double layer is Similar to that of ion-ion interactions in Solution

→According to this model, the potential, drop at distance from the electrode is Given b

where

C = Concentration of solution

Ψx = outer potential difference blw a point (x) from the electrode

€0 = permitivity of medium

€r = dielectric constant of medium

z = charge of ion

K = Boltzmann Constant

T = Temperature

→The above relates the electric field and electric potential at a distance x from the electrod

1) Due to the diffusion of ions from outer, helm holtz plane into the solution. The Structure of double layer is changed.

2)The electrical double layer behaves as Condensor and the potential drop blw two plates is curved nature.

Draw backs :

1)In this model ion-ion interactions are play an important role in the determination of structure of double layer But incase of low concentration Solutions, the ion-ion interactions negligable.

2)very serious error in this model is the assumption of ions as Point charges

3) Stern model :

→The Stern model is a combination of Helmholtz- perrin parallel plate model and Gouy-chapmann model.

→In Stern model the point charges are eliminated.

→The stern theory may be divided into two contributions.

i)A part of charge (as) on, solution is equal to the sum of charge on metal electrode and charge on outer helmholtz plane.

$$qs = qm + qH$$

ii) The same charge is Spread out in the electrolyte solution. From these two point it can be clear that the charge on solution is equal to the sum of charges of helmholtz -perrin and Gouy-Chapmann Charges.

The potential graph between double layer is given

$\Phi m - \Phi bulk = (\Phi m-\Phi H) + (\Phi H- \Phi bulk)$ ------------------(1)

Where Φm= inner potential at metal electrode

ΦH = inner potential of outer Helmholtz plane

$\Phi bulk$ = inner potential of solution.

The separation of charges and potential region produced a separation of differential capacities.

Each term in the above information reciprocal of differential capacitor.

$1/C = 1/CH+ 1/CG$

Where CH =Capacity for Helmholtz model

CG = Capacity for gouy-chapmann mode

from the above discussion we concluded than an electrical double layer has a total differential Capacity which is Given by helmholtz and GouyChapmann Capacities in series.

****

Over potential-Butler-Volmer equation (or) High field Approximation :

→If the cell is balanced against external Source, the galvanic potential difference can be identified tou as electrode potential.

→over potential may be defined as it is the extra driving force to cause the chemical reaction at the surface of electrode.

→It is denoted by Ƞ.

→The over potential is also complemen corresponding to current density of Cathode (ic) and the Current density of anode (ia)

→The net current density i = ic-ia

at equilibrium ic= ia

Butler-Volmer equation :

→this equation was proposed by Buttler and Volmer.

→Kinetics of electroding reactions are explained on the bases of Butter-Volmer equation.

→This equation Gives the Relation ship blw current density and over potential.

→This equation is also explain the reversible electrodic reactions.

→The Derivation of Buttler-Volmer equation is based on the kinetics of electrodic reactions.

let us consider the following redox reaction.

O+ne → Red (R)

Where Kf = Rate constant for forward reaction.

Kb= Rate constant for backward reaction.

→The current density of cathode for the a bove reaction is Given by.

$ic = nFK^{\circ}[0].e\ \alpha nf\eta/RT$ ---------------- (1)

where $\eta = E\text{-}Eo$

The current density at anode for the above reaction is Given by.

$ia = nFKo\ [R]\ e\ (1\text{-}\alpha)nF\eta/RT$ ---------------------- (2)

where n=no of electrons involved in reaction.

F=Faraday = 96,500 column

ko = Rate Constant

α=polarisation constant

R = universal constant

T = Temperature

[o] ^ * = oxidation species in activated form

[R] ^ * Reducted species in activated form

→The Net current density.

$i = i_{c} - i_{a}$

$i=nFk^{\circ}\ [0]\ e\ \text{-}\alpha\ nF\eta/RT - nFko(R)\ e\ (1\text{-}\alpha)nF\eta/RT$------------------- (3)

At equilibrium the aboce equation becomes

$i/io = \{e\ (1\text{-}\alpha)\ nF\eta/RT - e\text{-}\alpha nF\eta/RT$

$i = io\ \{\ e\ (1\text{-}\alpha)nF\eta/RT\text{-}e\ \text{-}\alpha nF\eta/RT$

→This equation is called Buttler-Volmer equation.

****

Tafel equation :

(OR)

Low field Approximation.

→ It is a special case of Butter-volmer equation

→ According to Butter-volmer equation we may write that

$i=io\ \{e\ (1\text{-}\alpha)nF\eta/RT - e\text{-}\alpha nF\eta/RT\}$ ------------------- (1)

Sine the lower potential δ is very small, So that the value is $\eta F/RT <<< 1$

Now we expand the a bove equation Series we get.

$i=io \{1+(1-\alpha)nF\eta/RT+---------)-(1-\alpha)nF\eta/RT+-------------\}$

Since $\eta F/RT <<<1$. So we neglect the remaining terms in the above expantion

$I=io\ n\eta F/RT$

This is called Tafel equation.

Case (1)

When ovenpotential 'η ' is large and the, the second term in the eq(1) is much smaller than that of first term so we neglect the second term in the eq (1)

$i=io\ e(1-\alpha)n\eta F/RT$ ------------------ (2)

Case 2

when overpotential 'η is lange,- ve thanthe first term in the a bove equation ismuch smaller than that of second term in the eq(1)

$i= - io\ e-\alpha n\eta F/RT$

This is known as Tafel equation.

****

Effect of electrolyte concentration on electrode potential Nernest equation :

→Consider an electrolyte consists of a metal in contact with a solution of its own ions.

Eg : Let us take a zinc rod in contact with a Znso4 Solution then the following equilibrium can be established.

$Zn(s) \rightarrow Zn2+ +2e-$

The emf of the electrode is Given by

$Eele = Eeleo – RT/nFLn \{(Zn2+)/Zn)\}$

Eele = electrode potential for Zn electrode under operating Conditions

Eele = Standard electrode potential of zn' electrode

let us consider the following Half cell reaction

$Ag+ (aq) +1e- \rightarrow Ag(s)$

The electrode potential half cell is for the a bove half cell is

****

Concentration polarisation-voltametry. (Polarograph) :

→Polarography is a electro Analytical technique. Cwhich makes use of Current Voltage Curves under Conditions of concentration Polarisation of an indicator electrode This also known as voltammetry.

→Polarography is the Study of the relation between Current flowing through a electrolyte solution and the voltage applied across the two electrodes in the Solution.

→A plot of current against applied voltage for a sample solution is called a polarogram.

→Heyrousky derive polarographic, method of analysis by using Droping mercury electrode (OME).

→G is the Galvanometer which measures the current strength.

→N2 gas is passed through the sample Gothich removes Sample the dissolved O2 from the sample.

Advantages of Droping mercury electrode :

→Mercury forms Amalgums with many metals and hence it reduce the reduction potential of metals.

→Hydrogen has a high over voltage on mercury.

→The diffused current atains a series state Volume.

→The surface of mercury drop is reprodu cable So it is more convienement to record the current voltage.

Applications of polarography :

→Polarography Con be used to estimate the Catiory and onions in the presence of various interfering ions.

→It is used to direct determination of dissolved oxygen in aqueous solutions and organic Solvents.

→To determine the oxidation states of metal ions in solution.

→The fonic solution of various element Can be analysied by polarographic technique

→The potential at cutiich the current is half of the limiting Current is called Holf wave potential.