

**NOTES FOR REVISION STUDIES**

**CY6151 - ENGINEERING CHEMISTRY -I**

**UNIT - 3 PHOTOCHEMISTRY AND SPECTROSCOPY**

**LESSON PLAN**

**3.1) Introduction - Photochemical and Thermal reactions.**

**3.2) Laws of Photochemistry:**

- a) Beer Lamberts Law**
- b) Grotthuss - Draper Law**
- c) Stark - Einstein Law**

**3.3) Quantum Efficiency (Quantum Yield)**

- a) High and Low yield**
- b) Determination of quantum efficiency by actinometer**

**3.4) Photo Physical Process**

- a) Fluorescence**
- b) Phosphorescence**

**3.5) Mechanism of Photo physical process by JABLONSKI diagram:**

- a) Non radiative transitions (Internal Conversion & Inter System Crossing)**
- b) Radiative transitions (Fluorescence, Phosphorescence)**

**3.6) Photo Chemical Process**

- a) Photosensitization & quenching**
- b) Chemiluminescence**

**3.7) Spectroscopy - Introduction**

- a) Electro Magnetic Radiations**
- b) Energy level diagrams**

**3.8) Absorption of radiation- Electronic, Vibrational & rotational transition**

**3.9) Ultraviolet (UV) spectroscopy - Principle, Instrumentation and application.**

**3.10) Infrared (IR) spectroscopy - Principle, Instrumentation and application.**

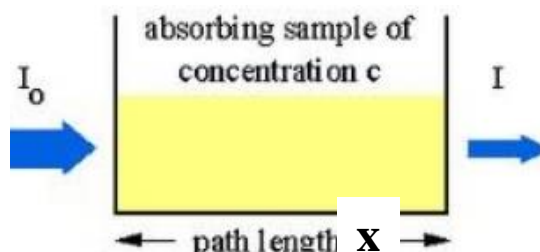
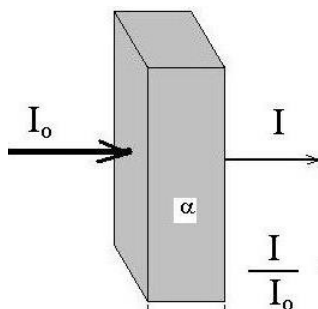
### 3.1) INTRODUCTION

The Chemical reactions occurring by absorbing UV , Visible radiations are known as Photochemical reactions. The study about the rate and mechanism of photochemical reactions is Photochemistry. These radiations are having the wavelength from 200 – 800 nm.

S. N O	PHOTOCHEMICAL REACTIONS	THERMAL REACTIONS
1	Presence of light is important condition.	Presence of heat energy is important condition.
2	Involves absorption of light radiation	Involves absorption or liberation of heat energy.
3	Reaction rate is Temperature independent.	Reaction rate is Temperature dependent.
4	$\Delta G$ may be Positive or Negative. Because the radiation in photosynthesis may be converted to free energy and makes $\Delta G$ positive.	$\Delta G$ is always Negative.
5	Reactions are initiated by absorption of radiations of energy $h\nu$ .	Reactions are initiated by molecular collisions.
6	Eg. HCl formation $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$ No reaction in darkness	Decomposition of $\text{CaCO}_3$ $\text{CaCO}_3 \xrightarrow{900^\circ\text{C}} \text{CaO} + \text{CO}_2$

### 3.2) LAWS OF PHOTOCHEMISTRY

#### 3.2) -a) BEER LAMBERT'S LAW (PHOTO PHYSICAL LAW)



**Lambert's law:** Lambert's law states that " When a beam of monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease of intensity of the radiation ( $-dI$ ) with thickness of absorbing medium ( $dx$ ) is proportional to the intensity of incident radiation ( $I$ ).

$$\text{i.e., } \frac{-dI}{dx} \propto I$$

$$\frac{-dI}{dx} = K I$$

(Where  $K$  = absorption coefficient.)

Integrating on both sides,  $\frac{-dI}{I} = K dx$

$$-\ln I / I_0 = K x$$

$$2.303 \log I_0 / I = K.x$$

$$\log \frac{I_0}{I} = \frac{K}{2.303} \cdot x$$

$$\boxed{A = \epsilon x}$$

The above equation is known as Lambert's law.

**Beer's law:** This is used for dilute solution. When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation (-dI) with thickness of the absorbing solution (dx) is proportional to the intensity of incident radiation (I) as well as the concentration of the solution (C).

i.e.,  $\frac{-dI}{dx} \propto I.C$

$$\frac{-dI}{dx} = K I.C \quad (\text{Where } K = \text{absorption coefficient}).$$

Integrating on both sides,

$$\frac{-dI}{I} = K.C dx$$

$$-\ln I / I_0 = K.C x$$

$$\ln I_0 / I = K C x$$

$$2.303 \log I_0 / I = K.C.x$$

$$\log \frac{I_0}{I} = \frac{K}{2.303} \cdot C \cdot x$$

$$\boxed{A = \epsilon C x}$$

This is called Beer Lambert's law.

Where,  $\log \frac{I_0}{I} = A$ , Absorbance (or) Optical activity

And,  $\frac{K}{2.303} = \epsilon$ , molar absorptivity constant.

### Application of Beer-Lambert's law:

Using this Beer – Lambert's law, the concentration of any unknown solution can be easily found out.

#### Step 1:

A standard solution of concentration  $C_S$  is taken . Its absorbance is found out. It is denoted as  $A_S$ .

As per Beer Lambert's law, we can write,  $A_S = \epsilon C_S x$  ,

$$\frac{A_S}{C_S} = \epsilon x \quad \text{-----(1)}$$

#### Step 2:

Now the unknown sample solution is taken . Let us assume its concentration as  $C_U$ . Its absorbance is noted by a colorimeter. It is denoted as  $A_U$ .

As per Beer Lambert's law, we can write,

$$A_U = \epsilon C_U x ,$$

$$\frac{A_U}{C_U} = \epsilon x \quad \text{-----(2)}$$

Comparing the equations, (1) and (2)

$$\frac{A_U}{C_U} = \frac{A_S}{C_S}$$

$$\text{Therefore , } C_U = A_U \cdot \frac{C_S}{A_S}$$

Thus the unknown concentration can be calculated.

### Limitations of Beer-Lambert's law:

1. It is used only for dilute solution.
2. If the solution contains any impurity or any suspended particles, the law fails.
3. There should be no change in temperature.
4. Only monochromatic light should be used.
5. Deviation occurs if the solution undergoes polymerization or dissociation.

### 3.2- B) GROTHUSS DRAPER LAW

1. It is also known as the Principle of Photochemical activation.
2. When the light radiation falls on any substance, only the fraction of absorbed light can cause a photo chemical change.
3. But, when the conditions are not favouring for such changes, the radiation may be reflected, transmitted or re-emitted.

### Limitations of Grothuss Draper Law:

1. It is purely qualitative. It does not give any relationship between the amount of light absorbed and the number of molecules reacted in a system.
2. It mainly concerns about the primary process of a photochemical reaction. In secondary process it may fail.

### 3.2 - C) STARK EINSTEIN LAW

1. **Statement:** In a primary photochemical process ( I step) each molecule is activated by absorption of one quantum of radiation.

2. **Steps Involved:**

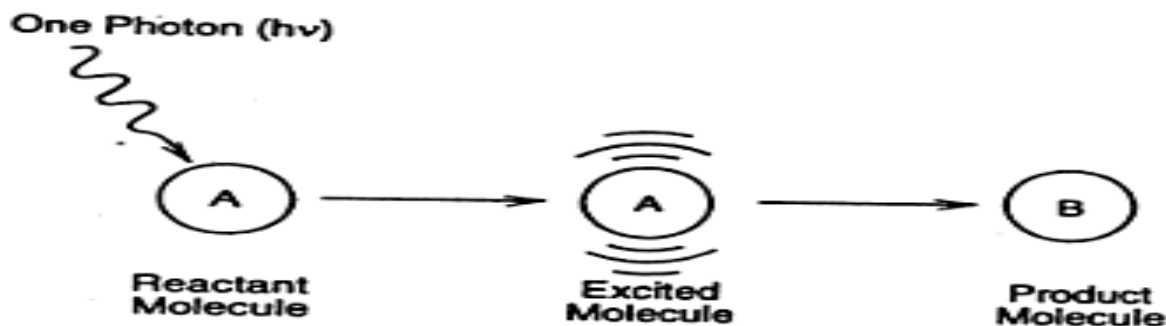
a) When a molecule absorbs a photon, it forms activated molecule. This is known as primary process of photochemical reaction.

b) This activated molecule further may or maynot react. If it reacts, it may cause chain of reactions also. This is known as secondary process of photochemical reaction.

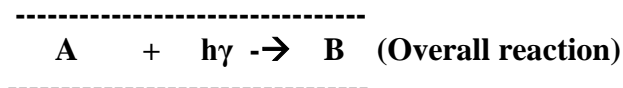
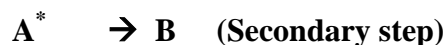
c) In primary process, one molecule absorbs one photon or one quantum of radiation of energy  $h\gamma$ .

(Where  $h$  = Plank's constant =  $6.62 \times 10^{-34}$  erg.sec       $\gamma$  = frequency)

3. **Illustration:**



From the diagram, it is evident A absorbs a photon of light and gets activated. This is primary step. The activated molecule  $A^*$  then decomposes to yield B.



4. **Other Important relations derived from Stark- Einstein Law:**

Photons = quanta =  $E = h\gamma$

1 molecule absorbs = 1 Photon

1 mole of substance absorbs = 1 mole of photon

$6.023 \times 10^{23}$  molecule absorbs =  $6.023 \times 10^{23}$  photons = 1 Einstein

i.e., Amount of energy (E) absorbed per mole of substance is called as Einstein.

$$1 \text{ Einstein} = N_A \cdot h\gamma = N_A \cdot \frac{hC}{\lambda}$$

where  $C$  = velocity of light =  $3 \times 10^{10}$  cm / sec

### 3.3) QUANTUM EFFICIENCY (OR) QUANTUM YIELD

1) Quantum yield is defined as ‘the number of reactant molecules reacted or product molecules formed per quantum of light absorbed.’ It is denoted as ( $\phi$ ).

2) Quantum yield  $\phi = \frac{\text{Number of molecules reacted (or) formed}}{\text{Number of Photons absorbed}}$

3)  $\phi$  value varies from 0 to  $10^6$ .

4) If a reaction obeys Einstein’s law, then one molecule is decomposed per photon.

Quantum yield  $\phi = \frac{\text{Number of molecules reacted (or) formed}}{\text{Number of Photons absorbed}} = \frac{1}{1} = 1$

5) If yield is less than 1, it is called low quantum yield. If yield is greater than 1, it is called a high quantum yield.

#### 3.3 - A) HIGH QUANTUM YIELD AND LOW QUANTUM YIELD: Conditions to get proper quantum yield:

- All the molecules should have equal reactivity.
  - Reactivity of the molecule is temperature independent.
  - The activated molecules should decompose to form product.
- If these conditions are violated, it leads to deviation in expected quantum yield.

#### Reasons for high yield:

- In primary step absorption, Free radicals are produced to cause chain reaction.
- Collision of active molecules with other molecules also cause chain reaction
- Intermediate products formed may act as catalysts.
- The exothermic reaction evolving heat may activate further molecules.

#### Example : Formation of HCl

Step 1:  $\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$  ( $1^\circ$  reaction)

Step 2:  $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$  ( $2^\circ$  reaction)

Step 3:  $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$  ( $2^\circ$  reaction)

The Cl consumed in step (2) is regenerated in step (3) and the reaction is becoming a chain reaction with  $\phi = 10^4$  to  $10^6$ .

#### Reasons for Low yield:

- Excited molecules may lose energy by collision with non-excited molecules.
- Molecules may not receive sufficient energy to react.
- Primary step may be reversible.
- Recombination of dissociated fragments to form reactants.

Example: - Dimerisation of anthracene.



As per theory, it should have  $\phi = 2$ . But practically found to be  $\phi = 0.5$ .

This is because the reaction is reversible.

#### Classification of Photochemical reactions based on quantum yield

No	Condition	Type	Examples
1	$\Phi =$ small integers like 1,2	Normal quantum yield reactions	1) Dissociation of HI, 2) Dissociation of HBr
2	$\Phi < 1$	Low quantum yield reactions	1) Anthracene dimerisation (0.5) 2) Dissociation of $\text{NH}_3$ , (0.2)
3	$\Phi$ is very high ( $10^2$ to $10^6$ )	High quantum yield reactions	1) Combination of $\text{H}_2 + \text{Cl}_2$ ( $10^6$ ) Combination of $\text{CO} + \text{Cl}_2$ ( $10^3$ )

### 3.3 - B) DETERMINATION OF QUANTUM YIELD:

Determination of quantum yield can be done in two steps.

- Measuring the number of molecules decomposed or formed.
- Measuring the amount of quanta absorbed.

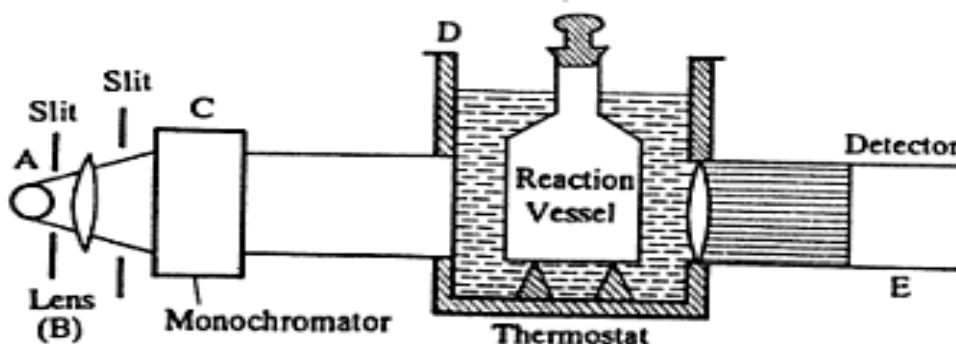
#### a) Measuring the number of molecules decomposed or formed:

This is determined by chemical kinetics method. Small quantities of samples are periodically pipette out from the reaction mixture. Then its concentration is determined by volumetric analysis. The concentration can also be determined by absorption techniques, refractive index measurement and optical activity measurement.

#### b) Measuring the amount of quanta absorbed:

Light from a suitable source (A) ( eg. Sunlight, Tungsten filament, Mercury vapour lamp) is sent through the lens (B) and Monochromator (C). From there, light enters into the sample cell (D). The cell is kept in a thermostat. The cell contains reaction mixture. The light transmitted through D falls on Detector ( E ) to calculate its intensity ( $I_1$ ). The same experiment is repeated with empty cell and its intensity is measured. ( $I_2$ ). The difference between the two readings ( $I_2 - I_1$ ) will give the amount of energy absorbed. Generally Chemical actinometers are used as detector.

(eg) Uranyl oxalate actinometer, Ferrioxalate actinometer



#### Uranyl Oxalate Actinometer:

##### Principle:

A chemical actinometer consists of a solution which is sensitive to light. When light falls on it, a chemical reaction will take place. The extent of reaction is a direct measure of energy absorbed by the reaction.

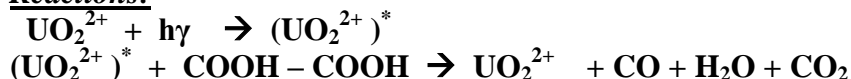
##### Construction and working:

It is used for radiations of 200 – 500 nm wavelength and  $\phi = 0.5$ .

It contains 0.05M oxalic acid and 0.01M Uranyl sulphate. On falling light oxalic acid dissociates to CO, H<sub>2</sub>O and CO<sub>2</sub>.

The extent of decomposition of oxalic acid is a measure of intensity of light absorbed. The progress of the reaction is determined by KMnO<sub>4</sub> before and after exposure to light.

##### Reactions:



##### Calculation:

Absorbed energy = Total incident energy – Residual energy

Absorbed energy = Empty cell reading – Reaction mixture cell reading

### **3.4) PHOTO PHYSICAL PROCESS:**

Molecules go to excited state by absorption of radiation. If the absorbed radiation is not used to produce the reaction, it will be re-emitted as light of longer wavelength. This process is known as Photo physical process.

Types of Photo physical process:

- a) Fluorescence
- b) Phosphorescence

### **3.4- A) FLUORESCENCE:**

**1.Definition:** When a radiation is passed on certain substances, they get excited. On coming back to ground state, it re-emits excess energy. If the emission is stopped as soon as the incident radiation is cut off, such phenomenon is known as Fluorescence.

2. The substances showing this property are ‘ fluorescent substances’. (eg) Fluorite, Eosin dye, Fluorscein dye, chlorophyll, riboflavin

### **3. Applications of fluorescence:**

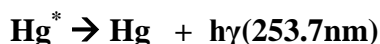
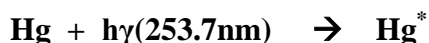
- a) Used in fluorescent lamps
- b) Different inks show different types of fluorescence. So, forged documents are found out.
- c) When UV light is sent through newly laid eggs, they fluoresce with rose colour while decayed eggs appear in blue colour.
- d) To prevent accidents, reflectors are used in High ways. They use the principle of fluorescence .

### **4) Types of Fluorescence:**

- a) Resonance fluorescence
- b) Sensitized fluorescence

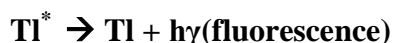
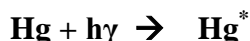
a) **Resonance fluorescence:** In fluorescence process, if incident and re-emitted radiations are of same wavelength, then it is known as Resonance fluorescence.

Eg. Mercury vapours absorb radiation of 253.7nm and get excited. On coming back to its ground state , it re-emits the radiation of same wavelength 253.7 nm.



b) **Sensitized fluorescence:** A non- fluorescent substance may be made as fluorescent substance by the presence of a foreign fluorescent substance. The foreign substance is known as Fluorescent Sensitizer. The process is known as Sensitized fluorescence.

Eg. Thallium is non- fluorescent substance. When adding Mercury, Thallium becomes fluorescent substance.





### 3.4 - B) PHOSPHORESCENCE:

When a radiation is passed on certain substances, they get excited. On coming back to ground state, they emit visible light continuously for some time even after the incident light is cut off. This delayed fluorescence is known as 'Phosphorescence'.

Eg. Ruby, emarlad, Cadmium Sulphide, Barium Sulphide

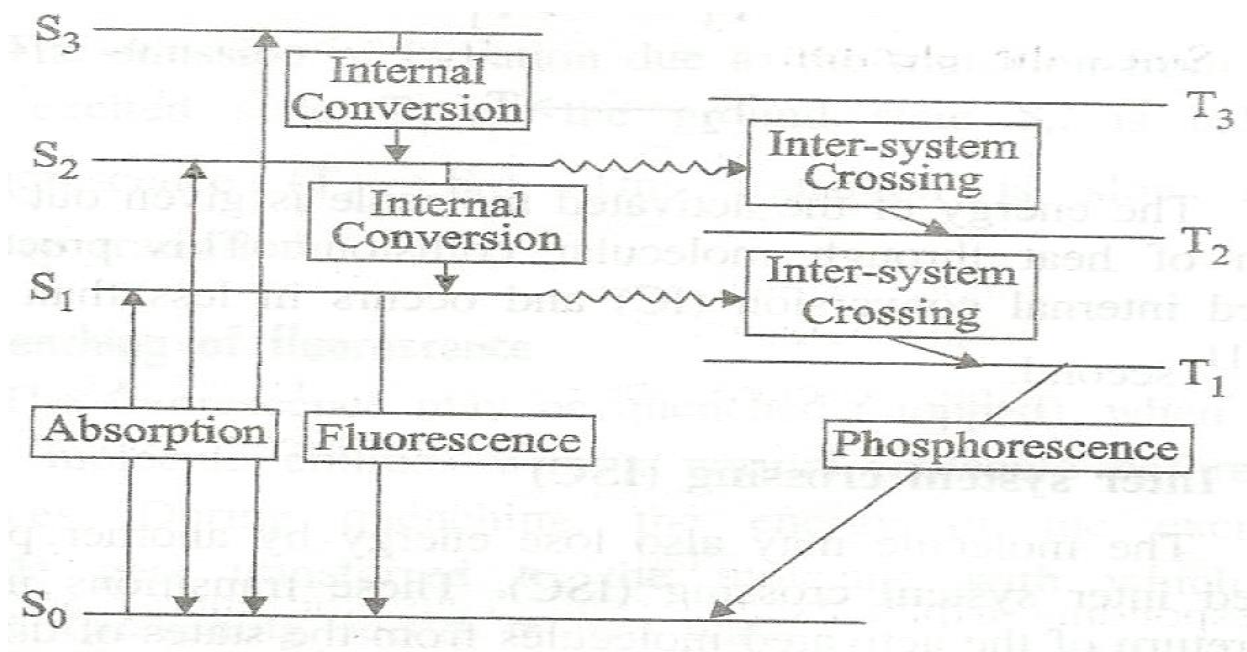
Uses: 1) In dials of clocks and watches as they glow in dark.

2) Luminous paints are used in painting watches, electric switches and advertisement boards.

#### **Differences between Fluorescence and Phosphorescence:**

No	FLUORESCENCE	PHOSPHORESCENCE
1	The emitted radiation stops as soon as the incident radiation is cut off.	The emitted radiation continues for sometime even after the incident radiation is cut off.
2	It is a fast process. Occurs in $10^{-8}$ sec.	It is slow process. Takes time of $10^{-3}$ to 10 seconds.
3	It is allowed transition.	It is forbidden transition.
4	It is due to transition of $S_1 \rightarrow S_0$	It is due to transition of $T_1 \rightarrow S_0$
5	Eg. Fluorite, Eosin dye, Fluorscein dye, chlorophyll, riboflavin	Eg. Ruby, emarlad, Cadmium Sulphide, Barium Sulphide
6	Used in fluorescent lamps, detection of forged documents, detection of decayed eggs.	Used in dials of clocks and watches , painting watches, electric switches and advertisement boards.

### 3.5) MECHANISM OF PHOTO PHYSICAL PROCESS BY JABLONSKI DIAGRAM



Jablonski diagram is used to explain mechanism of photo physical process. It involves Non radiative transitions ( Internal conversion, Inter System Crossing) and radiative transitions ( Fluorescence, Phosphorescence) .

**Singlet and Triplet States:**

$(2S + 1)$  is known as spin multiplicity.

If  $(2S + 1) = 1$ , it is singlet state.

If  $(2S + 1) = 3$ , it is triplet state.

**Ground state:**

Before absorbing energy, molecules have paired electrons in ground state. ( $\uparrow\downarrow$ ). The Upward orientation spin gets cancelled by downward orientation spin.

$$\text{i.e., } S_1 = +\frac{1}{2} \quad S_2 = -\frac{1}{2}$$

$$S = S_1 + S_2 = 0$$

Hence,  $2S + 1 = 2(0) + 1 = 1$ , This is singlet ground state.

**Excited state:**

On absorbing energy, one of the paired electrons goes to excited state with Parallel orientation ( $\uparrow\uparrow$ ) or Anti-parallel orientation ( $\uparrow\downarrow$ ).

For parallel Orientation,  $S_1 = +\frac{1}{2} \quad S_2 = +\frac{1}{2}$

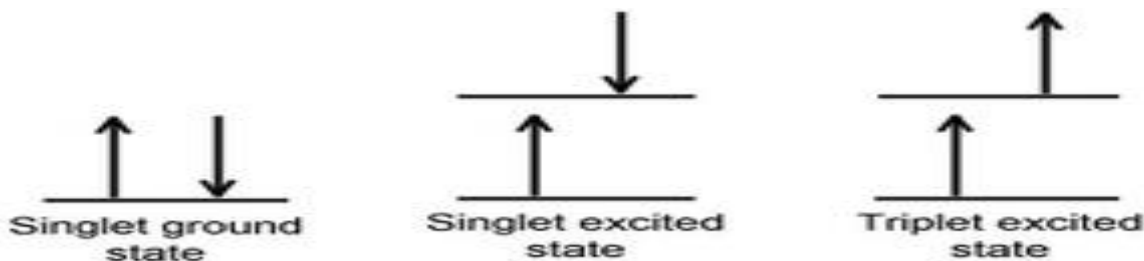
$$S = S_1 + S_2 = 1$$

Hence,  $2S + 1 = 2(1) + 1 = 3$ , This is Triplet excited state.

For Anti - parallel Orientation,  $S_1 = +\frac{1}{2} \quad S_2 = -\frac{1}{2}$

$$S = S_1 + S_2 = 0$$

Hence,  $2S + 1 = 2(0) + 1 = 1$ , This is Singlet excited state.



### Non- Radiative transitions:

If the excited molecules come to lower state without emitting radiation, it is known as non-radiative transition. Here, the energy is lost as heat. This occur within excited states only.

- a) **Internal Conversion**: If the transition is between higher excited state to first excited state of same spins, it is known as Internal Conversion. ( $T_3 \rightarrow T_1$  ,  $T_2 \rightarrow T_1$  ,  $S_3 \rightarrow S_1$ ,  $S_2 \rightarrow S_1$ ). It occurs in less than  $10^{-11}$  seconds.
- b) **Inter System Crossing**: If the transition takes place between excited states of different spins, it is known as Inter System Crossing. (ISC). ( $S_1 \rightarrow T_1$  ,  $S_2 \rightarrow T_2$  ,  $S_3 \rightarrow T_3$ ). It is forbidden process. It occurs very slowly.

### Radiative transitions:

If the excited molecules come to ground state by emitting radiation, it is known as radiative transition. Here, the energy is emitted as light.

- a) **Fluorescence** : If the transition is between excited state to ground state of same spins, it is known as Fluorescence. It is allowed transition and occurs fast i.e., in ( $10^{-8}$ ) seconds. ( $S_1 \rightarrow S_0$ ).
- b) **Phosphorescence**: If the transition is between excited state to ground state of different spins, it is known as Phosphorescence. It is forbidden transition and occurs very slowly i.e., in ( $10^{-3}$  to  $10$ ) seconds. ( $T_1 \rightarrow S_0$ ).

**Quenching of Fluorescence**: Stopping the process of fluorescence is known as “quenching”.

- a) **Internal quenching**: If molecule is changed its spin state from  $S_1$  to  $T_1$ , then fluorescence will be stopped. This is known as ‘internal quenching of fluorescence’.
- b) **External quenching**: If quenching is stopped by adding external substance which absorbs energy from excited molecule, then it is known as ‘External quenching of fluorescence’.

The transitions can be tabulated as follows:

No	Type of Transition	Name	Transition involved	Nature of Transition
1	Non- Radiative	Internal Conversion	$T_3 \rightarrow T_1$ , $T_2 \rightarrow T_1$ , $S_3 \rightarrow S_1$ , $S_2 \rightarrow S_1$	Allowed
2		Inter System Crossing	$S_1 \rightarrow T_1$ , $S_2 \rightarrow T_2$ , $S_3 \rightarrow T_3$	Forbidden
3	Radiative	Fluorescence	$S_1 \rightarrow S_0$	Allowed
4		Phosphorescence	$T_1 \rightarrow S_0$	Forbidden

### 3.6) PHOTO CHEMICAL PROCESS

The Chemical reactions occurring by absorbing UV , Visible radiations are known as Photo chemical reactions.

#### 3.6-A) PHOTO SENSITIZATION:

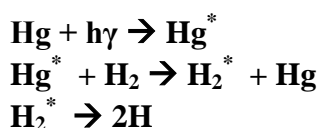
**Photo sensitization:** The foreign substance which absorbs the radiation and transfers the energy to the reactant is called photo sensitizer. The process is known as photo sensitization.

(eg) Mercury, Cadmium, Zinc, Benzophenone, Sulphur di oxide

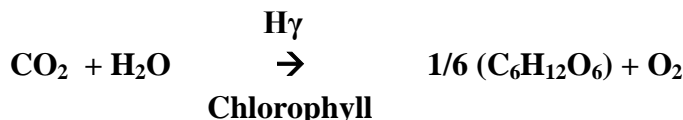
When the excited sensitizer loses its energy by collision with other molecules, it is called quenching of photo sensitization.

#### Examples of Photo sensitization:

a) Dissociation of Hydrogen: At 253.7 nm, H<sub>2</sub> does not absorb any radiation. But, on adding mercury vapour, the dissociation occurs because of photo sensitization.



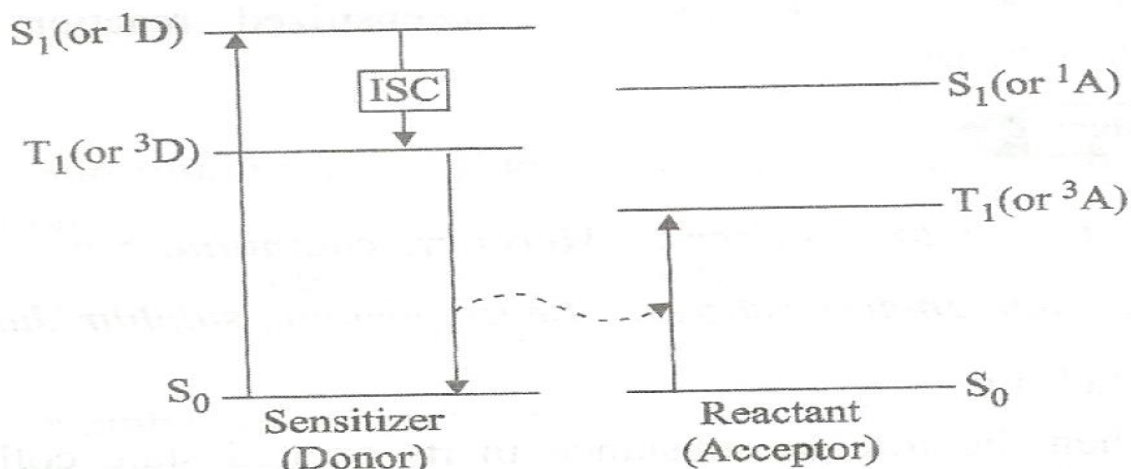
b) Photo synthesis in plants: CO<sub>2</sub> and H<sub>2</sub>O donot absorb sun light directly in the range of 600 – 700 nm. But in presence of chlorophyll, sun light is absorbed and photosynthesis is taking place.



#### Mechanism:

Let us consider a Donor – Acceptor system. Sensitizer is acting as Donor (D) and the reactant is acting as acceptor (A). The process involves some of the following steps:

Step	Reaction	Explanation
I	$\text{D} + h\nu \rightarrow {}^1\text{D}$	Donor absorbs energy and excites to singlet state ${}^1\text{D}$
II	${}^1\text{D} \rightarrow {}^3\text{D}$ ( By ISC )	By Inter system crossing, it crosses from singlet ( ${}^1\text{D}$ ) to triplet state( ${}^3\text{D}$ )
III	${}^3\text{D} + \text{A} \rightarrow {}^3\text{A} + \text{D}$	Triplet state donor ${}^3\text{D}$ collides with acceptor A and A goes to triplet excited state.
IV	${}^3\text{A} \rightarrow \text{Product}$	Triplet excited state acceptor gives the product. These entire process is known as Photo sensitization.
V	${}^3\text{D} \rightarrow \text{Product}$	Instead of sensitization, sometimes the sensitizer itself forms the product or it may lose its energy by colliding with another molecule. This is known as quenching.



### 3.6 - B- CHEMILUMINESCENCE:

Emission of light in a chemical reaction at ordinary temperature is known as 'chemiluminescence'.

Reactants  $\rightarrow$  Products +  $h\nu$

It is reverse process of photochemical reaction.

As the emission occurs at ordinary temperature, it is also known as 'cold light'.

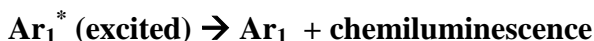
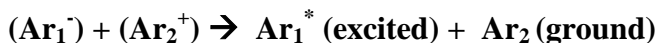
In this process chemical energy is converted to light energy.

#### Examples for chemiluminescence:

1. Grignard reagent on oxidation shows greenish blue light glow.
2. Phosphorous on oxidation shows greenish yellow light glow.
3. Pyrogallol + Formaldehyde + Hydrogen peroxide reaction mixture shows a red glow.
4. Glow of fireflies is due to oxidation of luciferon protein by luciferase enzyme. This is also known as bio – luminescence as it is found in biological system.

#### Mechanism of chemiluminescence:

Consider a reaction between aromatic anions ( $Ar_1^-$ ) and cations ( $Ar_2^+$ ).



Before reaction:

- 1) ( $Ar_1^-$ ) contains one set of paired electrons in Bonding Molecular Orbital (BMO) and one unpaired electron in Anti Bonding Molecular Orbital (ABMO).
- 2) ( $Ar_2^+$ ) contains one unpaired electron in BMO and one empty ABMO.

After reaction:

- 1) One electron is transferred from ABMO of ( $Ar_1^-$ ) to BMO of ( $Ar_2^+$ ).
- 2) ( $Ar_1^-$ ) is activated to ( $Ar_1^*$ ). It emits energy as chemiluminescence and coming to original state.

