UNIT –III Photochemistry

Photochemistry is the study of the interaction of electromagnetic radiation with matter resulting into a physical change or into a chemical reaction.

Primary Processes

- **One molecule is excited into an electronically excited state by absorption of a photon, it can undergo a number of different primary processes.**
- **Photochemical processes are those in which the excited species dissociates, isomerizes, rearranges, or react with another molecule.**
- **Photo physical processes include radiative transitions in which the excited molecule emits light in the form of fluorescence or phosphorescence and returns to the ground state, and intramolecular non-radiative transitions in which some or all of the energy of the absorbed photon is ultimately converted to heat.**

Laws Governing Absorption Of Light

Lambert's Law: **This law states that decrease in the intensity of monochromatic light with the thickness of the absorbing medium is proportional to the intensity of incident light.**

$$-dI/dx \propto I$$

$$-dI/dx = KI,$$

on integration changes to

$$I = I_0 e^{-Kx}$$

Where , I_0 = intensity of incident light.

I=intensity of transmitted light.

K= absorption coefficient.

Beer's Law :

It states that decrease in the intensity of monochromatic light with the thickness of the solution is not only proportional to the intensity of the incident light but also to the concentration 'c' of the solution.

Mathematically, $-dI/dx \propto Ic$

$$-dI/dx = \epsilon Ic$$

on integration $I = I_0 e^{-\epsilon cx}$

Where,

ϵ = molar absorption coefficient or molar extinction coefficient

Numerical value of Einstein

- **In CGS Units**

  $E = 2.86/\lambda(cm)$ **cal per mole**

  or

  $= 2.86 \times 10^5 / \lambda(A^0)$ **K cal per mole**

- **In SI units**

  $E = 0.1197/\lambda(m) J\ mol^{-1}$

Grotthuss-Draper Law(First Law of Photochemistry):

Only the light which is absorbed by a molecule can be effective in producing photochemical changes in the molecule.

Stark-Einstein's Law (Second Law of Photochemistry):

It states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction.

The energy absorbed by one mole of the reacting molecules is

$$E=Nh\nu.$$

This energy is called one einstein.

Or

$$=11.97X10^{-5}/\lambda(m)KJ\ mol^{-1}$$

Processes of photochemical reactions

1. **Primary Process: Atoms or molecules activated by actual absorption of radiation.**

   Or, the excitation of the species from the ground electronic state to excited state.

2. **Secondary process: Activated species undergoes chemical reaction.**

   ---Does not involve the absorption of light.

Eg., Photochemical combination of Cl_2 and H_2 *(It is chain mechanism)*

   a. *Primary Process*

$Cl_2 + h\nu \rightarrow 2Cl^{\cdot}$ Chain Initiation step

Photochemical equivalence is applicable to this step

b. Secondary process

Propagation reaction and Chain terminating step

Utility of the Laws

1. **Calculation of the rates of formation of reactive intermediates in photochemical reactions**
2. **The study of the mechanisms of photochemical reactions.**

Interpretation of Einstein's Law

In terms of Quantum efficiency:

Quantum Efficieny

$$\phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No.of quantas of light absorbed in the same time}}$$

Experimentally,

$$\Phi = \frac{\text{rate of chemical reaction}}{\text{quanta absorbed per second.}}$$

Quantum efficiency :

It expresses the efficiency of a photochemical reaction.
A photochemical reaction strictly obey the laws of photochemical equivalence Φ should be unity.

Because the ratio between the reacting molecules & no. of quanta absorbed =1:1
Only few reactions, $\Phi = 1$ eg. $SO_2 + Cl_2 \rightarrow SO_2Cl_2$
But in major cases, $\Phi \neq 1$

Because, all the primary process (photo activation) does not lead to the secondary process (thermal reaction).

Quantum Yield

- In the photolysis of Cl_2 and H_2, Φ_{HCl} can be as high as 1 million.

$$Cl_2 + h\nu \rightarrow 2Cl^{\cdot}$$

$$Cl^{\cdot} + H_2 \rightarrow HCl + H \text{ (exothermic)}$$

$$H + Cl_2 \rightarrow HCl + Cl^{\cdot}$$

- In the photolysis of Br_2 and H_2, Φ_{HBr} is very low i.e about 0.01

$$Br_2 + h\nu \rightarrow 2Br$$

$$Br + H_2 \rightarrow HBr + H \text{ (endothermic)}$$

$$H + Br_2 \rightarrow HBr + Br$$

The hydrogen- chlorine reaction

We are considering the photolysis of Cl_2 and H_2

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)} (\text{radiation}, \lambda = 4800 A^0)$$

Its quantum yield $=10^4$ to 10^6 ,because it is a chain reaction

Chain reaction : A chain reaction is one in which a single photoactivated molecule sets off a sequence of reactions so that a very large number of reactant molecule react through a chain reaction.

Primary process, involve the decomposition of chlorine molecule into chlorine radicals.

$$Cl_2 + h\nu \rightarrow 2Cl^{\cdot} \qquad (1) \text{ Chain Initiation step}$$

In secondary process **- propagate the chain by their continued reaction gives a large no. of HCl molecules.**

$$Cl^{\cdot} + H_2 \rightarrow HCl + H^{\cdot}$$

$$H^{\cdot} + Cl_2 \rightarrow HCl + Cl^{\cdot} \quad \text{Propagation reaction}$$

Exothermic and low activation energy hence large no. of HCl molecule is formed before terminating the reaction.

Hence the no of Cl_2 molecules that undergoes reaction per each quantum of radiation absorbed is very large, ie, 104 to 106 .

So the reaction has very high quantum yield.

The chain is finally terminated by the combination of chlorine radicals on the walls of the vessels or in gas phase.

$$Cl. + Cl. \rightarrow Cl_2 \quad \text{(Chain terminating step)}$$

Photosensitization

Photosensitized reactions:An electronically excited molecule can transfer its energy to a second species which then undergoes a photochemical process even though it was not itself directly excited.

eg, 1. Mercury acting as a photosensitizer:

$$Hg+hv \rightarrow Hg^* \qquad Hg^*+H_2 \rightarrow H_2^* + Hg$$

$$H_2^* \rightarrow 2H^{\cdot}$$

2. Chlorophyll acting as a photosensitizer

$$\text{Chlorophyll} + hv \rightarrow \text{Chlorophyll}^*$$

$$6CO_2+6H_2O+ \text{Chlorophyll}^* \rightarrow C_6H_{12}O_6 + 6O_2 + \text{Chlorophyll}$$

3 Chlorine photosenstizes the reaction of ozone to oxygen.

$$Cl_2 + h\nu \rightarrow Cl_2^*$$

$$Cl_2^* + O_3 \rightarrow Cl_2 + O_2 + O$$

$$O + O_3 \rightarrow 2O_2$$

Luminescence

The glow produced in the body by methods other than action of heat i.e. the production of cold light is called Luminescence.

It is of three types,

1. Chemiluminescence: The emission of light in chemical reaction at ordinary temperature is called Chemiluminescence

e.g. The light emitted by glow-worms

2. Fluorescence: Certain substances when exposed to light or certain other radiations absorb the energy and then immediately start re-emitting the energy.

Such substances are called fluorescent substances and the phenomenon is called fluorescence .

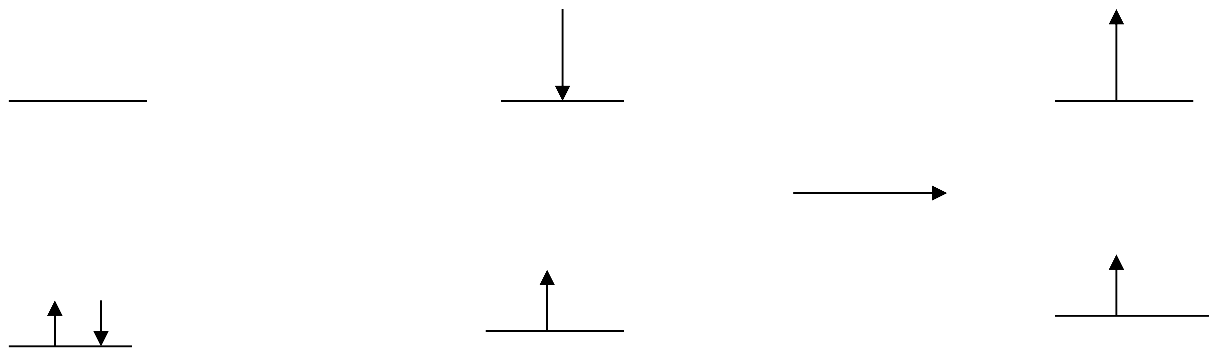
e.g Organic dyes such as eosin,fluorescein etc.

vapour of sodium,mercury,iodine etc.

3. Phosphorescence: There are certain substances which continue to glow for some time even after the external light is cut off.

Thus, phosphorescence is a slow fluorescence.

Fluorescence and phosphorescence in terms of excitation of electrons



Singlet ground state S_o

Singlet excited state S_1 (pair of electrons with Opposite spins but each in different orbital)

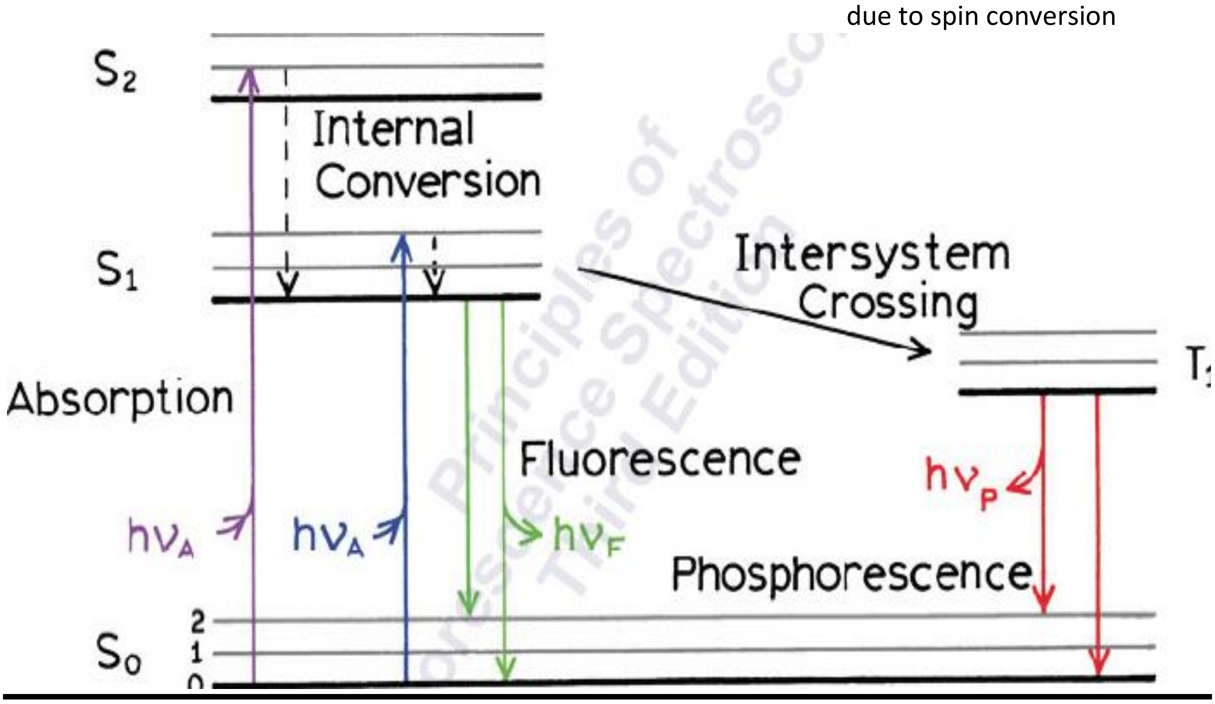
Triplet excited state T_1 (pair of electrons with parallel spins in different Orbital's)

The excited species can return to the ground state by losing all of its excess energy by any one of the paths shown in Jablonski diagram.

Jablonski Diagram for various photophysical processes

Allowed singlet states:

Forbidden triplet states due to spin conversion



Explanation of Jablonski Diagram

<u>First step</u>: is the transition from higher excited singlet states (S_2, S_3, …) to the lowest excited singlet state S_1.This is called internal conversion (IC).

It is a non-radiative process and occurs in less than 10-11 second.

Now from S_1 the molecule returns to ground state by any of the following paths.

Path I : The molecule may lose rest of the energy also in the form of heat so that the complete path is non-radiative or radiation less transitions.

Path II: Molecule releases energy in the form of light or uv radiation. This is called Fluorescence

Path III : Some energy may be lost in transfer from S_1 to T_1 in the form of heat. It is called intersystem crossing (ISC).

This process involves transition between states of different spins (parallel to antiparallel), ie, different multiplicity.

This path is non-radiative.

Path IV : After ISC, the molecule may lose energy in the form of light in going from the excited triplet state to the ground state. This is called phosphorescence.

<u>Chemical reaction</u>

The activated molecule loses energy by undergoing chemical reaction.

Since the molecules in singlet excited sates returns quickly to the G.S, it gets no chance to react chemically.

However the molecules in the triplet state returns to the G.S. slowly, has a opportunity to the activated molecule undergoes chemical reaction.

i.e., the molecule which undergoes chemical reaction is one which is previously present in a triplet state.

Distinction between Fluorescence and Phosphorescence

Fluorescence	**Phosphorescence**
(a)If a system absorbs radiant energy and then emits it partially or completely almost instantaneously(within 10^{-8} S) in the form of radiation.	(a)If a system absorbs radiant energy and then emits partially or completely after a time lag in the form of radiation.
(b)Its emission ceases as soon as the source of exciting radiation is removed.	(b)It continues for some time even after the source of exciting radiation is removed.
©It can be stimulated in gases, liquids and solids.	©It mainly exhibited by solids.
(d)It is caused by $S_1 \rightarrow S_0$ transitions which is a quantum mechanically allowed transition	(d)It is caused by $T_1 \rightarrow T_0$ transitions which is a quantum mechanically forbidden transition

<u>Chemiluminescence</u>

- **Chemiluminescence: The emission of light in chemical reaction at ordinary temperature is called Chemiluminescence**

  e.g. The light emitted by glow-worms.

It is the reverse of a chemical reaction.

- **Chemical reaction—results from the absorption of light**
- **Chemiluminescence— emission of light from a chemical reaction.**

Quantum Efficieny (ϕ)=

$$\phi = \frac{\text{No. of photons emitted in a given time}}{\text{No. of molecules of the reactant consumed in the same time}}$$

ϕ is less than 1.

Explanation

- **Excited products undergoes deactivation and the excess energy is emitted as radiation**
- **If the wavelength of the emitted light falls in the visible region, Chemiluminscence is observed.**

$$A \rightarrow B^* \rightarrow B + hv$$

- **The exothermic reaction can produce one of the product to the electronically excited state, it shows chemilumincescence.**

Examples:

1. **Phosphorus glows in air with faint greenish colour due to its oxidation.**

P oxidizes to phosphorus trioxide (P_2O_3 exists as dimer P_4O_6) oxidises to phosphorus pentoxide(P_2O_5 exists as dimer P_4O_{10})

$$4P + 3O_2 \rightarrow P_4O_6^* \rightarrow P_4O_6 + hv$$

$$P_4O_6^* + 2O_2 \rightarrow P_4O_{10}^* \rightarrow P_4O_{10} + hv$$

Natural Example:

Photosensitization is that by chlorophyll in the Photosynthesis of carbohydrates in plants.

$$\text{Chlorophyll} + hv \rightarrow \text{Chlorophyll}^*$$

$6CO_2+6H_2O+\text{Chlorophyll}\ ^* \rightarrow C6H12O6+O_2 + \text{Chlorophyll}$

Bioluminescence

Emission of visible light accompanies a chemical reaction that occurs in the living organism.

Or it is the chemiluminescence from a biological system.

egs: Glow of fire files

Emission of light results from the oxidation of a protein called luciferin in their body by atmospheric oxygen in the presence of enzyme luciferase.

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Phosphorescence

If a system absorbs radiant energy and then emits partially or completely after a time lag in the form of radiation

It continues for some time even after the source of exciting radiation is removed.

It mainly exhibited by solids.

It is caused by $T_1 \rightarrow T_0$ transitions which is a quantum mechanically forbidden transition