Second law:- Einstein's law of photochemical equivalence:
Each quantum of radiation absorbed by molecules activates one in primary step of photochemical reacn.
The amount of chemical progress is expressed by quantum yield ϕ.

$AB \xrightarrow{h\nu} AB^* \longrightarrow$ product

$$\phi = \frac{\text{No. of molecules reacting}}{\text{No. of photons or quantum absorbed}}$$

$$= \frac{\text{No. of moles reacting}}{\text{No. of Einsteins absorbed}}$$

$$= \frac{\text{No. of moles reacting/sec}}{\text{No. of Einstein absorbed/sec}}$$

$$= \frac{\text{rate}}{\text{Intensity}} = \frac{dx/dt}{Ia}$$

one Einstein = Avogadro no. of photons.

Einstein means one mole photon.
1 Einstein = No. $h\nu$ = No. $h \cdot c/\lambda$

Quantum yield (ϕ):- A photon activates one molecule in the primary step of photochemical reaction and activated molecule undergoes chemical reaction.

$AB \xrightarrow{h\nu} AB^* \longrightarrow$ product

$$\phi = \frac{\text{No. of molecules reacting}}{\text{No. of photons absorbed}}$$

And if product undergoes no further chemical reaction, then $\phi = 1$.
Sometimes ϕ may be greater than one or less than one.
$\phi = 1$, is due to mainly some secondary processes.

$\phi > 1$:- Sometimes active radicals generated in the initiation step undergo secondary process to produce further active radicals. Hence we can get large number of product molecules.
Ex: Chain reacn: H_2-Cl_2 reacn, Decomposition of HBr.

$\phi < 1$: This is also due to some secondary process like collisional deactivation, reemission of light in the form of fluorescence and phosphorescence.

$AB \xrightarrow{h\nu} AB^* \longrightarrow$ product
collisional deactivation $\longrightarrow AB + h\nu'$

Due to these secondary proces we can get $\phi < 1$

Primary process in photochemical reaction:

This is basically absorption of radiation and molecule gets excited. Absorption of AB $\xrightarrow{h\nu}$ AB* light leads to the electric transition from one level to another. The electric transition of molecule is accompanied with vibrational and rotational from one level to another level and is governed by Fraock-condon principle. (During electronic transition internuclear distance remains unchanged).

Now excited molecule may behave in different ways:
i) physical process
ii) chemical process

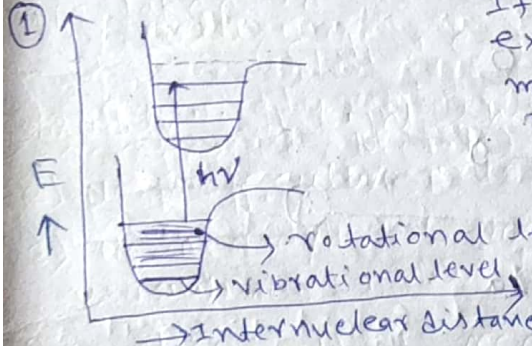
$AB \xrightarrow{h\nu} AB^* \xrightarrow{\text{chemical process}}$ product

AB^* → Collisional deactivation
AB^* → Fluorescence + Phosphorescence
AB^* → Thermally heated

(Collisional deactivation, Fluorescence + Phosphorescence, Thermally heated) → Physical process.

* From last page:-
Now a molecule may enter into the chemical reaction in four different following ways :→

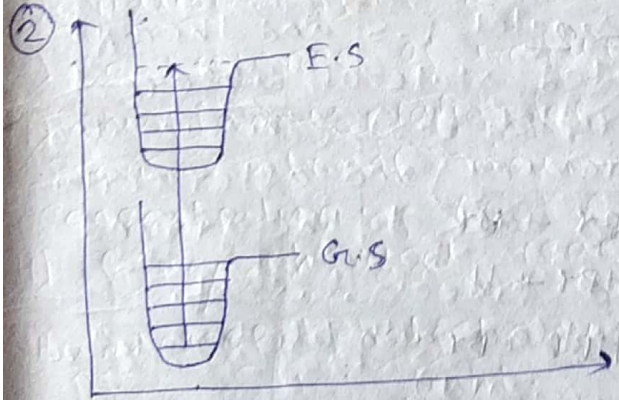
① If molecule is excited to stable excited state then excited molecule collide with another reactant to give products.



$NOCl \xrightarrow{h\nu} NOCl^*$

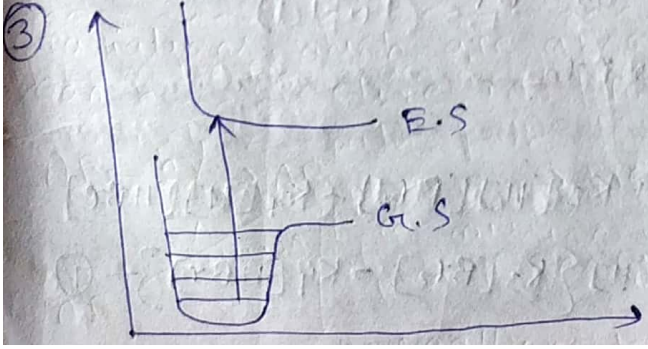
$NOCl^* + NOCl \rightarrow 2NO + Cl_2$

② If molecule is promoted to the topmost vibrational level of excited state, then it undergoes dissociation.

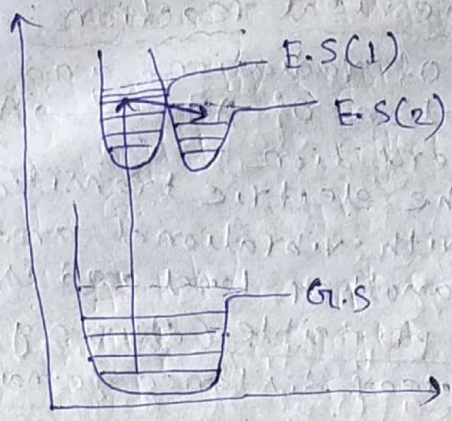


$Cl_2 \xrightarrow{h\nu} Cl + Cl$

③ If molecule is promoted to directly unstable excited state (anti-bonding) then it undergoes dissociation.



(4)



$AB \xrightarrow{h\nu} AB^*$ (stable)

$AB^* \xrightarrow{ISC} AB^{**} \longrightarrow A + B$

If a molecule possesses more than one excited state and if molecule gets excited to 1st stable excited state and now in order to get instability molecule comes to unstable level of another excited state and finally undergoes dissociation.

→ predissociation.

Kinetic study and calculation of quantum yield (ϕ):

1) Decomposition of HI :-

1st step : $HI \xrightarrow{h\nu} H + I$ $\quad \phi = \dfrac{dx/dt}{I_a}$

2nd step : $HI + H \xrightarrow{K_2} H_2 + I$

3rd step : $I + I \xrightarrow{K_3} I_2$

$$\text{rate} = -\frac{d[HI]}{dt} = I_a + K_2[HI][H] \quad \text{——(i)}$$

At steady state, $\dfrac{d[H]}{dt} = 0$

$$\therefore \frac{d[H]}{dt} = I_a - K_2[HI][H] = 0$$

$$\therefore K_2[HI][H] = I_a \quad \text{——(ii)}$$

$$-\frac{d[HI]}{dt} = I_a + I_a = 2I_a$$

$$\phi = \frac{-d[HI]/dt}{I_a} = 2$$

2) $H_2 - Br_2$ reaction :-

Step 1 : $Br_2 \xrightarrow{h\nu} Br + Br$

Step 2 : $H_2 + Br \xrightarrow{K_2} HBr + H$

Step 3 : $Br_2 + H \xrightarrow{K_3} HBr + Br$

Step 4 : $H + HBr \xrightarrow{K_4} H_2 + Br$

Step 5 : $Br + Br \xrightarrow{K_5} Br_2$

$$\frac{d[HBr]}{dt} = K_2[H_2][Br] + K_3[H][Br_2] - K_4[H][HBr]$$

$$= K_2[H_2][Br] + [H]\{K_3[Br_2] - K_4[HBr]\} \quad \text{——(i)}$$

At steady state, $\frac{d[H]}{dt} = 0$, $\frac{d[Br]}{dt} = 0$

$$\frac{d[H]}{dt} = k_2[H_2][Br] - k_3[Br_2][H] - k_4[H][HBr] = 0 \quad \text{— (ii)'}$$

$$\therefore [H] = \frac{k_2[H_2][Br]}{k_3[Br_2] + k_4[HBr]} \quad \text{— (ii)''}$$

$$\frac{d[Br]}{dt} = 2I_a - k_2[H_2][Br] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 = 0 \quad \text{— (ii)'''}$$

Using equation — (ii)' we get, in (ii)'''

$$2I_a - 2k_5[Br]^2 = 0$$

$$\therefore [Br] = \left(\frac{I_a}{k_5}\right)^{1/2} \quad \text{— (iii)}$$

From (i) using (ii) we get

$$\frac{d[HBr]}{dt} = k_2[H_2][Br] + \frac{k_2[H_2][Br](k_3[Br_2] - k_4[HBr])}{k_3[Br_2] + k_4[HBr]}$$

$$= \frac{2k_2k_3[H_2][Br][Br_2]}{k_3[Br_2] + k_4[HBr]}$$

$$= \frac{2k_2[H_2]}{1 + \frac{k_4[HBr]}{k_3[Br_2]}} \cdot [Br] = \frac{2k_2[H_2]}{1 + \frac{k_4[HBr]}{k_3[Br_2]}} \times \left(\frac{I_a}{k_5}\right)^{1/2}$$

$$\phi = \frac{d[HBr]/dt}{I_a} = \frac{2k_2[H_2]}{1 + \frac{k_4[HBr]}{k_3[Br_2]}} \cdot \left(\frac{1}{I_a \cdot k_5}\right)^{1/2}$$

Luminescence:- This is the emission of light or radiation caused by some agency other than heat or temperature.

Types: (i) Photoluminescence — a) Fluorescence
b) Phosphorescence

$A \rightarrow A^*$ (ii) Electroluminescence
$\downarrow$ (iii) chemoluminescence
$A + h\nu$ (iv) cathodoluminescence

Photoluminescence:- This is luminescence caused by radiation or light energy.

Fluorescence & phosphorescence :-

Fl: $A \xrightarrow{h\nu} A^* \longrightarrow A + h\nu'$

A (Singlet G.S) → A^* (Singlet E.S) → $A + h\nu'$ (Singlet G.S)

Time span $= 10^{-8} - 10^{-4}$ sec

$\nu' \leq \nu$

Ph: $A \xrightarrow{h\nu} A^* \xrightarrow{ISC} A^{**} \longrightarrow A + h\nu''$

A (Singlet G.S) → A^* (Singlet E.S) → A^{**} (Triplet E.S) → $A + h\nu''$ (singlet G.S)

Time span: 10^{-4} - 20 sec

Fluorescence:- Fluorescence is the radiative transition between two states of same spin multiplicity. At first a molecule/atom is excited from ground state to singlet excited state and then quickly comes back to the ground state with emitting the radiation of same or quite different frequencies.

$A \xrightarrow{h\nu} A^* \longrightarrow A + h\nu$ (R.F) $\nu' = \nu$, resonence fluorescence

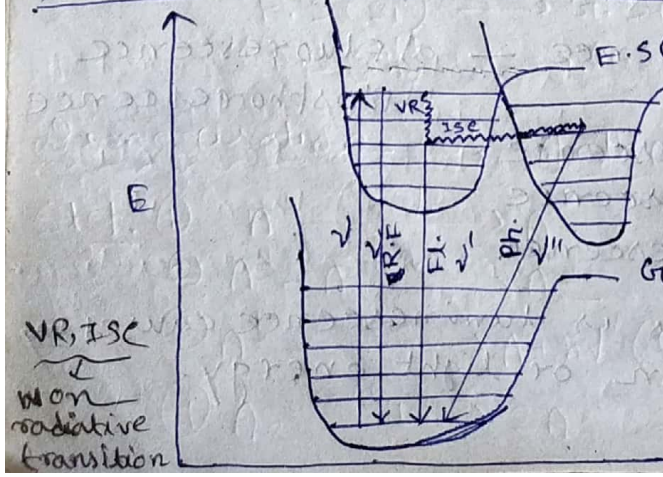
Singlet Singlet

$AB^* \xrightarrow{VR} AB^{**} \; AB^{*/*} \longrightarrow AB + h\nu'$ $\nu' < \nu$ → Fluorescence

It is very faster process with life time $10^{-4} - 10^{-8}$ sec. It is faster as spin allowed transition takes place. If emitted radiational frequency is same with absorbed frequency then the process is called resonance fluorescence.

Phosphorescence:- Phosphorescence is the radiative transition between two state of different spin multiplicity.

A molecule/atom at first is excited from ground state to singlet E.S and then after certain lapse of time it comes to another excited state of different spin multiplicity (ie, triplet E.S), (this is also called inter system crossing) and after certain lapse of time it comes back to the ground state. This is spin forbidden transition and that is why it is delayed process, as spin forbidden transition takes place with life time 10^{-4} - 20 sec



Spin allowed transition (ΔS=0)
" forbidden " (ΔS≠0)

by releasing of radiation in different freq. (ν''') as that of absorbing radiation.

Quenching of fluorescence:- This is the decrease of intensity of fluorescence due to molecular collision, phosphoreseence or non radiative transition.

Some times excited molecule may collide with another molecule and gets deexcited. (This is collisional deactivation)

$$A \xrightarrow{h\nu} A^* \qquad A^* + A \longrightarrow A + A$$

collisional deactivation increases, ie, intensity of fluoreseence decreases at high pressure or at high concentration. In presence of foreign particles intensity of fluoreseence may decrease.

$$A^* + B \longrightarrow A + B$$

Some times excited particle comes back to ground state through non radiative transition.

Sensitised fluorescence:- Some molecules/atoms (element) themselves do not show fluorescence but they can exhibit fluorescence in presence of suitable foreign particle, which is photoactive.

Ex: Tl does not show fluoreseence but if we take mixture Tl + Hg, then both exhibite fluoreseence.

How? $Hg \xrightarrow{h\nu} Hg^*$; $Tl \xrightarrow{h\nu} \times$

$$Tl + Hg^* \longrightarrow Tl^* + Hg$$

$$Tl^* \longrightarrow Tl + h\nu' \text{ (fl.)}$$
$$Hg^* \longrightarrow Hg + h\nu'' \text{ (fl.)}$$

Here foreign particle or Hg is the sensitiser. The fluorescence of Hg is quenched by Tl and Tl is sensitised to show fluoreseence by Hg.

Photosensitised reaction:-

$$H_2 + O_2 \xrightarrow{h\nu} \times \rightarrow H_2O \quad ; \quad H_2 + O_2 \xrightarrow[Hg]{h\nu} H_2O$$

$$CO_2 + H_2O \xrightarrow{h\nu} \times \rightarrow \text{glucose} \quad ; \quad CO_2 + H_2O \xrightarrow[\text{chlorophyll}]{h\nu} C_6H_{12}O_6$$

Some reactions are generally not happened in presence of suitable light, but it may happen in presence of suitable foreign element or particle, which is photoactive. these reaction are called photosensitised reaction.

$$H_2 + O_2 \xrightarrow{h\nu} \times \rightarrow H_2O$$

10,320 cal ; 11,700 cal ; $\lambda = 2537 A^\circ$ ~ 10,700 cal

* H_2 & O_2 both are insensitive towards light, Energy of light is sufficient to breaking H–H bond, but *

In presence of Hg, H_2O is produced.

$Hg \xrightarrow{h\nu} Hg^*$

$Hg^* + H_2 \longrightarrow 2H$

$2H + O_2 \longrightarrow H_2O$

Photosynthesis is a good example of photosensitised reaction.

$CO_2 + H_2O \xrightarrow{h\nu} glucose$ (Mg in chlorophile is photosentiser the $h\nu$ chlorophile (mg))

Photostationary State :- This is equilibrium state of photochemical reaction. Here at least one step is light dependent. Here rate = 0

Ex: $2HI \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} H_2 + I_2$

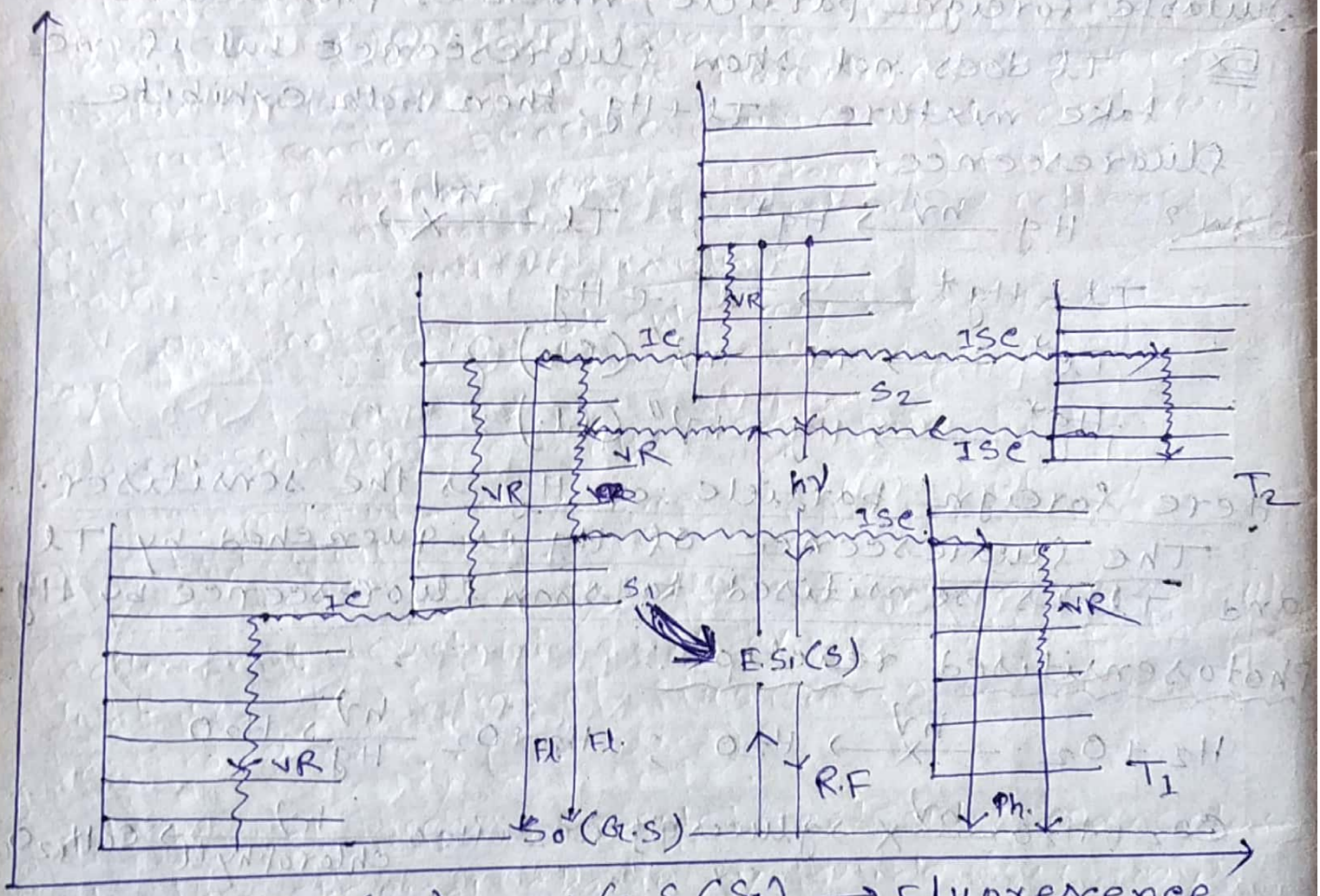
In case of thermal reaction or dark reacn both steps are thermal ie, tempr. dependent.

$Br_2 + H_2 \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} 2HBr$

$CO + Cl_2 \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} COCl_2$

chemical equilm :- $2A \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} A_2$ $\quad 2A \overset{\text{thermal}}{\rightleftharpoons} A_2$ (thermal)

Jablonski Diagram :→



$E.S(S_1) \longrightarrow G.S(S_0) \longrightarrow$ Fluorescence

$E.S(T_1) \longrightarrow G.S(S_0) \longrightarrow$ Phosphorescence

4) a) What is an actinometer? Describe and explain the working principle of any one chemical actinometer.

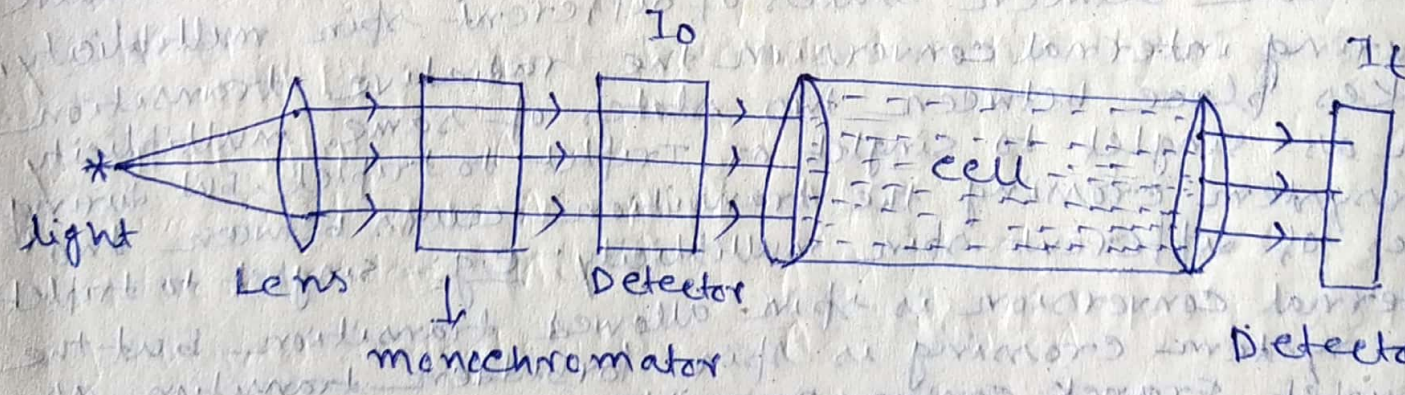
Actinometer:- It is a device, which can determine intensity of light absorbed, quantum yield and rate of reaction.

Chemical actinometer:- A chemical actinometer uses a chemical reaction whose rate can be determined easily. It depends on the use of photochemical reaction of known quantum yield. One such simple device is Uranyl oxalate actinometer. It contains 0.05 M oxalic acid and 0.01 M Uranyl sulphate in water. When it is exposed to radiative oxalic acid is decomposed to CO_2, CO and H_2O.

$$UO_2^{2+} + h\nu \longrightarrow (UO_2^{2+})^*$$

$$(UO_2^{2+})^* + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The conen of oxalic acid that remain can be found by titration with standard $KMnO_4$ solution. The used up conen of oxalic acid is a measured of intensity of radiation.



Chemical actinometer

b) State Franck condon principle.

i) Electronic transition will always take place from S state to S state and from T to T state. But never from singlet to triplet or triplet to singlet. It is the selection rule for electronic transition.

ii) The massive nuclei don't respond during electronic transition as they are highly heavier than the electrons.

iii) Electronic transition will not occur if $\int \psi_f^* \hat{H}_{int} \psi_i \, d\tau = 0$. Therefore one essential condition for the electronic transition is $\int \psi_f^* \hat{H}_{int} \psi_i \, d\tau \neq 0$. The greater the value of the integral, more prominant will be the transition.

iv) Always electronic transition takes place from $v=0$ vibrational level in the G.S as the population of the electrons is maximum in this state.

c) An actinometer contains 20cc of 0.05 moles/litre oxalic acid through which light of 350 nm was passed for 2 hours. The light was absorbed by uranyl oxalate. After exposure the solution required 34cc $KMnO_4$ to titrate the undecomposed oxalic acid. The same volume ie, 20cc required 40cc of $KMnO_4$ before exposure. Calculate the energy absorbed in Joule/sec. If $\phi = 0.6$

20cc of 0.05 moles/litre i.e 0.10 (N) oxalic acid $\equiv$ 40cc $KMnO_4$.

so strength of $KMnO_4 = \frac{20 \times 0.1}{40} = 0.05$ (N)

Finally this solution required 34cc $KMnO_4$. So oxalic acid equivalent to (40 - 34) = 6 cc 0.05 (N) was decomposed by light. But 6cc of 0.05 (N) sol^n contained

$= \frac{6 \times 0.05}{1000} = 3 \times 10^{-4}$ equivalent

so 3×10^{-4} equiv oxalic acid i.e 1.5×10^{-4} mole has been decomposed.

Now, ϕ (Quantum efficiency) = $\frac{\text{No. of moles decomposed}}{\text{No. of einstein absorbed}}$

So, $0.6 = \frac{1.50 \times 10^{-4}}{\text{No. of einstein absorbed}}$

so, No. of einstein absorbed = 2.5×10^{-4} mole

Here one einstein contain in 2 hours

$$\frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34} \text{ J.sec} \times 3 \times 10^8 \text{ m/sec}}{350 \times 10^{-9} \text{ m} \times 2 \times 60 \times 60 \text{ sec}}$$

$= 47.50999762$ J/sec

Hence energy absorbed in Joule/sec is

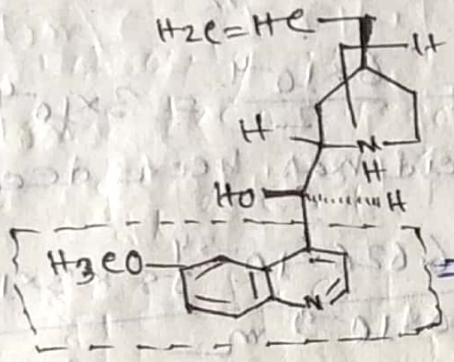
$2.5 \times 10^{-4} \times 47.50999762$ J/sec

$= 1.19 \times 10^{-2}$ Joule/sec

3) a) Substitution of a carboxylic acid or carbonyl group on an aromatic ring generally inhibits fluorescence — Explain.

Such type of groups are, -I and as well as -R groups, which reduce the electron density on the aromatic ring, hence fluorescence intensity will be inhibited.

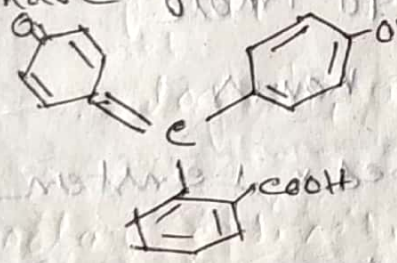
b) Predict with explanation the part of the given quinine molecule that is most likely to behave as the chromophore and fluorescent centre.

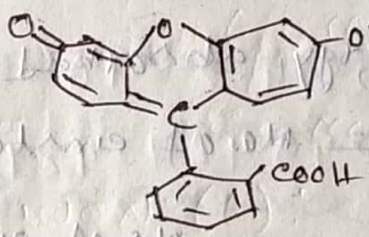


⇒ Quinoline part

The quinoline part of the molecule behaves as chromophore as well as fluorescent centre. This part of the molecule is the electron rich centre and there are so many possibilities of $\pi \rightarrow \pi^*$ transition so it can behave as fluorescent centre.

c) Explain which of the two compounds is expected to have greater quantum yield of phosphorescence?





In the second molecule conjugated system with oxygen (O) is present, so the presence of oxygen increases the density of molecule & hence we can expect, the second molecule show phosphorescence.

(c) When gaseous HI is irradiated by a radiation of wave length 253 nm, 0.0185 moles of HI decompose per Kcal of radiant energy absorbed. calculate the quantum yield.

$$\lambda = 253\ nm = 253 \times 10^{-9}\ m$$

$$1\ Einstein = \frac{No.\ hc}{\lambda} = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^{8}}{253 \times 10^{-9}}$$

$$= 473,222.1107\ Joule/mole$$

Amount of energy absorbed = 1 Kcal = 1000 cal

$$= 1000 \times 4.2\ Joule$$

$$= 4200\ Joule$$

There no. of einstein absorbed $= \frac{4200}{473222.1107}$ mole

Now, $\phi = \frac{\text{No. of moles of HI decomposed}}{\text{No. of einstein absorbed}}$

$$= \frac{0.0185 \times 4200}{473222.1107}$$

$$= 1.64 \times 10^{-4}$$

Hence quantum yield = 1.64×10^{-4}.

d) The extinction co-efficient of $K_3[Fe(CN)_6]$ at 419 nm is $1020\ cm^2 mol^{-1}$. what percentage of light is transmitted from a cell of thickness 2 cm containing 1×10^{-4} m $K_3[Fe(CN)_6]$ solution?

$\epsilon = 1020\ cm^2 mol^{-1}$; $l = 2$ cm ; $c = 1 \times 10^{-4}$ m

Absorbance $(A) = \log \frac{I_0}{I_t} = \epsilon c l$ $\quad I_0 = 100$, $I_t = ?$

$\Rightarrow \log \frac{100}{I_t} = 1020 \times 2 \times 10^{-4}$

$\Rightarrow I_t = 62.517$

Hence percent of light is transmitted from a cell of thickness 2 cm containing 1×10^{-4} m $K_3[Fe(CN)_6]$ solution is

$62.517\ \%$ or $\frac{I_t}{I_0} \times 100$

$= \frac{62.517}{100} \times 100$

$= 62.517\ \%$

e) Is Lambert-Beer's law applicable in any radiation range UV-VIS and IR? Give explanation.

Yes, the Lambert-Beer's law applicable in any radiation range, UV-VIS & IR, but the radiation should be monochromatic in nature.

L.B law is based on the concept of absorption of photon leading to the electronic transition from one energy level to another energy level. The energy corresponds to UV, VIS range is very much comparable with energy required for electronic transition.

But energy corresponds to IR is not sufficient for electronic transition rather it can change the vibration of molecule only. So L.B law is not applicable for IR radiation.

d) In the photochemical reaction.

$CH_2ClCOOH + H_2O \xrightarrow{h\nu} CH_2OH.COOH + HCl$

it was found that after irradiating the solution at 2537 Å for 837 minutes 3.436×10^8 ergs of energy was absorbed and 2.296×10^{-5} mole of HCl were formed. Calculate the quantum yield of the reaction.

$$\lambda = 253.7 \text{ nm} = 253.7 \times 10^{-9} \text{ m}$$

$$\phi = \frac{\text{Rate of reaction}}{\text{Intensity of light absorbed}}$$

$$= \frac{\text{No. of HCl produced/sec}}{\text{No. of Einstein absorbed}}$$

∴ No. of HCl produced per second

$$= \frac{2.296 \times 10^{-5}}{837 \times 60} \text{ mole}$$

$$1 \text{ Einstein} = \frac{\text{No. } hc}{\lambda}$$

$$= \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-27} \text{ erg sec} \times 3 \times 10^8 \text{ m/s}}{253.7 \times 10^{-9} \text{ m}}$$

$$= 4.719 \times 10^{12} \text{ erg/mole}$$

Now No. of einstein absorbed

$$= \frac{3.436 \times 10^8}{4.719 \times 10^{12}} \text{ mole}$$

$$= 7.28 \times 10^{-5} \text{ mole}$$

$$\therefore \phi = \frac{2.296 \times 10^{-5}}{837 \times 60} \times \frac{1}{7.28 \times 10^{-5}}$$

$$= 6.28 \times 10^{-6}$$

7) g) Is the einstein law of photochemical equivalence always valid?

If there are secondary process along with primary process then the law will be violated. Even for primary process the law may be invalid for LASER beam. LASER beam contains a very high density of photons and a substance may absorb more than one photon. Sometime a single photon can excite two molecules. So this law is not valid always.

5] a) Photostationary equilibrium:- The photostationary state is a steady state which arises if the forward or backward or both reactions are affected by the radiation. In that case, the thermal equilm state may be shifted to another minium which remains the same as long as radiation is not cut off. one of the well-known examples of photostationary equilm is the dimerisation of Anthracene(A).

Anthracene absorbs radiation to give the dimer and hence the equilm state between A and A_2 is shifted more towards A_2 in comparison to thermal conversion.

Fluorescence	Phosphorescence
i) It is the radiative transition between two states of same spin multiplicity.	i) It is the radiative transition between two states of different spin multiplicity.
ii) Excited state singlet to ground state singlet transition takes place.	ii) E.S (triplet) to G.S (singlet) transition takes place.
iii) This is faster process.	iii) This is slower process.
iv) Spin allowed transition takes place, $\Delta S = 0$	iv) Spin forbidden transition takes place, $\Delta S \neq 0$.
v) Relaxation time $10^{-8} - 10^{-4}$ sec	v) Relaxation time $10^{-4} - 20$ sec

3) b) Distinguish between internal conversion (I.C) and intersystem crossing (ISC).

I.C is the internal conversion - non radiative transition between states of same spin multiplicity (higher → lower).

I.S.C is the internal system crossing - non radiative transition between states of different spin multiplicity.

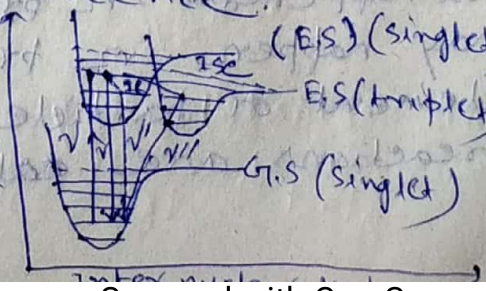
(*) (i) During internal conversion the radiative transition takes place between two states of same multiplicity such as singlet to singlet or Triplet to triplet, but during Intersystem crossing the transition occurs between two states of different spin multiplicity; E.g:- singlet to triplet.

(ii) Internal conversion is spin allowed transition but the intersystem crossing is spin forbidden transition as it violet Franck condon prineiple.

(iii) Internal conversion may be observed from every molecule if sufficient energy is supplied.
But for a molecule to show inter system crossing, it must have high molecular weight so that spin transition can take place.

(iv) Internal conversion is observed during fluorescence but the inter system crossing is observed during phosphoreseence.

(Diagram)



(d) what are the essential steps for a photochemical chain reaction? Illustrate with the help of an example.

The essential steps for a photochemical chain reaction is ——

(i) chain Initiation step

(ii) chain propagation "

(iii) Termination "

chain inhibition may or may not be present.

chain reaction:- This is the type of reaction, where reaction proceeds stepwise and continuously forming products after first initiating reaction and it is continued, ~~and~~ unless it is regenerated.

(i) chain initiation:- In this step some active radicals or atoms/ions are generated.

(ii) chain propagation:- Active radicals those are generated in initiation step react with one of the reactant to form product and also some other active radicals.

(iii) chain inhibition:- Here active radicals combine with product to product reactant molecule back.

(iv) Termination:- These radicals are generated in the initiation step may recombine together or deactivated by collision with wall.

Example:- H_2-Br_2 reaction.

chain initiation:- $Br_2 \xrightarrow{h\nu} Br + Br$

chain propagation:- $H_2 + Br \xrightarrow{K_2} HBr + H$

$Br_2 + H \xrightarrow{K_3} HBr + Br$

Chain inhibition:- $H + HBr \xrightarrow{K_4} H_2 + Br$

Chain Termination:- $Br + Br \xrightarrow{K_5} Br_2$