Laws of Photochemistry

Photochemistry is the study of the chemical reaction initiated by absorption of energy in the form of light.

Photochemical Reaction	Thermal Reaction
These reactions involve absorption of light radiations.	These reactions involve absorption or evolution of heat energy.
Presence of light is the primary requirement.	These reactions can take place in light as well as in dark.
Temperature has very small effect.	Temperature has significant effect.
ΔG may be +ve or –ve.	ΔG is always –ve.
Photochemical activation is highly selective process.	Thermal activation is not selective in nature.

Laws of Photochemistry

Grotthus Draper Law:-

"Only those radiations which are absorbed by a reacting substance or system are responsible for producing chemical change."

According to this law, all light radiations are not bringing the chemical reaction. Some are increase the kinetic energy of molecule while some are re-emitted. (i.e. fluorescence).

Stark–Einstein Law or Einstein law of photochemical equivalence

"Each molecule of absorbing substance absorb one photon (or quantum) of the radiation in primary process."

Explanation:-

A molecule acquire energy by absorbing photon as,

$$A + h\upsilon \;\text{----------}> A^*$$

Thus energy of photon is,

$$E = h\upsilon$$

Where υ = frequency of absorbing photon.

h = plank's constant $= 6.624 \times 10^{-34}$ J.s

The energy of 1 mol photon (i.e. Einstein) is given by,

$$E = N.h.\upsilon$$

But, $\upsilon = C/\lambda$

$$E = \frac{N.h.C}{\lambda}$$

N= Avogagro's no. = 6.023×10^{23} mol⁻ .
C= velocity of light. = 3×10^{8} m/s.

$$E = \frac{6.023 \times 10^{23} \times 6.624 \times 10^{-34} \times 3 \times 10^{8}}{\lambda \times 10^{-9}}$$

$$E = \frac{1.1962 \times 10^{8}}{\lambda} \text{ J/mol} = \frac{119620}{\lambda} \text{ KJ/mol}$$

λ should be in cm

Lamberts law:-

When a monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease in the intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident radiation.

$$\Rightarrow \qquad \frac{I}{Io} = 10^{-a.x}$$

I_0 = initial intensity before passing absorbing medium.
I = intensity after passing absorbing medium.
x = thickness of absorbing medium.
a = extinction coefficient.
$\frac{I}{Io}$ = transmission or transmittance (T).

Lamberts–Beer's law (or Beer's law):-

When a monochromatic radiation is passed through a solution of absorbing medium, the rate of decrease in the intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident radiation and concentration of the solution.

$$\Rightarrow \quad \log_{10}\frac{I}{Io} = -\epsilon.c.x$$

I_0 = initial intensity before passing absorbing medium.

I = intensity after passing absorbing medium.

x = thickness of absorbing medium.

ϵ = molecular extinction coefficient

Quantum yield or Quantum efficiency (Φ)

It is defined as the ratio of number of molecules reacting in given time to the number of quanta absorbed in the same time.

$$\Phi = \frac{\text{number of molecules undergoing the process}}{\text{number of quanta absorbed}}$$

Reasons for unite Quantum yield:

According to Einstein law of photochemical equivalence , in primary process each molecule absorbs one quanta. Hence Quantum yield is unity.

Reasons for high Quantum yield: $\Phi > 1$

- The product of primary process may collide with 2^{nd} molecule & transfer energy. 2^{nd} to 3^{rd} and so on. Thus chain reaction starts and no. of reacting molecule will be high.
- Due formation of intermediate product which act as a catalyst.
- Exothermic reaction may activate more molecules.

Eg. Reaction between Hydrogen and Halogen.

Reasons for low Quantum yield: $\Phi<1$

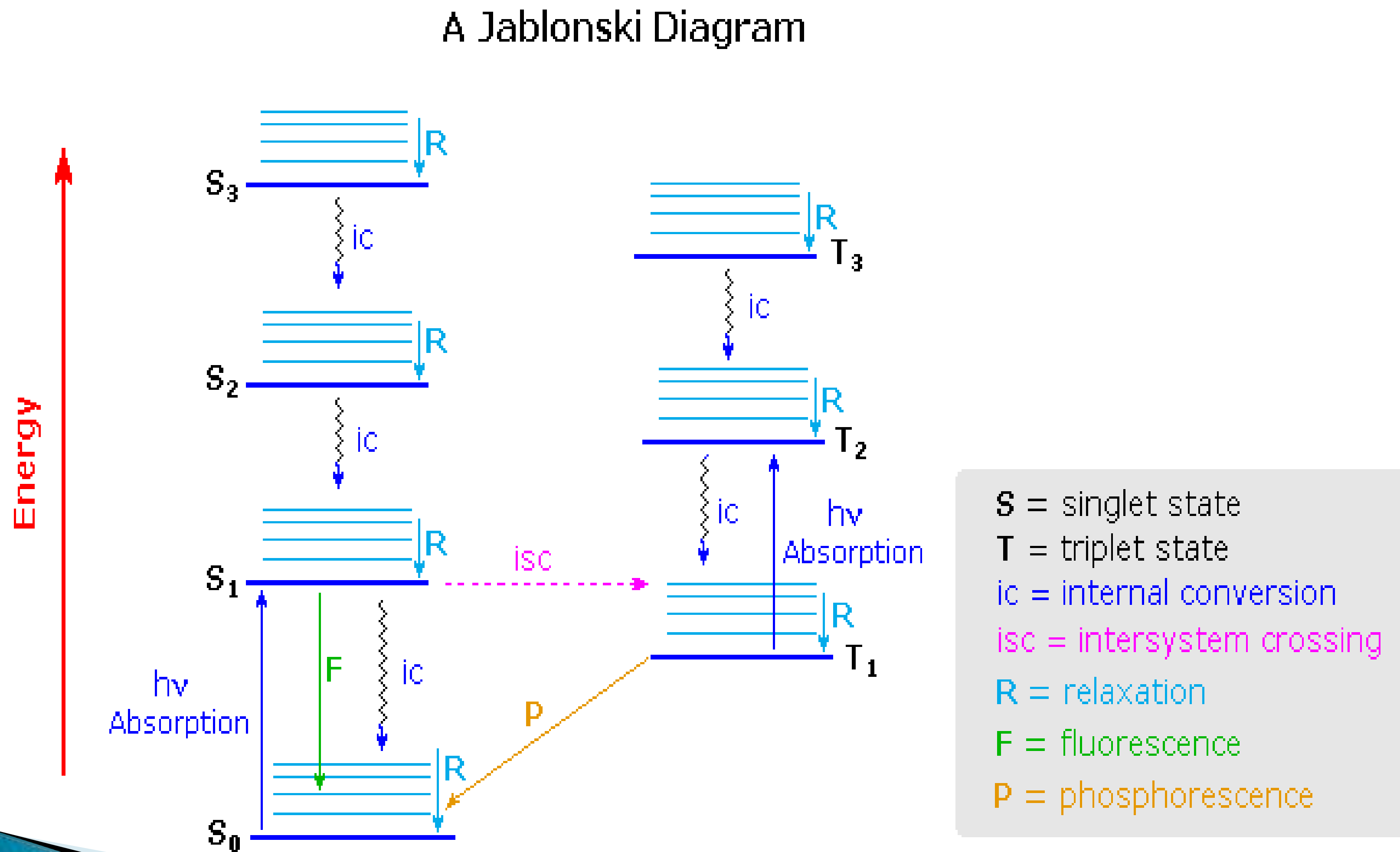
- In some reaction deactivation of activated molecule take place in primary process before transfer to product.
- The product of primary process may react back to form reactants.

Eg. Decomposition of HI and HBr,
Polymerization of anthracene.

Factors affecting quantum yield:-

- All primary photochemical process is endothermic. Hence, quantum yield increases with temperature.
- We know energy absorbed by molecule is inversely proportional to wavelength. Hence, quantum yield will be higher at the lower wavelength and vice versa.
- As speed of photochemical reaction is proportional to intensity of light. Hence, quantum yield increases with intensity and vice versa.
- The addition of inert gas in photochemical reaction the quantum yield.

Jablonski Diagram

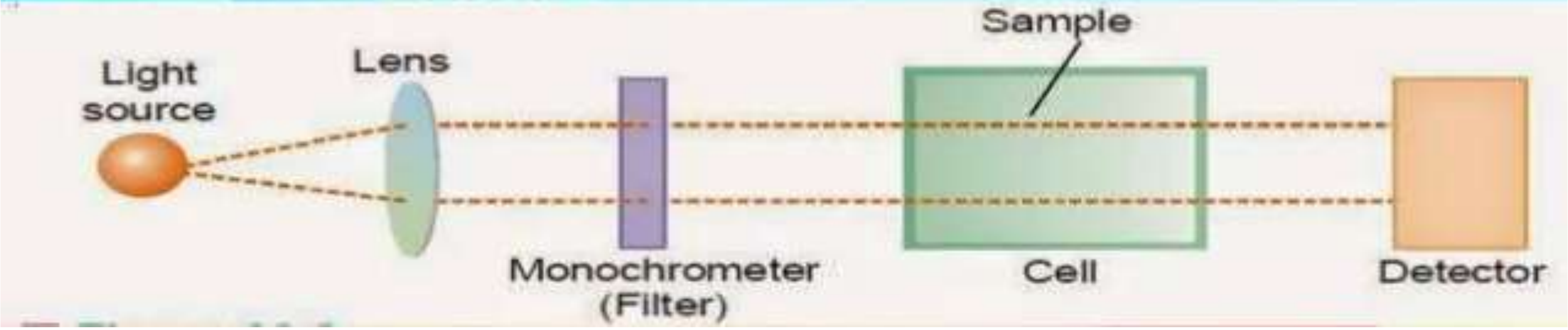


Experimental Determination of Quantum Yield

1. Determination of number of moles reacted.

2. Determination of number of Einstein's absorbed.

3.
   Source of light
   Monochromator
   Reaction cell
   Detector



$$\Phi = \frac{\text{number of molecules undergoing the process}}{\text{number of quanta absorbed}}$$

The reaction may be represented as $H_2 + Br_2 \rightarrow 2\ HBr$

- Photosynthesis of HBr i.e. Photochemical combination of Hydrogen and Bromine to form HBr.The reaction may be represented as

$$H_2 + Br_2 \rightarrow 2\ HBr$$

The quantum efficiency of this reaction is very low i.e. about 0.01 at ordinary temperatures. This is explained by proposing the following mechanism for the above reaction :

(a)Primary process ;$Br_2 + h\nu \rightarrow 2\ Br$

(b)Secondary Process :

(i) $Br + H_2$ endo$\rightarrow HBr + H$

(ii) $H + Br_2 \rightarrow HBr + Br$

(iii)$H + HBr \rightarrow H_2 + Br$(iv) $Br + Br \rightarrow Br_2$

Photosynthesis of HCl from H2 and Cl2

- This is an example of a reaction whose quantum yeild is very high i.e to This reaction may be represented as

$$H_2 + Cl_2 \rightarrow 2HCl$$

The high quantum yield of this reaction is explained by the chain mechanism (proposed by Nernst in 1918). The different steps involved are as follows :

(a) Primary process :$Cl_2 + h\nu \rightarrow 2Cl$

Chain initiating step i.e. a chlorine molecule absorbs one quantum of light and dissociates to give Cl atoms.

(b) Secondary process :

(i) $Cl + H_2 \rightarrow HCl + H$ | Chain propagating steps

(ii) $H + Cl_2 \rightarrow HCl + Cl$ I

(iii) $Cl + Cl \rightarrow Cl_2$ } Chain terminating step

- It is interesting to note that the mechanism of the above reaction is similar to that of the photosynthesis of HBr, yet the quantum yield of this reaction is very high whereas that of the photosnthesis of HBr is very low.
- The difference is explained on the basis of the reaction (i) of the secondary processes.
- In the present reaction, the reaction (i) of the secondary processes which immediately follows the primary process is exothermic and therefore, takes place very easily and consequently the chain reaction is set up very easily.
- In the photosynthesis of HBr, the reaction (i) of the secondary process is endothermic and thus has very little tendency to take place .

Photosensitized Reaction

- Photosensitization is a reaction to light that is mediated by a light-absorbing molecule, which is not the ultimate target. There are many substances that do not normally react when exposed to light. If, however, another substance is added to it, photochemical reaction readily proceeds.
- The substance thus added does not undergo any chemical change. It merely absorbs light energy and then passes it on to the reactant substance. The added substance is called a photosensitizer since it sensitizes the reaction. The process is termed as photo-sensitization.

The photosensitizer acts as a carrier of energy from the excited molecule to the reactant molecule. Photosensitization can involve reactions within living cells or tissues, or they can occur in pure chemical systems.

- If only hydrogen gas is irradiated by the ultraviolet light of $\lambda = 253.70$ nm the molecules do not dissociate to the atoms.
- But if the same radiation acts on hydrogen in presence of Hg-vapour, the hydrogen molecules undergo dissociation to the hydrogen atoms.
- $Hg + hv \rightarrow Hg^{*}$
- $Hg^{*} + H_2 \rightarrow Hg + 2H$