CHAPTER-9

Photochemistry

9.1. INTRODUCTION – INTERACTION OF RADIATION WITH MATTER

The term radiation includes all types of electromagnetic waves from very low frequency microwaves to medium frequency infrared, visible and ultraviolet radiation to high frequency X-rays and γ-rays. However, the visible and UV radiations having wave length lying between 8000-2000 Å (800-200 nm) are more important. The bond dissociation energy per mole for most of the molecules lies between 150 kJ and 600 kJ. These energies are available from the visible and UV radiations. Therefore, if a molecule absorbs a quantum of visible or UV radiations, a chemical reaction can occur. Absorption of a photon of light may raise a molecule to an excited electronic state which essentially involves the promotion of an electron from a bonding molecular orbital (BMO) to an antibonding molecular orbital (ABMO). In the excited state, the atom or the molecule is more likely to undergo a chemical reaction in the ground state.

The branch of chemistry which deals with the study of interaction of radiation with matter resulting into a physical change or into a chemical reaction is called photochemistry. The reactions which are brought about directly or indirectly by light radiations are known as Photochemical reactions.

The two main types of processes studied under photochemistry are :

(*i*) *Photophysical processes*

(*ii*) *Photochemical processes or photochemical reactions.*

Photophysical processes. These are the processes which take place in the presence of light radiations but do not result into any chemical reaction. Some important examples of photophysical processes are fluorescence into phosphoresecence and photoelectric effect. These processes arise on account of the absorption of light by substances followed by the emission of the absorbed light. The process is known as **fluorescence**, if the absorbed light is emitted **instaneously.** If the absorbed light is emitted after some *time lag*, the process is called **phosphorescence.** Further, if the energy of the absorbed light is sufficiently high, it may lead to the emission of electrons from the atoms and the process is called **photoelectric effect.**

Photochemical reactions. These are the reactions which are brought about by the absorption of light by the reacting substances. These reactions are usually brought about by the light radiations of the visible and ultra violet region (having wave lengths between 800-200 nm). In the photochemical reactions, the light energy absorbed is stored within the substance and then used for bringing about the reaction.

Some important examples of photochemical reactions are :

(*i*) **Dissociation :** $2HBr \rightarrow H_2 + Br_2$

(*ii*) **Combination :** $H_2 + Cl_2 \rightarrow 2HCl$

(*iii*) **Decomposition :** $2O_3 \rightleftharpoons 3O_2$

(*iv*) **Double decomposition :** $C_6H_{12} + Br_2 \rightarrow C_6H_{11}Br + HBr$

(*v*) **Addition reaction :** $(C_6H_5)_2C = C(C_6H_5)_2 + Br_2 \rightarrow (C_6H_5)_2CBr - CBr(C_6H_5)_2$

(*vi*) **Polymerisation :** $n\, C_2H_2 \rightarrow (C_2H_2)_n$

(*vii*) **Rearrangement :** Fumaric acid → Maleic acid (*viii*) **Photo-catalytic reactions :** Photosynthesis of carbohydrates in plants in the presence of chlorophyll, the green colouring matter of leaves of plants.

$$\underbrace{6CO_2 + 6H_2O}_{\text{From air}} \xrightarrow[\text{chlorphyll}]{\text{Light}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

9.2. DIFFERENCE BETWEEN THERMOCHEMICAL REACTIONS (OR THERMAL REACTIONS) AND PHOTOCHEMICAL REACTIONS

Photochemical reactions differ from ordinary thermochemical (or dark) reactions as summarised in Table 9.1.

Table 9.1 Difference between Photochemical and Thermochemical reactions

	Dark or Thermochemical Reactions	Photochemical Reactions
(*i*)	These reactions involve the evolution or absorption of heat.	These reactions involve the absorption of photons of light.
(*ii*)	The presence of light is not necessary for the reaction to take place.	The presence of light is an essential requirement for the reaction to take place.
(*iii*)	Temperature has significant effect on the rate of a thermochemical reaction.	Temperature has no significant effect on the rate of a photochemical reaction. On the other hand, the intensity of light has a marked effect on the rate of a photochemical reaction.
(*iv*)	Free energy change (ΔG) of a thermochemical reaction is always negative.	The free energy change (ΔG) of a photochemical reaction is not negative in all cases. For example, in the synthesis of carbohydrates by plants and decomposition of HCl into H_2 and Cl_2 and Cl_2, ΔG is positive but the reaction is spontaneous.
(*v*)	In these reactions, the required activation energy is provided by inter-molecular collisions or is supplied in the form of heat.	In these reactions, the required activation energy is gained through the absorption of quanta of visible or ultraviolet light.
(*vi*)	In thermal reactions, exposure to heat radiations, increases, in a random manner, the translational, rotational and vibrational energies of all the molecules to almost the same extent i.e. there is no selectivity. For example, exposure of a mixture of H_2 and Br_2 to heat radiations would cause the excitation of both the bromine and hydrogen molecules.	In photochemical reactions only a single selected species (atom or molecule) can be promoted to an excited state independent of other species present in the reactions. For example, exposure of a mixture of H_2 and Br_2 to radiaions of wave lengths between 450 nm and 550 nm, results in the excitation of only the bromine molecules.

Key Facts

(*i*) In spontaneous reactions, the light acts essentially as a catalyst and speeds up the reaction.

(*ii*) In non-spontaneous reactions, energy associated with light radiations increases the free energy of the reactant molecules sufficiently so that ΔG becomes negative.

9.3. LAWS GOVERNING ABSORPTION OF LIGHT

1. Lambert's Law. This law put forward by Lambert (1760) states that :

When a beam of monochromatic light is passed through a pure homogeneous absorbing medium, the rate of decrease of intensity of the radiation with thickness of absorbing medium is proportional to the intensity of the incident light. Mathematically, Lambert's law may be expressed as :

$$-\frac{dI}{dx} \propto I \qquad \text{or} \qquad -\frac{dI}{dx} = kI$$

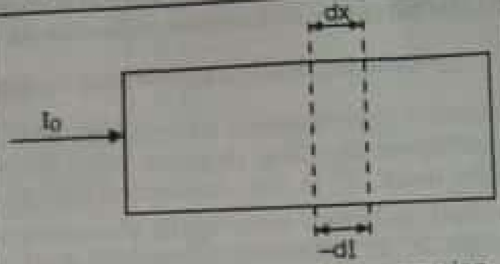


Fig. 9.1 Decrease in intensity on passing through a medium.

where dI is the small decrease in intensity of the light on passing through a small thickness dx, I is the intensity of light after passing through a thickness x of the absorbing medium. The proportionality constant k is called the **absorption coefficient** and its value depends upon the nature of the absorbing medium.

If 'I_0' is the intensity of light radiation before entering the absorbing medium (*i.e.*, when $x = 0$), then the intensity of radiation 'I' at any point 'X' at a distance x from the start of the medium can be obtained from equation (1) as follows :

Rearranging equation (1), we get, $\frac{dI}{I} = -k dx$

when

$$x = 0, I = I_0 ; x = x, I = I \qquad \text{...(2)}$$

Integrating equation (2) between the limits x = 0 to x and $I = I_0$ to I, we get

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} k dx \qquad \text{or} \qquad \ln \frac{I}{I_0} = -kx \qquad \text{...(3)}$$

Taking antilog $\frac{I}{I_0} = e^{-kx}$ ...(4) or $\boxed{I = I_0 \cdot e^{-kx}}$ ...(5)

where 'I_0' is the original intensity and 'I' is the intensity after passing through a thickness 'x' of the medium. Therefore, the intensity of light absorbed (I_{abs}) is given by

$$I_{abs} = I_0 - I \qquad \text{...(6)}$$

Substituting the value of 'I' from equation (5) we get

$$I_{abs} = I_0 - I_0 e^{-kx} \qquad \text{or} \qquad I_{abs} = I_0(1 - e^{-kx}) \qquad \text{...(7)}$$

On changing the natural logarithm to base 10, the equation (3) can be written as :

$$2.303 \log_{10} \frac{I}{I_0} = -kx \qquad \text{or} \qquad \log_{10} \frac{I}{I_0} = -\frac{k}{2.303} x$$

or $\log_{10} \frac{I}{I_0} = -k'x$ ...(8) or $\frac{I}{I_0} = 10^{-k'x}$ or $\boxed{I = I_0 \times 10^{-k'x}}$ ...(9)

where k' is called **extinction coefficient or absorptivity** of the absorbing medium and is related to absorption coefficient k by the expression.

$$k' = \frac{k}{2.303} \qquad \text{...(10)}$$

Physical significance of the absorptivity or extinction coefficient. Rearranging equation (8), we get

$$k' = -\frac{1}{x} \log_{10} \frac{I}{I_0} = \frac{1}{x} \log_{10} \frac{I_0}{I} \qquad \text{...(11)}$$

Now $k' = \frac{1}{x}$ if $\log_{10} \frac{I_0}{I} = 1$

But $\log_{10} \frac{I_0}{I} = 1$ only when $\frac{I_0}{I} = 10$ *i.e.*, $I = \frac{1}{10} I_0$.

Hence absorptivity or extinction coefficient may be defined as :

The reciprocal of the thickness of that layer of the absorbing medium at which the intensity of light is reduced to one–tenth of its original value.

2. Beer's Law. This law which is an extension of Lambert's law is used when the absorbing substance is present in solution. This law states that :

When a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as to the concentration of the solution.

Mathematically, the law may be expressed as $-\frac{dI}{dx} \propto I \times C$ or $-\frac{dI}{dx} = \varepsilon IC$ ...(12)

where ε (pronounced as epsylon) is a constant of proportionality and is called **molar absorption coefficient**. Its value depends upon the nature of the absorbing substance and the wavelength of the light used. 'C' is the concentration of the solution in moles per litre. Let I_0 be the intensity of the radiations before entering the absorbing solution (*i.e.*, when $x = 0$), then intensity of radiation I at any point 'X' at a distance x from the start of medium can be obtained by integrating the equation (12) between the limits $x = 0$ to x and $I = I_0$ to I.

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} \varepsilon C dx \quad \text{or} \quad \ln \frac{I}{I_0} = -\varepsilon Cx \qquad ...(13)$$

or

$$\frac{I}{I_0} = e^{-\varepsilon Cx} \qquad ...(14) \quad \text{or} \quad \boxed{I = I_0 e^{-\varepsilon Cx}} \qquad ...(15)$$

As before, $I_{abs} = I_0 - I = I_0 - I_0 e^{-\varepsilon Cx} = I_0(1 - e^{-\varepsilon Cx})$

Changing the natural logarithm to the base 10, equation (13) may be written as

$$2.303 \log_{10} \frac{I}{I_0} = -\varepsilon Cx \quad \text{or} \quad \log_{10} \frac{I}{I_0} = -\frac{\varepsilon}{2.303} C.x \quad \text{or} \quad \log_{10} \frac{I}{I_0} = -\varepsilon' Cx \qquad ...(16)$$

or

$$\frac{I}{I_0} = 10^{-\varepsilon' Cx} \quad \text{or} \quad \boxed{I = I_0 . 10^{-\varepsilon' Cx}} \qquad ...(17)$$

where $\varepsilon' = \frac{\varepsilon}{2.303}$ is called **molar extinction coefficient** of the absorbing solution. These days, ε' is called **molar absorption coefficient or molar absorptivity. Its C.G.S. unit is (litre/ mole) cm^{-1} or M^{-1} cm^{-1} whereas its S.I. unit is m^2 mol^{-1}.**

Physical significance of molar extinction coefficient or molar absorptivity. Rearranging equation (16), we get

$$\varepsilon' = -\frac{1}{Cx} \log_{10} \frac{I}{I_0} = \frac{1}{Cx} \log_{10} \frac{I_0}{I}$$

If $\log_{10} \frac{I_0}{I} = 1$ and $C = 1$ M, then $\varepsilon' = \frac{1}{x}$. But $\log_{10} \frac{I_0}{I} = 1$ means that $\frac{I_0}{I} = 10$ or $I = \frac{1}{10} I_0$

Hence, molar exitinction coefficient or molar absorptivity may be defined as :

The reciprocal of the thickness of the solution layer of 1 molar concentration which reduces the intensity of the light passing through it to one tenth of its original value.

The product $\varepsilon' Cx$ or $-\log_{10} I/I_0$ is called the optical density (A) or absorbance of the sample and I/I_0 is called transmittance (T).

Thus, eq (16) becomes, $\varepsilon' Cx = -\log_{10} \frac{I}{I_0} = -\log_{10} T = A$ or D ...(18)

This is the expression for the **Lambert-Beer law.**

Also $\quad \% T = (I/I_0) \times 100 \quad$ or $\quad \frac{I_0}{I} = \frac{10^2}{(\% T)}$

or
$$\log_{10}(I_0/I) = 2 - \log_{10}(\%\,T) \quad \text{or} \quad A = 2 - \log_{10}(\%\,T) \qquad ...(19)$$

Thus a plot of absorbance, A versus concentration, C will be a straight line passing through the origin, with slope $= \varepsilon' x$ (Fig. 9.2). The dotted portion of the curve represents deviation from linearity at higher concentrations.

Limitations of Beer-Lambert Law

1. It is not obeyed if the radiation used is not monochromatic.

2. It is applicable only to dilute solutions. In case the solute is an electrolyte then at higher concentrations, the interionic interactions can drastically alter the ability of a solute to absorb a given wavelength of the incident radiation. Thus at higher concentrations there are deviations from linearity (Fig. 9.2).

3. The temperature of the system should remain almost constant. This is because too much rise in temperature shifts the absorption band towards longer wave length (called **bathochromic effect**).

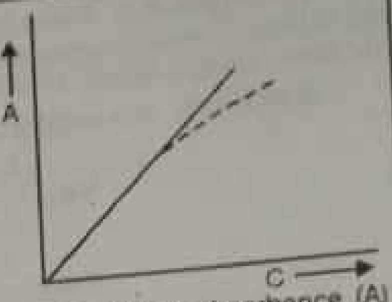


Fig. 9.2 Plot of absorbance (A) versus concentration (c) of solution.

Numerical Problems

Formulae and Units

1. *For light passing through a pure homogeneous medium* (**Lambert's Law**),

$$ln\frac{I}{I_0} = -kx \qquad \text{or} \qquad \log_{10} I_0 = -\frac{kx}{2.303} = -k'x$$

where I_0 = Intensity of incident light, I = Intensity of light after passing through a distance x in the medium ; k' = absorption coefficient or absorptivity or extinction coefficient of absorbing medium.

If x is the total length of medium, $I = I_t$, the intensity of transmitted light.

2. *For light passing through a solution* (**Beer's law**),

$$ln\frac{I}{I_0} = -\varepsilon c x \qquad \text{or} \qquad \log_{10}\frac{I}{I_0} = -\frac{\varepsilon}{2.303}cx = -\varepsilon' cx$$

where I_0 and I are the intensity of incident radiation and intensity after passing through a distance x in the medium, c is the concentration of solution in mol L^{-1} and ε' is the molar absorption coefficient or molar extinction coefficient.

3. $I_{abs} = I_0 - I_t$ 4. $-\log_{10}\frac{I}{I_0} = -\log T = A(\text{or } D) = \varepsilon' cx$

where $\frac{I}{I_0} = T$ (Transmittance), A is called absorbance and D is called optical density.

5. $\%\,T = \frac{I}{I_0} \times 100$ or $\frac{I_0}{I} = \frac{10^2}{(\%T)}$

Example 9.1. *When an incident beam of wavelength 3000 Å was allowed to pass through 2 mm thick pyrex glass, the intensity of radiation was reduced to one-tenth of its incident value. What part of same beam will be transmitted through 1 mm thick same pyrex glass sheet ?* **(Pbi. U. 2003)**

Solution. According to Lambert's law, **in the first case,**

$$\log_{10}\frac{I_t}{I_0} = -k'x \;;\; I_t = 10\% \text{ of } I_0 \text{ or } \frac{I_t}{I_0} = \frac{10}{100} = \frac{1}{10}$$

$$x = 2mm = 0.2 \text{ cm} \;;\; \therefore \log_{10}\frac{1}{10} = -k'(0.2 \text{ cm}) \text{ or } k' = \frac{1}{0.2 \text{ cm}} = 5 \text{ cm}^{-1}$$

In the second case, $x = 1mm = 0.1$ cm

Substituting $k' = 5 \text{ cm}^{-1}$ in the expression for Lambert's law, we have

$$\log_{10}\frac{I_t}{I_0} = -5\ \text{cm}^{-1} \times 0.1\ \text{cm} = -0.5\ \therefore \frac{I_t}{I_0} = \text{antilog}_{10}(-0.5) = \text{antilog}(\bar{1}.5) = 0.3162$$

$\therefore I_t = 0.3162 \times I_0$ or intensity of transmitting light = **31.62% of the intensity of incident light.**

Example 9.2. *When beam of light (5000 Å) was allowed to pass through 4 mm thick glass sheet, the intensity of the transmitted light was reduced to 20% of the initial value. What percentage of light of the same radiation will be absorbed by 2 mm thick glass sheet?* (P.U. 2003)

Solution. According to Lambert's law in the first case,

$$\log_{10}\frac{I_t}{I_0} = -k'x\ ;\ I_t = 20\%\ \text{of}\ I_0\ \text{or}\ \frac{I_t}{I_0} = \frac{20}{100} = \frac{2}{10}\ ;\ x = 4mm = 0.4\ \text{cm}$$

$$\therefore \qquad \log_{10}\frac{2}{10} = -k'(0.4\ \text{cm}) \qquad \text{or} \qquad \log_{10}\frac{10}{2} = k'(0.4\ \text{cm})$$

$$\text{or} \qquad (1 - 0.3010) = k'(0.4\ \text{cm})\ \text{or}\ k' = \frac{0.6990}{0.4}\ \text{cm}^{-1} = 1.747\ \text{cm}^{-1}$$

In the second case, $x = 2\,mm = 0.2$ cm

Substituting $k' = 1.747\ \text{cm}^{-1}$ in the expression for Lambert's law, we have

$$\log_{10}\frac{I_t}{I_0} = -1.747\ \text{cm}^{-1} \times 0.2\ \text{cm} = -0.3494$$

$$\frac{I_t}{I_0} = \text{Antilog}_{10}(-0.3494) = \text{Antilog}_{10}(\bar{1}.6506) = 0.4473$$

$$I_t = 0.4473 \times I_0\ ;\ I_{abs} = I_0 - I_t = I_0 - 0.4473\, I_0 = 0.5527\, I_0$$

or $I_{abs} = 55.27\%$ **of the intensity of incident light.**

Example 9.3. *In a cell of certain length and at a pressure of 100 mm Hg, gaseous acetone transmits 25.1 per cent of the incident radiation of wavelength 265 nm. Assuming Beer's law to apply, calculate the pressure at which 98% of the incident radiation will be absorbed by acetone in the same cell at the same temperature.*

Solution. For a gaseous system ; C in Beer's law may be replaced by p. Thus, we have

$$\log_{10}\frac{I}{I_0} = -\varepsilon' px$$

Since at 100 mm Hg, transmittance is 25.1%, we have

$$\frac{I}{I_0} = \frac{25.1}{100} = 0.251\ ;\ \therefore\ \log_{10}(0.251) = -\varepsilon' x\,(100\text{mm Hg})$$

$$\text{or} \qquad \varepsilon' x = -\log_{10} 0.251/100\ \text{mm Hg} = 0.006\ (\text{mm Hg})^{-1}$$

For 98% absorption or 2% transmittance, we have

$$\log_{10}(0.02) = -(\varepsilon' x)p = -0.006\ (\text{mm Hg})^{-1}p\ \text{ or }\ p = -\frac{\log(0.02)}{0.006\ (\text{mm Hg})^{-1}} = 283\ \text{mm Hg}$$

Example 9.4. *A 0.01 M solution of a compound transmits 20% of the radiation in a container with path length equal to 1.5 cm. Calculate the molar extinction coefficient of the compound.* (G.N.D.U. 2002)

Solution. Here $\dfrac{I_t}{I_0} = \dfrac{20}{100} = 0.2$

Where I_0 = Intensity of incident light and I_t = Intensity of transmitted light

Hence, absorbance $A = -\log_{10}\dfrac{I_t}{I_0} = \varepsilon' cx$, or $-\log_{10}(0.2) = \varepsilon' \times 0.01\ \text{M} \times 1.5\ \text{cm}$

Problem 9.6. *The intensity of a light beam is halved on traversing a 1.0 cm thickness of an absorbing medium. What thickness must be traversed to reduce the emergent intensity to (a) one-fourth (b) one-tenth of incident intensity ?* [**Ans.** (*a*) 2.0 cm (*b*) 3.32 cm]

Problem 9.7. *An aqueous solution of a coloured compound has molar absorptivity (ε') of 3200 at 525 nm. Calculate optical density (A) and % transmittance of a 3.4×10^{-4} M solution if a 1.00 cm cell is used.* [**Ans.** A = 1.088, % T = 8.17]

[**Hint.** To calculate % T, use A = 2 – log % T]

Problem 9.8. *A compound when dissolved in water, a 10^{-2} M concentration absorbs 10% of an incident radiation in a path of 0.01 m length. What should be the concentration of solution in order to absorb 90% of the same incident radiation. ?* [**Ans.** 0.218 M]

Problem 9.9. *Calculate the transmittance, absorbance and molar absorption coefficient of a solution which absorbs 85% of a certain wavelength of light beam passed through a 1.5 cm cell containing 0.20 M solution.* (**P.U. 2000**) [**Ans.** T = 0.15, A = 0.8239, ε' = 2.746 M^{-1} cm^{-1}]

$$\left[\textbf{Hint. } T = \frac{I_t}{I_o} = \frac{100-85}{100},\quad A = -\log_{10}\left(\frac{I_t}{I_o}\right) = \varepsilon' Cx\right]$$

Problem 9.10. *The molar absorbing coefficient of a solute absorbing at a wave length of 540 nm is 286 M^{-1} cm^{-1}. When the same light passes through 6.5 mm cell containing the solute of unknown concentration, 46.5% of the light is absorbed. Calculate the concentration of the solute.*

(**Phi. U. 2002**) [**Ans.** 1.46×10^{-3} M]

Problem 9.11. *A 2×10^{-3} m thick glass sheet transmits 10% of the incident light of the same wave length 300 nm. What percentage of light of the same wavelength will be absorbed by 1×10^{-3} m thick glass sheet ?* [**Ans.** 68.38%]

Problem 9.12. *Calculate the transmittance, absorbance and absorption coefficient of a solution which absorbs 90% of a certain wavelength of light beam passed through a 1 cm cell containing 0.25 M solution.* [**Ans.** A = 1, T = 0.10, ε' = 4L mol^{-1} cm^{-1}]

9.4. PHOTOCHEMICAL PRINCIPLES

1. Grotthus-Draper Principle of Photochemical Activation. Prior to 1817, photochemical changes such as photosynthesis in plants, blackening of silver halides and photofading of coloured materials etc. was observed and studied qualitatively. The quantitative approach to photochemistry was initiated by Grotthus and Draper (1818-1819). They pointed out that all the incident light was not effective in bringing about a chemical change. They formulated the first law of photochemistry. This law now known as **Grotthus-Draper** law states that :

When light falls on an object, a part of it is reflected, a part of it is transmitted and the rest is absorbed. It is only the light absorbed by the reacting system which is effective in bringing about a chemical reaction.

However, it does not necessarily follow from the above law that the absorbed light will always bring about the chemical reaction. In several cases, the absorbed light is converted into the kinetic energy of the absorbing molecules and only heat effects are produced. For example, $KMnO_4$ solution strongly absorbs light but no chemical change is produced. In many cases, the absorbed light is re-emitted as **fluorescence or phosphorescence** (For details refer to section 9.9).

2. Stark-Einsein Law of Photochemical Equivalence. The second law of photochemistry known as Stark-Einstein law sates that :

In a photochemical reaction, each light absorbing molecule obsorbs only one quantum of radiation which causes that particular reaction.

If ν is the frequency of absorbed light, the corresponding quantum of energy absorbed per molecule is given by Planck's relation $E = h\nu$.

The energy E absorbed per mole of the reacting substance is, therefore, given by $E = N_A h\nu$

where N_A = Avogadro's number $= 6.022 \times 10^{23}$ and $h = 6.626 \times 10^{-34}$ Js

$$\therefore \quad E = 6.022 \times 10^{23} \times 6.626 \times 10^{-34}\ \nu = \frac{39.90 \times 10^{-11} \times c}{\lambda}$$

$$= \frac{39.90 \times 10^{-11} \times 3 \times 10^{8}\ \text{mol}^{-1}}{\lambda} = \frac{0.1197}{\lambda}$$

where λ is the wavelength of the absorbed light in metres.

The quantity E, *i.e.*, **the energy absorbed per mol of the reacting substance is called an einstein. The numerical value of einstein is inversely proportional to the wavelength of the light absorbed.**

$$\boxed{E = \frac{0.1197}{\lambda}\ \text{J mol}^{-1}\ \text{when } \lambda \text{ is in metres} = \frac{0.1197}{\lambda} \times 10^{10}\ \text{J mol}^{-1} = \frac{11.97 \times 10^{5}}{\lambda}\ \text{kJ mol}^{-1}}$$

when λ is expressed in Å units (1 Å $= 10^{-10}$ m).

The values of einstein for radiations having different wavelengths are given in Table 9.2.

Table 9.2 Values of einstein for radiations of different wavelengths

Wave length (nm)	Colour range	Value of Einstein (kJ mol^{-1})
800	Near infrared	149.6
700	Red	171.0
600	Yellow-green	199.5
500	Blue-green	239.4
400	Violet	299.3
300	Ultraviolet	399.0
200	Ultraviolet	598.5

Numerical Problems

Formulae and Units In S.I. Units

1. Eienstein of Energy (E) $= \frac{0.1197}{\lambda}$ J mol^{-1} $= 11.97 \times 10^{-5}$ kJ mol^{-1}

when λ is the wave length of the absorbed light in metres.

2. $E = \frac{11.97 \times 10^{5}}{\lambda}$ kJ mol^{-1} when λ is expressed in Å units (1Å $= 10^{-10}$ *m*)

3. **In C.G.S. Units,**

$$E = Nh \cdot \frac{C}{\lambda} = \frac{6.022 \times 10^{23} \times 6.626 \times 10^{-27}\ \text{erg sec} \times 3.0 \times 10^{10}\ \text{cms}^{-1}}{\lambda}$$

$$= \frac{119.7 \times 10^{6}\ \text{erg}}{\lambda}\ \text{per mole} = \frac{119.7 \times 10^{6}}{4.184 \times 10^{7}\lambda} \qquad [\because 4.184 \times 10^{7}\ \text{ergs} = 1\ \text{cal}]$$

$$= \frac{2.86}{\lambda}\ \text{cal per mole.}$$

Here λ is expressed in cm.

$$E = \frac{2.86}{\lambda} \times 10^{8}\ \text{cal per mole} = \frac{2.86}{\lambda} \times 10^{5}\ \text{kcal per mole when } \lambda \text{ is expressed in Å units}$$

$[\because 1\ \text{Å} = 10^{-8}\ \text{cm}]$

4. The unit of energy used most frequently in photochemistry is electron volt (eV) where 1 eV s the energy acquired by an electron when a potential difference of one volt is applied to it.

5. Relationship between different energy units is as follows :

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}; \text{eV/mole} = 96.48 \text{ kJ mol}^{-1} = 23.06 \text{ kcal mol}^{-1}.$$

Example 9.6. *Calculate the energy (in eV) of an einstein of radiation of wavelength 300 nm. ($1 \text{ eV} = 1.6 \times 10^{-19}$ J).*

Solution. According to Stark-Einstein law, $E = N_A h\nu = N_A hc/\lambda$

$$= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (6.626 \times 10^{-34} \text{ Js}) \times (3 \times 10^{8} \text{ ms}^{-1})}{(300 \times 10^{-9} \text{ m})}$$

$$= 399017.7 \text{ J mol}^{-1} = \frac{399017.7 \text{ J mol}^{-1}}{1.6 \times 10^{-19} \text{ J/eV}} = \mathbf{2.49 \times 10^{24}\ eV\ mol^{-1}}$$

Example 9.7. *A radiation having wavelength 400 nm is completely absorbed by a reaction mixture. How many moles of the radiation are absorbed in 20 minutes if the intensity of the radiation is 50 W ?*

Solution. Energy absorbed by the reaction mixture in one second = 50 W = 50 Js $^{-1}$

Energy absorbed in 20 minutes = $(50 \text{ Js}^{-1}) \times (20 \times 60 \text{ s}) = 60{,}000$ J

Let the number of moles of photons absorbed be n, then the total energy absorbed $= nE$

or $\quad 60{,}000 \text{ J} = n . N_A h\nu = n N_A h\frac{c}{\lambda}$

$$\therefore \quad n = \frac{(60{,}000 \text{ J}) \times (400 \times 10^{-9} \text{ m})}{(6.022 \times 10^{23} \text{ mol}^{-1})(6.626 \times 10^{-34} \text{ Js})(3.0 \times 10^{8} \text{ ms}^{-1})} = \mathbf{0.200\ mol}$$

Practice Problems

Problem 9.13. *What is the energy in kcal mol^{-1} of one einstein of 2537 Å ?* [Ans. 112.77]

Problem 9.14. *Calculate the value of einstein for a radiation having wavelength 600 nm.*

[**Ans.** 199.5 kJ mol^{-1}]

Problem 9.15. *Calculate the energy of one photon of light of wavelength 2450 Å. Will it be able to dissociate a bond of diatomic molecule which absorbs this photon and has a bond energy equal to 95 kcal per mol ?*

[**Ans.** (*i*) 8.11×10^{-19} J or 1.938×10^{-19} cal, (*ii*) Energy required for the dissociation of bond $= 1.578 \times 10^{-19}$ cal. Hence the bond will be dissociated]

Problem 9.16. *If the value of an Einstein is 301.25 kJ, calculate the wavelength of the light.*

[**Ans.** 3972.2 Å]

9.5. QUANTUM YIELD (EFFICIENCY) OF A PHOTOCHEMICAL REACTION

The law of photochemical equivalence is applicable only to the absorption in primary photochemical process, *i.e.*, when as a result of absorption of light, only one molecule decomposes and the products enter no further reaction. However, if the primary process is accompanied by the subsequent reactions as in case of chain reactions, the absorption of one photon of light might lead to the decomposition of several molecules. Under such conditions, simple 1 : 1 ratio between the photons absorbed and the molecules decomposed does not hold. Again, in certain reactions where deactivation occurs, the number of molecules which undergo chemical reaction is less than the number of photons of light absorbed. To express the relationship between the number of molecules entering reaction and the number of photons absorbed, the concept of **quantum yield** (or **efficiency**), ϕ is introduced. This is defined as :

The number of molecules reacting in a given time per quantum of light absorbed, i.e.,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

or

$$\phi = \frac{\text{Number of moles reacting in a given time}}{\text{Number of einsteins of light absorbed in the same time}}$$

Thus, to determine the quantum yield of any photochemical reaction, we have to measure

(i) the quantum of light absorbed per second.

(ii) the number of moles of the light absorbing substance that react in one second.

An experimental arrangement for the study of a photochemical reaction is shown in Fig. 9.3.

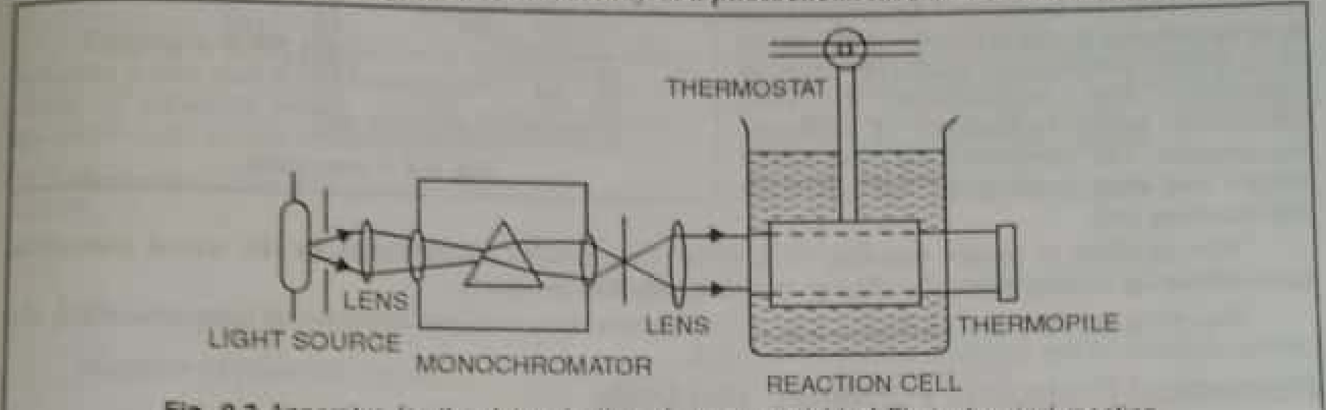


Fig. 9.3 Apparatus for the determination of quantum yield of Photochemical reaction

The apparatus used for the determination of the number of quanta of light absorbed consists of :

(*i*) a **light source** which emits radiation of suitable intensity in the desired spectral range. A common source of light used is mercury vapour lamp. Iron and carbon arcs and, in some cases, metal filament lamps are also used as source of light.

(*ii*) a **lens** of suitable focal length.

(*iii*) **monochromator** which cuts off all radiations except the radiations of desired wavelengths (λ).

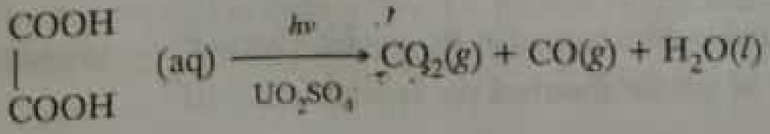
(*iv*) a **reaction cell** which is made of glass or quartz. Glass is used when the wavelength of the light used lies in the visible range. For light radiations having wavelength below 350 nm, only the quartz cell is used.

(*v*) **detector** which is usually a thermopile or an actinometer used to measure the intensity of light radiations.

A thermopile consists of a number of thermo-couples joined in series as shown in Fig. 9.4. A thermo-couple consists of two metal rods (say Ag and Bi) joined together. One set of junctions of the thermo-couple is saldered to metal strip blackned with platium black so as to absorb all the radiations. The other set is protected from radiations and maintained at constant temperature by placing the system in a box. The radiations falling on the blackened metal strip are almost completely absorbed by it. The heat radiations associated with light radiations absorbed by the blackened end, raise the temperature of this set of junctions. The temperature difference between the hot end and the cold end produces a current in the circuit. Thermoelectric current in the circuit can be measured by connecting a milliammeter to the thermopile. The intensity of light radiations absorbed can be measured by calibrating the thermopile with radiations of known intensity. From the intensity of light absorbed, the energy of incident radiations can be easily calculated.

The measurements are made before and after passing light through the cell. The difference of two measurements gives the energy of the radiation absorbed by the reacting substance.

The energy associated with radiations absorbed can also be measured by employing an actinometer. It is a device in which gas mixtures or solutions sensitive to light are used. An actinometer makes use of the fact that a definite amount of the radiation absorbed brings about a definite amount of chemical reaction. One of the actinometers, which is in common use, is the uranyl oxalate actinometer. It consists of 0.05 molar oxalic acid and 0.01 molar uranyl sulphate (UO_2SO_4) solutions in water. When exposed to light, the following reactions take place :



$$\begin{matrix}\text{COOH}\\ |\\ \text{COOH}\end{matrix}\,(aq) \xrightarrow[UO_2SO_4]{h\nu} CO_2(g) + CO(g) + H_2O(l)$$

Uranyl sulphate absorbs the light and then passes it on to oxalic acid. The extent of decomposition of oxalic acid is determined at the conclusion of the experiment by titration against potassium permanganate solution. For calculating the energy associated with a radiation, it is assumed that the amount of decomposition is proportional to the intensity of radiation of a given wavelength and the time of exposure. The actinometer is first calibrated using radiations of different wavelength. The measurements are made before and after passing the light through the reacting cell.

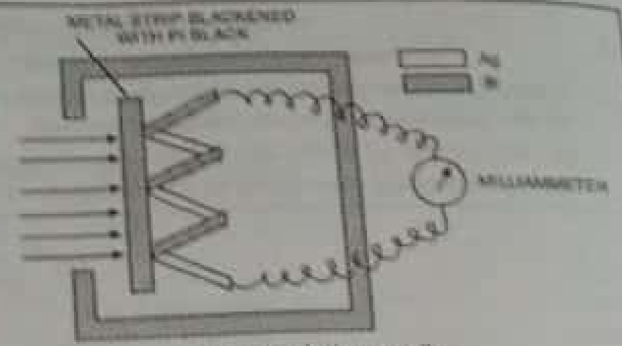


Fig. 9.4 A thermopile

The number of moles reacting in a given time can be determined by the usual analytical methods or by noting down the change in some physical property.

Knowing the number of moles reacting in a given time and the intensity of light absorbed, the quantum yield of the reaction can be calculated.

Numerical Problems Formulae and Units

1. 1 Joule = 10^7 ergs ; 4.184×10^7 ergs = 4.184 J = 1 cal

2. Quantum yield (ϕ) = $\dfrac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta absorbed in the same time}}$

3. Units of (ϕ) : Number of moles per quantum or moles per einstein.

4. Energy of one quantum $= h\nu = \dfrac{hc}{\lambda} = \dfrac{(6.62 \times 10^{-27}\ \text{ergs}) \times (3 \times 10^{10}\ \text{cms}^{-1})}{\lambda(\text{in cm})}$ ergs

$$= \frac{(6.62 \times 10^{-34}\ \text{Js})(3 \times 10^{8}\ \text{ms}^{-1})}{\lambda(\text{in } m)}$$

Example 9.8. *The irradiation of HI vapour with UV radiation of 207 nm leads to the formation of H_2 and I_2. If 4.4×10^{-4} g of HI is decomposed per joule of radiant energy absorbed, how many HI molecules are decomposed per quantum of absorbed radiation ?* **(G.N.D.U. 2004)**

Solution. The energy associated with a photon of wave length 207 nm (= 207×10^{-9} *m*)

$$= h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\text{Js} \times 3 \times 10^{8}\ \text{ms}^{-1}}{207 \times 10^{-9}\ m} = 9.6 \times 10^{-19}\ \text{J}$$

Total energy absorbed = 1 J

Number of photons absorbed $= \dfrac{1}{9.6 \times 10^{-19}} = 1.04 \times 10^{18}$

Molecular mass of HI = 1 + 126.9 = 127.9

Amount of HI decomposed $= 4.4 \times 10^{-4}\ \text{g} = \dfrac{4.4 \times 10^{-4}}{127.9} = 3.4 \times 10^{-6}$ mol

$= 3.4 \times 10^{-6} \times 6.023 \times 10^{23}$ molecules $= 2.048 \times 10^{18}$ molecules

Quantum yield (ϕ) $= \dfrac{\text{Number of molecules decomposed}}{\text{Number of photons absorbed}} = \dfrac{2.048 \times 10^{18}}{1.04 \times 10^{18}} = 1.97 = 2$

Hence HI molecules decomposed per quantum of absorbed radiation = 2

Example 9.9. *A certain system absorbs 3×10^{18} quanta of light per second. On irradiation, 0.002 moles of reactant was found to have reacted in 10 minutes. Calculate the quantum yield of the process.*

Solution. Number of quanta absorbed per second = 3×10^{18}

Number of moles reacting in 10 minutes = 0.002

$\therefore$ Number of molecules reacting in 10 minutes = $0.002 \times 6.023 \times 10^{23}$

$$\text{Number of molecules reacting per second} = \frac{0.002 \times 6.023 \times 10^{23}}{10 \times 60} = 2 \times 10^{18}$$

$$\text{Quantum yield } (\phi) = \frac{\text{Number of molecules reacting per second}}{\text{Number of quanta absorbed per second}} = \frac{2 \times 10^{18}}{3 \times 10^{18}} = \mathbf{0.66}$$

Example 9.10. *Radiation of wave length 2500 Å was passed through a cell containing 10 mL of a solution which was 0.05 molar in oxalic acid and 0.01 molar in uranyl sulphate. After absorption of 80 joules of radiation energy, the concentration of oxalic acid was reduced to 0.04 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.*

Solution. The energy associated with a photon of wavelength, 2500 Å($= 2500 \times 10^{-10}$ m)

$$= h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{Js} \times 3 \times 10^{8}\ \text{ms}^{-1}}{2500 \times 10^{-10}\ \text{m}} = 7.9512 \times 10^{-19}\ \text{J}$$

Total energy absorbed = 80 J

$$\text{Number of photons absorbed} = \frac{\text{E}}{h\nu} = \frac{80\ \text{J}}{7.9512 \times 10^{-19}\ \text{J}} = 1.006 \times 10^{20}$$

Number of moles of oxalic acid taken for irradiation

$$= \text{Number of moles present in 10 mL of 0.05 M solution} = \frac{0.05}{1000} \times 10 = 5 \times 10^{-4}$$

$$\text{Number of moles of oxalic acid left unreacted} = \frac{0.04}{1000} \times 10 = 4 \times 10^{-4}$$

Number of moles of oxalic acid decomposed = $5 \times 10^{-4} - 4 \times 10^{-4} = 1.0 \times 10^{-4}$

Number of molecules of oxalic acid decomposed = $1.0 \times 10^{-4} \times 6.022 \times 10^{23} = 6.022 \times 10^{19}$.

Quantum yield, ϕ, of the reaction

$$= \frac{\text{Number of molecules of oxalic acid decomposed}}{\text{Number of photons (quanta) of light absorbed}} = \frac{6.022 \times 10^{19}}{1.006 \times 10^{20}} = \mathbf{0.599}$$

Example 9.11. *In the photobromination of cinnamic acid to dibromocinnamic acid using blue light of 435.8 nm at 30.6°C, a light intensity of 1.4×10^{-3} J s^{-1} produced a decrease of 0.075 millimoles of Br_2 during an exposure of 1105 s. The solution absorbed 80.1% of light passing through it. Calculate the quantum yield.*

Solution. The energy absorbed in the photobromination process

$$= 1.4 \times 10^{-3}\ \text{J s}^{-1} \times 1105\ \text{s} \times \frac{80.1}{100} = 1.239\ \text{J} \qquad ...(a)$$

Let 'n' be the number of moles of photon of light absorbed.

Then, the energy of light absorbed in the process = $\text{E} = n\text{N}_\text{A}\, h\nu$

or $$\text{E} = n\ \text{N}_\text{A} \frac{hc}{\lambda} \quad \text{where N}_\text{A} = \text{Avogadro's number} = 6.022 \times 10^{23}$$

Here $\lambda = 435.8\ \text{nm} = 435.8 \times 10^{-9}\ \text{m}, c = 3 \times 10^{8}\ \text{m s}^{-1},\ h = 6.626 \times 10^{-34}\ \text{J s}$

$$\therefore \quad \text{E} = \frac{n \times 6.022 \times 10^{23} \times 6.626 \times 10^{-34}\ \text{J s} \times 3 \times 10^{8}\ \text{ms}^{-1}}{435.8 \times 10^{-9}\ \text{m}} = n \times 2.747 \times 10^{5}\ \text{J} \qquad ...(b)$$

Hence, from (a) and (b), we get $n \times 2.747 \times 10^{5}\ \text{J} = 1.239\ \text{J}$

or $$n = \text{number of moles of photons absorbed} = \frac{1.239}{2.747 \times 10^{5}} = 4.51 \times 10^{-6}$$

The number of moles of Br_2 reacted in the process = 0.075×10^{-3} moles

Therefore, quantum efficiency,

$$'\phi' = \frac{\text{No. of moles of } Br_2 \text{ reacted}}{\text{No. of moles of photons absorbed}} \text{ or } \phi = \frac{0.075 \times 10^{-3}}{4.51 \times 10^{-6}} = 16.63$$

Example 9.12. *In the photochemical combination of $H_2(g)$ and $Cl_2(g)$, a quantum efficiency of about 1.0×10^6 is obtained with a wavelength of 480 nm. What is the number of moles of HCl (g) produced if 1 J of radiant energy is absorbed ?* (Pbi. U. 2001)

Solution. An einstein corresponding to 480 nm = $N_A h \frac{c}{\lambda}$

$$= \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})}{(480 \times 10^{-9} \text{ m})} = 2.494 \times 10^5 \text{ J mol}^{-1}$$

Number of photons in 1 J = $\frac{1}{2.494 \times 10^5} = 4.013 \times 10^{-6}$ mol

$$\phi = \frac{\text{Amount of } Cl_2 \text{ (or } H_2\text{) reacted}}{\text{Amount of photons absorbed}} = 1.0 \times 10^6$$

Hence, amount of Cl_2 or H_2 reacted = $1.0 \times 10^6 \times 4.013 \times 10^{-6}$ mol = 4.013 mol.

In the photochemical combination of H_2 and Cl_2, 1 mol of H_2 combines with 1 mol of Cl_2 to produce 2 mol of HCl, i.e., $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

Hence amount of HCl produced is = 4.013 mol × 2 = **8.026 mol.**

Example 9.13. *In a photochemical reaction : $B \rightarrow C$, 1.00×10^{-5} moles of C are formed as a result of the absorption of 6.00×10^7 ergs at at 3600Å. Calculate the quantum yield.* (Pbi. U. 2000)

Solution. Number (n) of moles of photons of light absorbed = $\frac{E\lambda}{N_A hc}$

where $E = 6.00 \times 10^7$ *erg*, $\lambda = 3600\,\text{Å} = 3600 \times 10^{-8}$ *cm*,

$N_A = 6.022 \times 10^{23}$ *mol*$^{-1}$, $h = 6.626 \times 10^{-27}$ *erg s*, $c = 3 \times 10^{10}$ *cm s*$^{-1}$

$$\text{Putting, } n = \frac{6.00 \times 10^7 \text{ erg} \times 3600 \times 10^{-8} \text{ cm}}{6.022 \times 10^{23} \text{ mol}^{-1} \times 6.626 \times 10^{-27} \text{ erg. s} \times 3 \times 10^{10} \text{ cm s}^{-1}} = 1.8044 \times 10^{-5} \text{ moles}$$

Numbers of moles of C formed = 1.00×10^{-5} *moles* ∴ Quantum yield, $'\phi' = \frac{1.00 \times 10^{-5}}{1.8044 \times 10^{-5}} = 0.554$

Practice Problem

Problem 9.17. *A certain system absorbs 3.0×10^{16} quanta of light per second. When it was irradiated for 10 minutes, it was found that 0.0002 mole of the reactant had reacted. What is the quantum yield of the reaction?* (P.U. 1996) [**Ans.** 6.691]

Problem 9.18. *In the photochemical dissociation of gaseous HI to form H_2 and I_2, it was found that the absorption of 2.36×10^2 J of radiant energy having wavelength 253.7 nm caused decomposition of 1.0×10^{-3} mole of HI. Calculate the quantum yield for the decomposition of HI.* [**Ans.** 2]

Problem 9.19. *In the photochemical reaction,*

$$CH_2ClCOOH + H_2O \xrightarrow{h\nu} CH_2OHCOOH + HCl,$$

it was found that after irradiating the solution at 253.7 nm for 837 minutes 34.36 J of energy was absorbed and 2.296×10^{-5} mol of HCl were formed. Calculate the quantum efficiency (yield) of the reaction.

[**Ans.** 0.314]

are formed as a
(Pbi. U. 2000)

10^{-5} *moles*

$= 0.554$

When it was
the quantum
[Ans. 6.691**]**
it was found

composition
[Ans. 2**]**

s absorbed
eaction.
Ans. 0.314**]**

9.6. SOME PHOTOCHEMICAL REACTIONS AND THEIR QUANTUM YIELDS

Bodenstein studied quantum yields of a large number of photochemical reactions. The quantum yields of some important photochemical reactions alongwith effective wavelengths are given in Table 9.3.

Table 9.3 Quantum Yields of some Photochemical Reactions

Reaction	Effective wavelengths (nm)	Quantum yield (ϕ)
1. *Those for which the quantum yield is a small integer*		
$CH_3COCH_3 \rightarrow C_2H_6 + CO$	250 – 310	1
$SO_2 + Cl_2 \rightarrow SO_2Cl_2$	420	1
$H_2S \rightarrow H_2 + S$	208	1
$2Fe^{2+} + I_2 \rightarrow 2Fe^{3+} + 2I^-$	579	1
$2HBr \rightarrow H_2 + Br_2$	207 – 253	2
$2HI \rightarrow H_2 + I_2$	207 – 282	2
$3O_2 \rightarrow 2O_3$	170 – 190	3
2. *Those for which the quantum yield is very large*		
$H_2 + Cl_2 \rightarrow 2HCl$	400 – 436	10^4 to 10^6
$CO + Cl_2 \rightarrow COCl_2$	400 – 436	10^3
3. *Those for which the quantum yield is very low*		
$H_2 + Br_2 \rightarrow 2HBr$	510	0.01
$2NH_3 \rightarrow N_2 + 3H_2$	210	0.2
$CH_3CHO \rightarrow CO + CH_4$	310	0.5
$2NO_2 \rightarrow 2NO + O_2$	405	0.7

From the above table, it is evident that **the law of photochemical equivalence is strictly valid for a very few reactions only**, *i.e.*, **quantum yield is one for a very few reactions.** On the basis of their quantum yields, the photochemical reactions can be divided into three categories :

1. *Those for which quantum yield is small integer.* 2. *Those for which quantum yield is very large.* 3. *Those for which the quantum yield is very low.*

In order to explain the variation in quantum yield, Bodenstein pointed out that photochemical reactions involve two distinct processes ; *i.e.*, primary process and a secondary process.

PRIMARY PROCESS IN PHOTOCHEMICAL REACTIONS

The first step in a photochemical reaction is the absorption of a quantum of radiation by the molecule giving rise to the formation of an excited atom or an excited molecule, as the case may be. Thus

$$\underset{\text{Atom or molecule}}{A} + \underset{\text{One quantum of light}}{h\nu} \longrightarrow \underset{\text{Excited atom or excited molecule}}{A^*}$$

This absorption of radiation by an atom or molecule to form an excited atom or excited molecule is known as primary process in photochemistry. The excited atom or molecule formed by the absorption may then behave in different ways. There are four distinct possibilities of excitation of the molecule as shown in Fig. 9.5.

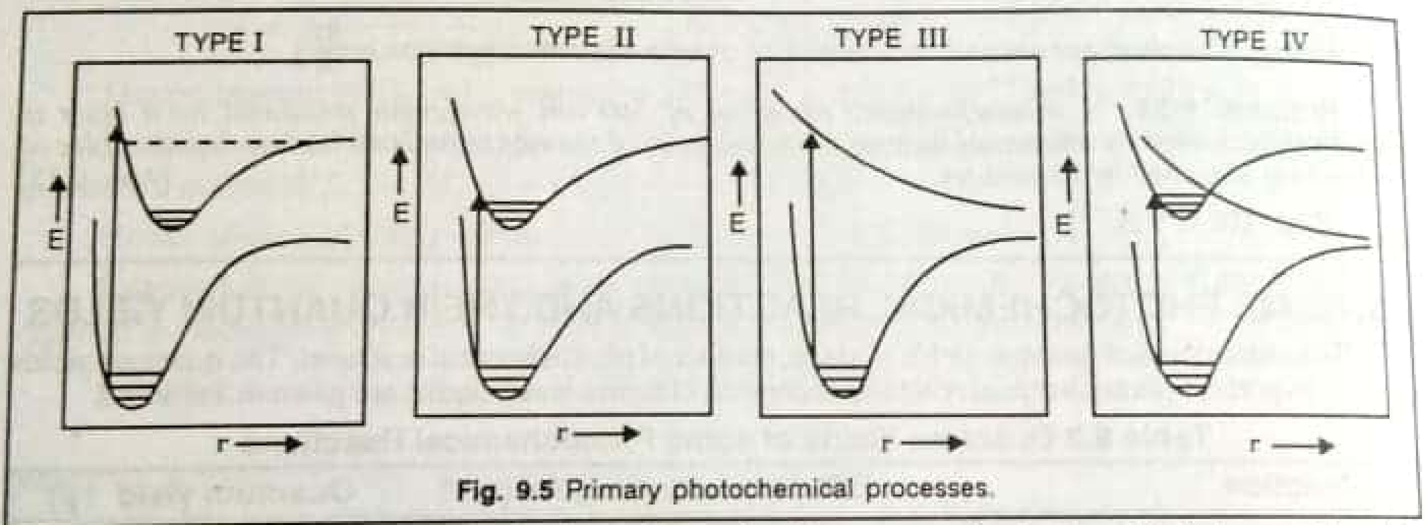


Fig. 9.5 Primary photochemical processes.

(*i*) **In type I,** energy absorbed raises the molecule to an excited state which is unstable. The molecule breaks up into atoms or radicals immediately on absorption of photon, *i.e.*, **dissociation** of the molecule takes place. The fragments obtained are associated with different kinetic energy and a continuous spectrum is obtained without any fine structure.

(*ii*) **In type II,** the electronic transition is from a stable ground state to stable excited state. There will be no direct dissociation of the molecule. This is indicated by the corresponding spectrum consisting of discontinuous bands with a fine structure.

(*iii*) **In type III,** the molecule is raised to a higher level. The energy acquired is more than the binding energy. Therefore, molecule would undergo dissociation and the spectrum will be continuous throughout.

(*iv*) **In type IV,** transition occurs from the lower level to a stable upper level. During the course of vibration, the molecule may shift from stable to the unstable state. When a shift of this type takes place, the molecule would dissociate producing atoms or radicals. This type of behaviour is referred to as **predissociation.** The spectrum would show fine structure. In the region of pre-dissociation, the rotational lines are absent and the rotational bands have a diffused appearance.

SECONDARY PHOTOCHEMICAL PROCESS

The activated molecules or the products of primary process may react with other molecules to form products or the activated molecules may emit the radiation of either the same or of different frequency. These processes are known as secondary processes.

In the light of above discussion, mechanism of some important photochemical reactions is given next page :

1. Kinetics and Mechanism of Photochemical decomposition of hydrogen iodide in the gaseous phase (Photolysis of hydrogen iodide). On exposure to radiations having wavelength in the range 207-253 nm, the decomposition of hydrogen iodide takes place. The quantum yield of the reaction is 2. This has been explained with the help of mechanism given below :

(*a*) *Primary Process* :

(*i*) $HI \xrightarrow{h\nu} \dot{H} + \dot{I}$

(*b*) *Secondary Process* :

(*ii*) $\dot{H} + HI \longrightarrow H_2 + \dot{I}$ (*iii*) $\dot{I} + \dot{I} \longrightarrow I_2$

Possibility of other secondary processes such as

(*iv*) $I + HI \longrightarrow I_2 + H$ (*v*) $\dot{H} + \dot{H} \longrightarrow H_2$ (*vi*) $\dot{I} + \dot{H} \longrightarrow HI$

is ruled out because the reaction (*iv*) is endothermic and takes place slowly and reactions (*v*) and (*vi*) are highly exothermic. The heat produced results into the dissociation of the products of these reactions. The overall reaction is, therefore, obtained by adding reactions (*i*), (*ii*) and (*iii*).

$$2\,HI + h\nu \longrightarrow H_2 + I_2$$

Thus, for every one quantum of light absorbed, two molecules of HI are decomposed. Hence the quantum yield of reaction is 2. It may be noted that while adding the equation (*i*), (*ii*) and (*iii*), no distinction has been made between the excited iodine atom and normal iodine atom.

The quantum yield for the photochemical decomposition of HBr is also 2 which suggests that the mechanism of this reaction is exactly similar to that of photolysis of HI as discussed above.

2. Photochemical combination of hydrogen and bromine to form HBr. When a mixture of hydrogen and bromine is exposed to radiations having 450–550 nm, they combine to form hydrobromic acid and the reaction may be represented as :

$$H_2 + Br_2 \longrightarrow 2HBr$$

The quantum yield of the reaction is very low, *i.e.*, 0.01. The low quantum yield may be explained by the mechanism given below :

(*a*) *Primary Process.* Bromine absorbs light in the green region of the spectrum (450 – 550 nm) and molecule dissociates into atoms :

(*i*) $Br_2 + h\nu \longrightarrow 2\,Br$

(*b*) *Secondary Processes*

(*ii*) $\dot{B}r + H_2 \xrightarrow{\text{Endo}} HBr + \dot{H}$ (*iii*) $\dot{H} + Br_2 \longrightarrow HBr + \dot{B}r$

(*iv*) $\dot{H} + HBr \longrightarrow H_2 + \dot{B}r$ (*v*) $\dot{B}r + \dot{B}r \longrightarrow Br_2$

The bromine atoms formed in primary process step (*i*) attack hydrogen molecule yielding hydrogen bromide and a hydrogen atom. The hydrogen atom then attacks bromine forming another molecule of hydrogen bromide and another bromine atom. As a result, reactions (*ii*) and (*iii*) should repeat over and again, *i.e.*, a chain reaction should be set up and the quantum yield of the reaction should be very high. However, in actual practice, the quantum yield is very low. This is explained as follows :

The step (*ii*) is highly endothermic and requires high energy of activation. This step is, therefore, very slow at ordinary temperatures. The step (*iii*) which depends upon step (*ii*), therefore, is also slow. Step (*iv*) which is the reverse of step (*ii*) becomes increasingly important and the rate of formation of HBr decreases. The step (*v*) is the only important secondary process in which the bromine atoms recombine to form Br_2 molecules readily. It is just the reversal of primary process. As a result, the quantum yield of the reaction is very low at ordinary temperatures.

The quantum yield of the photochemical combination of hydrogen and bromine increases with increase in temperature. This is because the reaction (*ii*) is endothermic and requires high energy of activation. On increasing temperature, the required energy of activation becomes available in the form of heat. Hence, the reaction becomes faster at high temperatures.

3. Photolysis of Ammonia. The photochemical decomposition of ammonia vapours has been found to take place by radiations of wavelength 210 nm. Its quantum yield is about 0.2 at ordinary temperatures and pressures. This can be explained with the help of mechanism given below :

(*a*) **Primary Process.**

(*i*) $NH_3 + h\nu \longrightarrow NH_2 + H$

(*b*) **Secondary Processes.** Since the final products of the photolysis of ammonia have been found to be nitrogen, hydrogen and hydrazine, the probable secondary processes are represented by the following equations :

(*ii*) $NH_2 + NH_2 \longrightarrow N_2 + 2H_2$

(*iii*) $\dot{N}H_2 + \dot{N}H_2 \longrightarrow N_2H_4$ (Hydrazine)

(*iv*) $\dot{H} + \dot{H} \longrightarrow H_2$

(*v*) $\dot{N}H_2 + \dot{H} \longrightarrow NH_3$.

The low observed quantum yield may be due to the fact that products of the primary process, *i.e.*, NH_2 and H recombine to form ammonia.

4. The hydrogen-chlorine reaction. When a mixture of hydrogen and chlorine is exposed to visible or ultra-violet light of wavelength less than 480 nm ($\sim$ 406 nm), a fast reaction takes place resulting in the formation of hydrogen chloride. The quantum yield of the reaction is exceptionally high (10^4 to 10^6). The presence of oxygen slows down the rate of the reaction and lowers the quantum yield also.

The extremely high quantum yield can be explained by the chain mechanism proposed by Nernst in 1918. The different steps involved are as follows :

(*a*) **Primary process.** According to Nernst's mechanism, the primary process is the dissociation of chlorine molecules into atoms as a result of absorption of light. Thus

(*i*) $Cl_2 + h\nu \longrightarrow \dot{C}l + \dot{C}l$] Chain initiating step

(*b*) **Secondary processes :**

(*ii*) $\dot{C}l + H_2 \xrightarrow{\text{Exo}} HCl + \dot{H}$]

(*iii*) $\dot{H} + Cl_2 \longrightarrow HCl + \dot{C}l$] Chain propagating Steps

(*iv*) $\dot{H} + HCl \longrightarrow H_2 + \dot{C}l$

(*v*) $\dot{C}l + \dot{C}l \longrightarrow Cl_2$] Chain terminating step

The steps (*ii*), (*iii*) and (*iv*) get repeated giving rise to a **chain reaction.** According to the mechanism proposed above, there is possibility of the formation of an infinite number of molecules of HCl due to the absorption of a single quantum of radiation. The reaction stops when the Cl atoms left off combine with each other to form Cl_2 according to the step (*v*). This reaction takes place on the walls of the reaction vessel.

The primary process in hydrogen-chlorine reaction is called *chain initating step.* The reactions (*ii*), (*iii*) and (*iv*) are called chain *propagating steps* and the reaction (*v*) is called *chain terminating step.*

The reason for the high quantum yield is that the steps (*ii*) and (*iii*) are repeated a large number of times before the chain termination.

It is important to note that the quantum yield in the combination reaction of hydrogen with bromine is very low as compared to hydrogen-chlorine although the same mechanism was proposed for the combination of hydrogen and bromine to form gaseous hydrogen bromide. The reason for the difference in the quantum efficiency is that while the reaction between chlorine atom and hydrogen molecule immediately following primary process is exothermic and takes place readily whereas the corresponding reaction in hydrogen-bromine reaction is highly endothermic and, therefore, extremely slow at ordinary temperatures.

As already mentioned, the quantum yield of the reaction between hydrogen and chlorine decreases in presence of a small amount of oxygen. This is because in presence of O_2, the chain may be terminated by the reaction

$$\dot{H} + O_2 \longrightarrow \underset{\text{(radical)}}{H\dot{O}_2}$$

Substances like O_2 which reduce the quantum yield of photochemical reactions are called **photo-inhibitors.**

The chain mechanism for the photochemical combination of hydrogen and chlorine is supported by the following fact :

(i) The combination of hydrogen and chlorine can be brought about even in absence of light by introducing either hydrogen or chlorine atoms into the reaction vessel.

(iii) The quantum yield of the reaction, decreases considerably if the reaction is allowed to take place in capillary tubes. This confirms the view that the chain is terminated at the walls of the containing vessel.

5. Photolysis of acetadehyde. When acetaldehyde is exposed to ultraviolet radiations having wavelengths less than 300 nm, it is first excited to a higher quantum level and then it breaks up into radicals which start chain reaction. The various steps involved are :

(*a*) Primary process :

(*i*) $CH_3CHO + h\nu \longrightarrow \dot{C}H_3 + \dot{C}HO$

(*b*) Secondary processes :

(*ii*) $\dot{C}H_3 + CH_3CHO \longrightarrow CH_4 + CH_3\dot{C}O$ (*iii*) $CH_3\dot{C}O \longrightarrow CO + \dot{C}H_3$

(*iv*) $\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6$

Quantum yield is about 300 at 373 K indicating that the reaction is chain reaction.

6. Photolysis of acetone

$$\underset{\text{(gas phase)}}{CH_3COCH_3} \xrightarrow[373\text{ K}]{h\nu\ (\lambda = 253.7\text{ nm})} \dot{C}H_3 + CH_3\dot{C}O$$

$$CH_3\dot{C}O \longrightarrow \dot{C}H_3 + CO \ ; \quad \dot{C}H_3 + CH_3COCH_3 \longrightarrow CH_4 + \dot{C}H_2COCH_3$$

$$2\,\dot{C}H_3 \longrightarrow C_2H_6$$

9.7. PHOTOCHEMICAL EQUILIBRIUM OR PHOTOSTATIONARY STATE

In certain cases a photochemical reaction is followed by another photochemical or a thermal reaction in the backward direction. The rate of photochemical reaction is proportional to the intensity of light radiation and that of the thermal reaction is proportional to the concentration of photochemical product. Suppose a substance A changes to B by a photochemical process and then B again changes to A by a *photochemical process,* the situation may be represented as :

$$A \underset{\text{Light}}{\overset{\text{Light}}{\rightleftharpoons}} B$$

Now if A changes to B by a *photochemical process* and B changes to A by a *thermal process (dark reaction),* then the situation may be represented as :

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

In either case, the rate of forward reaction will become equal to the rate of backward reaction after some time and the absorption of light after this will produce no further chemical change. At this stage, the reaction is said to have attained a **photochemical equilibrium** or a **photo- stationary state.** Some examples of reactions involving photochemical equilibrium are :

(*i*) Photochemical decomposition of sulphur trioxide

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

(*iii*) **Dimerization of anthracene.** Anthracene dimerizes when its solution in benzene or toluene is exposed to ultraviolet light. In the dark, the reverse thermal reaction takes place

$$\underset{\text{Anthracene}}{2C_{14}H_{10}} \underset{\text{Dark}}{\overset{\text{u . v . light}}{\rightleftharpoons}} \underset{\text{Dianthracene}}{C_{28}H_{20}}$$

The proposed mechanism for the photochemical dimerization is as follows :

Primary process $\underset{\text{Anthracene}}{C_{14}H_{10}} + h\nu \longrightarrow \underset{\text{Excited molecule}}{C_{14}H_{10}^*}$

Secondary process

$$C_{14}H_{10}^* + C_{14}H_{10} \longrightarrow C_{28}H_{20}$$

The quantum yield, according to the above mechanism, should be 2. However, actually it is only about 0.5. This is due to the simultaneous occurrence of back thermal reaction.

(*iii*) **Isomeric transformation of maleic acid into fumaric acid**

$$\text{Maleic acid} \underset{\text{u . v . light}}{\overset{\text{u . v . light}}{\rightleftharpoons}} \text{Fumaric acid}$$

Equilibrium constant. The equilibrium constant of a photochemical equilibrium is quite different from that of an ordinary chemical equilibrium. This is because of the fact that the rate of a photochemical reaction depends upon the intensity of the light absorbed instead of the concentration of the reactants. Thus for the reaction :

$$A \underset{\text{thermal}}{\overset{\text{Light}}{\rightleftharpoons}} B$$

Rate of forward reaction $= k_1 \, I_{abs}$, where k_1 is the rate constant of photochemical reaction and I_{abs} is the intensity of absorbed radiation.

Rate of backward reaction $= k_2 \, [B]$, where k_2 is the rate constant of thermal reaction and [B] is the concentration of photo-chemical product.

when the reaction is in equilibrium, $r_f = r_b$, *i.e.*, $k_1 \, I_{abs} = k_2 \, [B]$ ...(1)

or $\dfrac{k_2}{k_1} = \dfrac{I_{abs}}{[B]}$ ...(2) or $K = \dfrac{I_{abs}}{[B]}$ ...(3)

where K is the **photochemical equilibrium constant.**

From equation (3), $[B] = \dfrac{k_1}{k_2} \cdot I_{abs}$

i.e., **the concentration of the product formed at the equilibrium state is directly proportional to the intensity of light absorbed.**

9.8. LUMINESCENCE

Usual methods of obtaining light involve the heating of solids or solid particles to sufficiently high temperatures. For example, by heating a tungsten, platinum or a carbon filament electrically or in flame, bright light can be obtained. *The process in which thermal energy is converted into light energy is called* **incandescence.** If, however, light is produced by processes other than involving heating, such light is called **luminescence light or cold light.**

When the emission of visible radiation occurs due to a cause other than the action of heat, the phenomenon is known as luminescence. *The body emitting the cold light is called* luminescent.

In luminscence as well incandescence, emission of light occurs due to the return of electrons from excited outer position to lesser excitation position or ground state. Luminescence is of the following types :

1. Chemiluminescence . In photochemical reactions, light is absorbed. However, there are certain chemical reactions in which light is emitted. Such reactions produce products in excited electronic states, which then decay with the emission of light. **The phenomenon of emission of light in a chemical reaction is called chemiluminescence.** The process of chemiluminescence is shown as :

$$X \rightarrow Y^{*} \longrightarrow Y + h\nu$$

In a way, this is the reverse of photochemical reaction. Since the above process may take place at ordinary temperature, the emitted light is called **"cold light"**. Some important examples of chemiluminescent reactions are :

(*i*) The greenish glow of slowly oxidising yellow phosphorus to give P_2O_5 at ordinary temperatures (– 10 to 40°C).

(*ii*) The greenish blue glow of aerial oxidation of a solution of magnesium parabromophenyl bromide in ether.

(*iii*) The bright light green glow seen due to oxidation of alkaline solution of luminol.

(*iv*) Electron-transfer reactions.

(*v*) Oxidation-reduction reactions of hydrazine.

(*vi*) Reaction between alkaline solutions of H_2O_2 and either Cl_2 or hypochlorite ion which produces a red glow at a number of wave lengths.

(*vii*) Oxidation of decaying wood containing certain forms of bacteria.

(*viii*) The light emitted by the **firefly** and many deep-sea fish.

The cold light emission by glow worms (firefly) is an example of bioluminescent reaction involving the oxidation of **luciferon** – a protein, by atomospheric oxygen in the presence of an enzyme called **luciferase** which acts as a catalyst.

2. Fluorescene. When atoms of an element or molecules of a substance are exposed to radiation of short wavelength (high frequency) they are excited to higher electronic states. An electronically excited atom or molecule has a life period of about $10^{-7} - 10^{-8}$ sec. If during this brief period no collision occurs between excited particles, the excited particles may lose a part or all of extra energy in the form of radiations. **Instantaneous emission of radiation by an excited atom or molecule is called fluorescence and the substances which absorb radiation and then immediately re-emit the energy in the form of radiation are called fluorescent substances.**

It may be noted that fluorescence starts as soon as the substance is exposed to light and the fluorescence has a lower frequency than the incident radiation. This is explained by assuming that the absorbing molecules initially in their lowest vibrational energy levels may acquire higher vibrational energy. Atoms because of the absence of vibrational energy, emit radiation of exactly the same frequency as the frequency of radiation absorbed. **This phenomenon in which the emitted radiation has the same wavelength as that of the absorbed light is known as resonance fluorescence**: An example of resonance fluorescence is furnished by mercury vapour exposed to radiations having wavelength 253.7 nm. In rare cases, the frequency of the emitted radiation may be greater than the frequency of radiation absorbed. This is explained by assuming that some kinetic energy has been converted into vibrational energy and has been radiated along with the excitation energy of the atom.

When a photochemically excited atom collides with another atom or molecule before it has a chance to fluoresce, the intensity of fluorescent radiation is diminished. This is known as quenching of fluorescence and is due to the transfer of energy from the excited atom to the colliding atom.

Examples of Fluorescence. A few examples of the substances showing the fluorescence are:

(*i*) Certain organic dyes such as eosin, fluorescein etc. when their solutions are placed in light, they show fluorescence from green to violet colour.

(*ii*) Petroleum
(*iii*) Chlorophyll
(*iv*) Fluorite, CaF_2
(*v*) uranyl sulphate, UO_2SO_4
(*iv*) Vapours of mercury
(*vii*) Ultramarines.

Applications of Fluorescence. The phenomenon of fluorescence has a number of applications as described below :

(i) the intense green fluorescence of aqueous fluorescein solution is used to detect leaks by adding it to water systems.

(ii) Small quantities of optical brightners are added to detergents and are retained by the fabric during washing. In sunlight, they fluoresce blue and add brightness to the fabric after washing.

(iii) Fluorescent material dissolve in solution or in solid plastic bases is used to detect radioactive decay. This forms the basis of scintillation counters.

(iv) The three-dimensional structure of proteins can be studied by measuring the proximity of known fluorescent groups within the protein.

(v) Fluorescent tubes are used for lighting purposes.

(vi) Fluorescent microscopes and fluoroscopes are used in X-ray diagnosis for testing conditions of food stuffs and detection of ring worms.

3. Phosphorescence . As already mentioned, the fluorescence stops as soon as the external light is cut off. However, there are certain substances which continue to glow for some time, of the order of seconds or more after the source of light is removed. **This phenomenon of delayed fluorescence is called phosphorescence and the substances which exhibit phosphorescence are called phosphors or phosphorescent substances.** Phosphorescence is more intense from solids.

Some important examples of substances exhibiting phosphorescence are zinc sulphide and alkaline earth metal sulphides. A mixture of BaS or SrS containing about 2.5% NaCl or KCl and a trace of a heavy metal sulphide exhibits phosphorescence and is used to paint watch dials and electric switches etc. Further, it has been found that the fluorescent substances become phosphorescent if fixed by suitable methods. For example, many dyes (which show fluorescence) when dissolved in fused boric acid or glycerol and then cooled to a rigid mass become phosphorescent.

Difference between fluorescence and phosphorescence

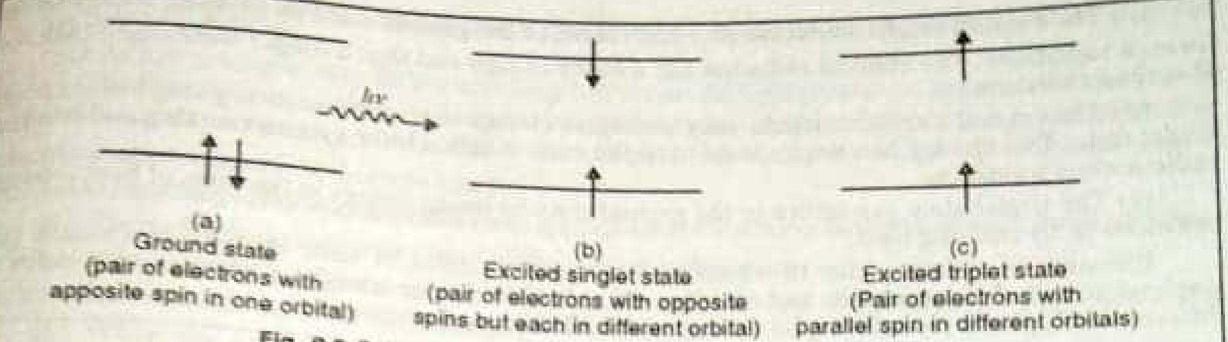
	Fluorescence		Phosphorescence
1.	Emission of radiation is rapid (decay time 10^{-6} to 10^{-8} s)	1.	Emission of radiation takes place slowly (decay time 10^{-4} to 100 s).
2.	It is the radiation emitted when transition between two states of same multiplicity takes place.	2.	It is the radiation emitted when transition between two states of different multiplicity takes place.
3.	It can be observed in solutions at room temperature.	3.	It is not observed in solutions at room temperature.

9.9. FLUORESCENCE AND PHOSPHORESCENCE IN TERMS OF EXCITATION OF ELECTRONS (JABLONSKI DIAGRAM)

When energy in the form of light radiations falls on certain molecules, some of the electrons present in them absorb energy and jump to the outer orbitals. The molecules are then said to be in the **excited state.** Most of the excited states have life times which are generally less than 10^{-6} second. They may either undergo a chemical change or return to the ground state.

Molecules may exist in several different excited states. The excitation of an electron involves absorption of photons. Most molecules have an even number of electrons and thus in the ground state, all the electrons are spin paired. The quantity 2S + 1, where S is the total electron spin, is known as the **spin multiplicity** of a state. *States in which the electrons are paired so that the total spin angular momentum (S) is zero* (Fig. 9.6 (*a*)] *and* $\left(s_1 = +\frac{1}{2}, s_2 = -\frac{1}{2} \text{ so that } S = s_1 + s_2 = \frac{1}{2} - \frac{1}{2} = 0\right)$ multiplicity (2S + 1) is unity are called **singlet ground states.**

When one of the paired electrons in the ground state absorbs a photon of suitable energy *hv* and goes to a higher energy level (excited state), the spin orientations of the two single electrons may be either anti parallel P (Fig. 4.6 *b*) or parallel [Fig. 9.6 *c*]. If the spins are parallel then



(a)
Ground state
(pair of electrons with apposite spin in one orbital)

(b)
Excited singlet state
(pair of electrons with opposite spins but each in different orbital)

(c)
Excited triplet state
(Pair of electrons with parallel spin in different orbitals)

Fig. 9.6 Spin orientation on the absorption of a light photon.

$$S = s_1 + s_2 = \frac{1}{2} + \frac{1}{2} = 1 \text{ so that } 2S + 1 = 3$$

If the two electrons have parallel spins so that the total spin angular momentum S is unity and multiplicity (2S + 1) is three then the molecule is in the ***triplet*** *excited state.*

If, however, the spins are antiparallel, then $S = s_1 + s_2 = \frac{1}{2} - \frac{1}{2} = 0$ *so that* $2S + 1 = 1$, *the molecule is said to be in the* ***singlet*** *excited state.*

The ground electronic state of an organic molecule is generally a singlet state and the represented by S_0. When a molecule in the ground state absorbs a photon, it is raised to one of the several singlet excited states represented by S_1, S_2, S_3 as shown in Fig. 9.7. After the excitation, the two electrons which were originally in the same orbital are now in different orbitals and Pauli's exclusion principle is no longer applicable. Now the spin of one of the electrons may be inverted to produce a triplet state.

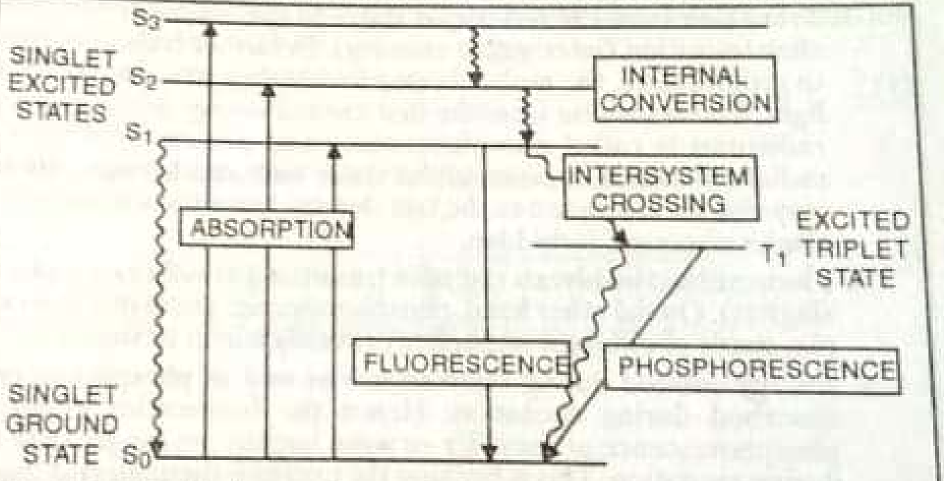


Fig. 9.7 Jablonski diagram for a molecule showing the various intramolecular processes resulting from the absorption of radiation. Wavy line (~) represents emission of energy in the form of heat.

For each singlet state there is a corresponding triplet state. For example, for singlet state S_1 there is a corresponding triplet state T_1. The energy of a triplet state is always lower than that of the corresponding single state. This is because of the fact that the electrons in the triplet state have same spin and, therefore, try to avoid each other by staying in different regions. Being far apart, electrons repel each other to lesser extent. Hence, the energy of the molecule decreases.

The excited molecules can return to the ground state by losing their excitation energy in any of the following ways :

(*a*) Excited molecules may lose the whole of excitation energy in the form of heat through collisions with other molecules so that the complete path is non-radiative.

(*b*) The excited molecules may lose a part of their excitation energy in the form of heat because of collision with other molecules. As a result, molecule moves to a electronic state having lower vibrational energy (say from S_3 to S_2 or from S_2 to S_1). This process is called **internal conversion.**

(*c*) The excited singlet molecule (S_1) can return to the ground state by emitting energy in the form of radiations. The emitted radiation has a lower energy and thus a longer wavelength than the absorbed radiation.

(*d*) The excited singlet molecule may undergo a change in spin orientation giving lower energy triplet state. This change of a singlet state to triplet state is called **inter-system crossing** and involves radiationless transition.

(*e*) The triplet state can return to the ground state by losing energy in the form of heat through collisions or by emitting light.

Emission of radiation due to transition between two states of same multiplicity (usually two singlets) is called **fluorescence** and emission of radiation due to transition between two states of different multiplicity (usually triplet to singlet) is called **phosphorescence.**

Key Facts

1. In all the steps described above, the first step is the transitions from higher excited states to the lowest excited singlet state S_1 (internal conversion).
2. The energy is lost in internal conversions only in the form of heat (shown by a wavy line in the diagram) due to the collision with other molecules. As it does not result into the emission of any radiation, it is therefore, called non-radiative or radiationless transition. It is a very fast process and occurs in less than about 10^{-11} second.
2. The molecule may lose rest of the energy in the form of heat so that the whole path is non-radiative or the molecule may release energy in the form of light or ultraviolet radiation. When the energy is lost in the form of light or *uv* radiations, the transition is a radiative transition and is called fluorescence. It occurs for about 10^{-8} second after absorption so that a substance fluoresces only in the presence of absorbed radiation.
3. Transition from excited singlet states to the excited triplet states is again a radiationless slow transition (intersystem crossing). In further transition from first excited triplet state to ground state, the molecule may lose energy either in the form of heat or in the form of light. The transition from the first excited energy to the ground state in the form of light radiations is called phosphorescence and persists even after the removal of absorbed radiation. This is because triplet states have much longer life times than singlet states. It may also be attributed to the fact that the transitions from excited triplet states to ground singlet states are forbidden.
4. Fluorescence involves a radiative transition between two states of multiplicity (usually two singlets). On the other hand, phosphorescence arises due to a radiative transistion between two states of different multiplicity (usually triplet to singlet).
5. Energy emitted during fluorescence as well as phosphorescence is less than the energy absorbed during excitation. Hence the frequencies emitted during fluorescence or phosphorescence are smaller or wave lengths are longer than those of the light absorbed during excitation. This is because the energy is dissipated as heat in the internal conversion and intersystem crossing.
6. Transitions from singlet excited states to ground state being very quick ($\approx 10^{-8}\ s$), there is no chance for a chemical reaction. However, transitions from the triplet excited states to ground state being slow, there is sufficient time available to the molecules to undergo a chemical reaction. Thus molecules undergoing chemical reaction are those which are first in the excited triplet state.

9.10. QUENCHING OF FLUORESCENCE (STERN-VOLMER EQUATION)

When a photochemically excited atom has a chance to undergo a collision with another atom or molecule before it fluoresces, the intensity of fluorescent radiation may be diminished or stopped. This process is known as quenching of fluorescence. The substances which are responsible for stopping the fluorescence are called **quenchers** and are usually represented by the symbol Q. Some facts about quenching of fluorescence are as follows :

(i) Quenching of fluorescence depends greatly on concentration of the fluorescent atom and of the quenching substance.

(ii) At low pressure, very little quenching will occur. At high pressures, appreciable quenching occurs. The fluorescence of gases and vapour is usually quenched when the total gas pressure exceeds a few millimeters of mercury, at which pressure collisions between the excited molecules and others take place at time intervals shorter than 10^{-8}

(iii) Quenching of fluorescence takes place appreciably in a liquid medium because of frequent collisions.

(iv) Quenching may occur in either of the two following ways :

(a) When the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called **internal quenching.**

(b) When the activated molecule transfers energy to the molecule with which it collids or quenching results from the presence of an externally added species (Quencher) which takes up energy from the excited state molecule. This is called **external quenching.**

Thus the various steps from activation to deactivation are as follows :

If Q is the quencher then

$$A + h\nu \longrightarrow A^* \qquad \text{(Activation)}$$

$$A^* \xrightarrow{k_1} A + h\nu \qquad \text{(Fluorescence)}$$

$$A^* \xrightarrow{k_2} A \qquad \text{(Internal quenching)}$$

$$A^* + Q \xrightarrow{k_3} A + Q' \qquad \text{(External quenching)}$$

Applying steady state principle to the concentration and remembering that the rate of reaction is directly proportional to the intensity of light, we have

$$I_a = k_1[A^*] + k_2[A^*] + k_3[A^*][Q] \qquad \text{...(1)}$$

where I_a is the intensity of light absorbed.

If I_f is the intensity of fluorescence, the quantum yield for fluoresence is givne by

$$\phi_f = \phi_Q = \frac{I_f}{I_a} = \frac{k_1[A^*]}{k_1[A^*] + k_2[A^*] + k_3[A^*][Q]} = \frac{k_1}{k_1 + k_2 + k_3 Q} \qquad \text{...(2)}$$

In the absence of quenching *i.e.* when $[Q] = 0$, the quantum yield, ϕ_0 is given by :

$$\phi_0 = \frac{k_1}{k_1 + k_2}$$

Hence the ratio of two quantum yields will be

$$\frac{\phi_0}{\phi_\theta} = \frac{k_1 + k_2 + k_3(Q)}{k_1 + k_2} = 1 + \frac{k_3}{k_1 + k_2}[Q] \qquad \text{...(4)}$$

Putting $\frac{1}{k_1 + k_2} = \Gamma$, called the life time of A^* in the absence of quencher, the equation (4) can be represented as :

$$\frac{\phi_0}{\phi_Q} = 1 + k_3\tau[Q] \quad \text{...(5)} \qquad \text{or} \qquad \frac{\phi_0}{\phi_Q} = 1 + k_{sv}[Q] \qquad \text{...(6)}$$

Equation (6) is known as the **Stern – Volmer equation** in which K_{sv} is called the **Stern – Volmer constant.** From the Stern-Volmer equation we see that ϕ_0/ϕ_Q depends linearly on [Q]. The slope of the line gives $k_3\tau$ from which Γ can be determined.

9.11. FLASH PHOTOLYSIS

In ordinary photochemical reactions, the reactants are continuously exposed to radiation of low intensity. As a result, the concentration of reactive intermediates such as free radicals is very low and their observation is difficult. In **flash photolysis,** the system is exposed to a very powerful beam of light for a very short duration, say 10^{-5} to 10^{-4} seconds. The powerful flash of light produces a much higher concentration of intermediates such as atoms or free radicals. The presence, concentration and state of these intermediates can now be ascertained by continuous observation of their absorption spectra. In certain cases, it is also possible to evaluate the rate constants of photochemical reactions involving these species.

Flash of light with energy up to 10^5 J and duration of about 10^{-4} seconds is obtained by discharging a bank of capacitors through an inert gas such as argon or krypton. However, these days laser is used for this purpose.

An example of the reaction studied by flash-photolysis is the reaction between Cl_2 and O_2. It is found that the only intermediate formed during flash photolysis is the chloromonoxy radical $C\dot{l}O$. This radical then decays to give Cl_2 and O_2 following the second order kinetics.

$$2C\dot{l}O \longrightarrow Cl_2 + O_2 \quad ; \quad -\frac{d[C\dot{l}O]}{dt} = k\,[ClO]^2$$

9.12. PHOTOSENSITIZATION-ENERGY TRANSFER PHOTOCHEMICAL REACTIONS

In some photochemical processes the reactant molecules do not absorb the radiation to which they are exposed and no reaction occurs. However, if a suitable foreign substance that absorbs radiations is added to the reaction mixture, the reaction takes place. The atoms of foreign substance absorb the radiation and pass it on to the reacting molecule and thereby imtiate the reaction. **Foreign substance which when added to a reaction mixture helps to start the photochemical reaction without undergoing any chemical change in itself is called a photosensitizer and the process is called photosensitization. Thus, a photosensitizer acts merely as carrier of energy. Commonly used photosensitizer are cadmium and mercury vapours.** Some important examples of photosensitized reactions are described below :

1. Dissociation of hydrogen molecule in presence of mercury vapour. A hydrogen molecule is unable to absorb the radiation of wavelength of 2537 Å that is emitted when an electrical discharge is passed through mercury vapour, *e.g.,* in a mercury vapour lamp. Consequently, this radiation cannot bring about dissociation of hydrogen. However, when mercury vapour is mixed with hydrogen and exposed to light from a mercury vapour lamp, the reaction is photosensitized by mercury vapour and can be presented as :

$$Hg + h\nu \rightarrow Hg^*; Hg^* + H_2 \rightarrow Hg + 2H$$

The hydrogen atom being highly reactive can easily reduce metallic oxides, carbon monoxide, etc. Dissociation of NH_3, PH_3, As H_3 and certain combination reactions such as :

$2H_2 + O_2 \rightarrow 2H_2O$; $N_2 + 3H_2 \rightarrow 2NH_3$; $3O_2 \rightarrow 2O_3$ etc. are photosensitized by mercury.

Two well known mercury photosensitized reactions involving dissociation of H_2 molecules into H-atoms are briefly described below.

(*a*) Combination between H_2 and O_2 to form H_2O and H_2O_2 :

(*i*) $Hg + h\nu \longrightarrow Hg^*$ (Activation)

(*ii*) $Hg^* + H_2 \longrightarrow Hg + 2H$ (Dissociation)

(*iii*) $H + O_2 \longrightarrow HO_2$

(*iv*) $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$

(*v*) $HO_2 + H_2 \longrightarrow H_2O_2 + H$ (resulting into a chain reaction)

Now H_2O_2 may either be isolated as such or further decomposed to form H_2O and O_2.

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

(b) Combination between CO and H_2. Photosensitized combination between CO and H_2 in presence of Hg yields **formaldehyde** and **glyoxal** in similar amounts. The quantum yield for this reaction is nearly 2 and it is believed take place as follows :

(i) $Hg + h\nu \longrightarrow Hg^*$ (Activation)

(ii) $Hg^* + H_2 \longrightarrow Hg + 2H$ (Dissociation)

(iii) $H + CO \longrightarrow HCO$

(iv) $HCO + H_2 \longrightarrow H + HCHO$ (Formaldehyde)

(v) $2HCO \longrightarrow HCHO + CO$

(vi) $2HCO \longrightarrow OHC - CHO$ (Glyoxal)

2. Photosynthesis of carbohydrates in plants. Photosynthesis is a process in which carbon dioxide and water vapour present in air combine in presence of chlorophyll (the green colouring matter of plants) and sunlight to form carbohydates.

$$CO_2 + H_2O + h\nu \xrightarrow{\text{chlorophyll}} \underset{\text{Glucose}}{\frac{1}{6} C_6H_{12}O_6} + O_2$$

Neither water nor carbon dioxide absorbs visible light radiations. However, chlorophyll-the green colouring matter absorbs over almost the whole range, and particularly in the blue-violet (470 nm) and red (650 to 700 nm) regions. Although the exact mechanism of the reaction is not certain, it is believed that the chlorophyll passes on the radiation energy absorbed by it to the carbon dioxide and water molecules which then combine to form carbohydrates. Thus **chlorophyll acts as a photosensitizer in the above reaction.**

3. Decomposition of oxalic acid in presence of uranyl ions UO_2^{2+}. As already discussed, the decomposition of oxalic acid into CO_2 and CO in presence of UO_2^{2+} ion forms the basis of the actinometer used to measure the intensity of radiation. The processes occurring are the excitation of the coloured UO_2^{2+} ion followed by transfer of energy to the colourless oxalic acid resulting in its decomposition. Thus

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

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

Thus uranyl ions, UO_2^{2+} act as photosensitizer and are used over and again.

4. Isomerization of cis-2-butene to trans-2-butene in presence of SO_2 as photosensitizer This isomerization on exposure of cis-2-butene to radiations of wave length 2573 Å in presence of SO_2 takes place as follows :

$$SO_2 \xrightarrow{h\nu} SO_2^*$$

$$\text{cis-But-2-ene} + SO_2^* \longrightarrow SO_2 + \text{cis} - \text{But} - 2 - \text{ene}^*.$$

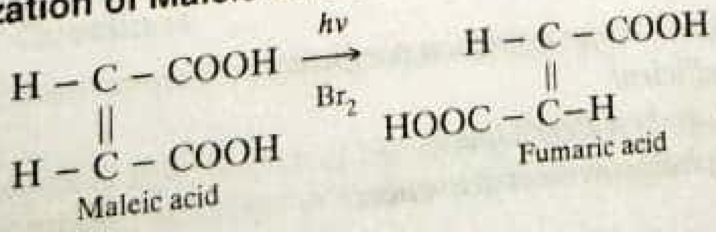
$$\text{cis-But-2-ene} \longrightarrow \text{trans}-\text{But}-2-\text{ene}^* \longrightarrow \text{trans}-\text{But}-2-\text{ene}$$

5. Decomposition of Diazomethane (CH_2N_2) in presence of Benzophenone as photosensitizer. The reaction is believed to take place as follows :

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

Benzophenone $Bz^* + CH_2N_2 \longrightarrow Bz + CH_2N_2^*$; $CH_2N_2^* \longrightarrow \underset{\text{Methylene}}{CH_2} + N_2$

6. Isomerization of Maleic acid to Fumaric acid using bromine as photosensitizer.



$$\underset{\text{Maleic acid}}{\begin{array}{c} H - C - COOH \\ \| \\ H - C - COOH \end{array}} \xrightarrow[Br_2]{h\nu} \underset{\text{Fumaric acid}}{\begin{array}{c} H - C - COOH \\ \| \\ HOOC - C - H \end{array}}$$

7. Decomposition of Ozone in presence of chlorine as photosensitizer. Decomposition of ozone under the influence of *uv* rays in presence of Cl_2 as photosensitizer is believed to follow the following mechanism :

(*i*) $Cl_2 + h\nu \longrightarrow 2Cl$ (*ii*) $Cl + O_3 + X \longrightarrow ClO_3^{\bullet} + X$

where X is any molecule capable of absorbing energy and then transferring it to the reactants.

The excited $ClO_3^{\bullet}$ radical may be absorbed on the walls of the containing vessel to form a mixture of Cl_2O_6, Cl_2 and O_2.

(*iii*) $ClO_3^{\bullet} + ClO_3^{\bullet} + M \longrightarrow Cl_2 + 3O_2 + M$

In addition to the above reactions, $ClO_3^{\bullet}$ in the gas phase may react to form ClO_2 and O_2

(*iv*) $ClO_3^{\bullet} + O_3 \longrightarrow ClO_2 + 2O_2$ (*v*) $ClO_2 + O_3 \longrightarrow ClO_3 + O_2$

The above mechanism is supported by the fact that in presence of moisture, acids $HClO_3$ and $HClO_4$ are found in the products. Also the polymer Cl_2O_6 has been isolated and identified.

8. Application of photosensitization in photography. A photographic plate coated with a simple emulsion of gelatin and silver bromide is sensitive only to the blue or blue-violet part of electromagnetic spectrum. However, it can be made sensitive even to green, yellow and orange light by the addition of suitable dyes. For example, a plate dyed yellow with aniline becomes sensitive to green, yellow and orange light. The dye linocyanol sensitizes the photographic plate to the red light while neocyanin sensitizes the photographic plates even to the infrared radiations. Photographic emulsions which are sensitive to the near infrared-radiations have made night photography possible.

9.13. PHOTO-INHIBITORS

There are certain substances which are able to retard the rate of a photochemical reaction when present in the reaction mixture in trace amounts. **Such substances which retard the rate of photochemical reactions are called photo-inhibitors.**

Some examples are :

(*i*) In the photochemical combination of H_2 and Cl_2, the presence of traces of oxygen reduces the quantum yield of this reaction (Section 9.6, reaction 4).

(*ii*) Traces of nitric oxide and propylene lower the quantum yield of the photochemical combination of hydrogen and chlorine.

(*iii*) Traces of impurities like NH_3 which when present in the hydrogen chlorine reaction lower its quantum yield from 10^6 to 10^4.

Explanation . It is generally accepted that these substances react with chain propagating atoms or radicals resulting into the chain termination. For example, in the photochemical combination of H_2 and Cl_2, O_2 reacts with H to form HO and interrupts the chain reaction.

DESCRIPTIVE QUESTIONS

A. Very Short Answer Questions

1. *What are photochemical reactions ?*
2. *What is photochemistry ?*
3. *Name two main type of processes studied under photochemistry.*
4. *Give four important examples of photochemical reactions.*
5. *State Lambert's law.*
6. *State Lambert-Beer's law.*
7. *Define extinction coefficient and molar extinction coefficient.*
8. *Define molar absorption coefficient.*
9. *What are the limitations of Lambert-Beer's law ?*
10. *State Grottus-Draper law of photochemical activation.*