PHOTOCHEMISTRY

4.1. INTRODUCTION – INTERACTION OF RADIATION WITH MATTER

Photochemistry *is defined as that branch of chemistry which deals with the study of interaction of radiation with matter resulting into a physical change or into a chemical reaction* (*called photochemical reaction*) *whose rates and mechanisms are studied after initiation by the radiant energy.* Though 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, the radiation of photochemical importance are those which lie in the visible and ultraviolet region from 8000 – 2000 Å (800 – 200 nm).

Thus the two main processes studied under photochemistry are :

(*i*) *Photophysical processes*

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

Photophysical processes *are those processes which take place in the presence of light but do not result into any chemical reaction*. These processes arise on account of the absorption of light by the substances followed by the emission of the absorbed light. If the absorbed light is emitted *instanteously*, the process is called **fluorescence**. If the absorbed light is emitted after some *time lag*, the process is called **phosphorescence**. Further, if the energy of the light absorbed is sufficiently high, the electrons may not only jump to the outer levels but may leave the atoms completely ; the process is called **photoelectric effect**. Thus photophysical processes include phenomena like fluorescence, phosphrescence and photoelectric effect.

Photochemical reactions *are those reactions which take place by absorption of light by the reacting substances*. These reactions are generally brought about by the absorption of light radiations of the visible and ultraviolet region which lie between 8000 – 2000 Å (800-200 nm) as already mentioned above. In these cases, the light energy absorbed is stored within the substance and then used for bringing about the reaction. A large number of different types of reactions can be brought about by exposure to suitable light e.g. synthesis, decomposition, oxidation, reduction, polymerisation, isomeric change etc. Two well known **examples** of photochemical reactions are given below :

(*i*) *Combination of hydrogen and chlorine to form hydrogen chloride*

$$H_2(g) + Cl_2(g) \xrightarrow{\text{Light}} 2HCl(g)$$

(*ii*) *Photosynthesis of carbohydrates in plants taking place in presence of chlorophyll, the green colouring matter present in the leaves*

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

3.1. ELECTROMAGNETIC RADIATION

The term 'electromagnetic radiation' represents the radiant energy emitted from any source in the form of light, heat etc. Some important characteristics of these electromagnetic radiations are given below :

(*i*) They have dual character *i.e.* particle character as well as wave character. For example, a beam of light is a stream of particles called photons moving through the space in the form of waves.

(*ii*) These waves are associated with electric and magnetic fields oscillating perpendicular to each other and also perpendicular to the direction of propagation, as shown in Fig. 3.1. That is why they are called electromagnetic waves.

(*iii*) All electromagnetic radiations travel with the velocity of light, c (= $2{\cdot}998 \times 10^8$ $ms^{-1} \simeq 3 \times 10^8$ ms^{-1}).

(*iv*) The wavelength λ of the electromagnetic radiation is related to their frequency (ν) and velocity (c) according to the equation $c = \nu\lambda$ or $\lambda = c/\nu$ or $\nu = c/\lambda$. As the quantity $1/\lambda = \bar{\nu}$ is called wave number, hence $\nu = c\bar{\nu}$. It is still very common to express $\bar{\nu}$ in terms of non-SI unit, cm^{-1} when λ is in cm and c is in cm s^{-1}. Frequency ν has the units s^{-1}.

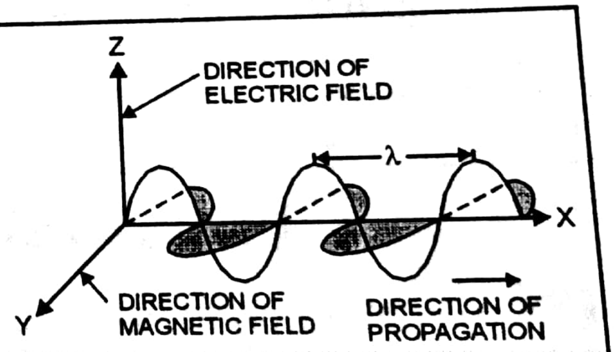


FIGURE 3.1

Electromagnetic radiation travelling in the form of waves and associated with electric and magnetic fields at right angles to each other.

(*v*) As stated earlier, electromagnetic radiations are made up of photons. Each photon is a packet of energy whose energy is given by Planck's equation viz. $E = h\nu$ where h is Planck's constant (= $6{\cdot}6262 \times 10^{-34}$ Js).

LAMBERT'S LAW :–

"When a beam of light is allowed to pass through a transparent medium, the rate of decrease of its intensity with the increase in the thickness of medium is directly proportional the intensity of incident light."

Mathematically, the Lambert's law may be stated as follows :

$$\frac{-dI}{dx} \propto I$$

or

$$\frac{-dI}{dx} = kI \qquad ...(1)$$

Here, 'dI' is the decrease in the intensity of light when it passes through small thickness 'dx' of the medium. 'I' denotes the intensity of incident light just before entering the medium of thickness dx is the thickness of medium and k is the constant of proportionality.

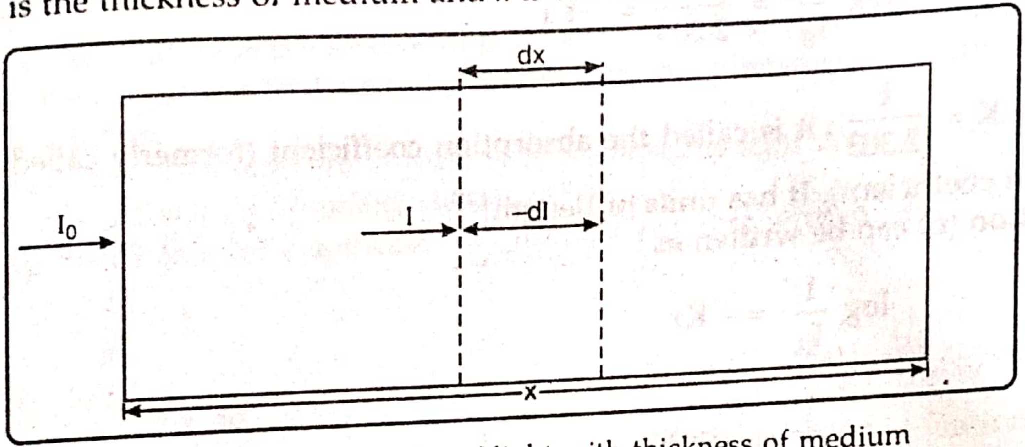


Fig. 2. Decrease in the intensity of light with thickness of medium

The intensity (I) at any point in the medium can be found as follows :

Equation (1) can be written as :

$$\frac{dI}{I} = -k\,dx \qquad ...(2)$$

At $x = x_0$, $I = I_0$

and at $x = x$, $I = I$

On integrating equation (2) between the limits of thickness of medium $x = 0$ to x and $I = I_0$ to I we get equation (3).

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

$$-[\ln I]_{I_0}^{I} = k[x]_0^x$$

$$-[\ln I - \ln I_0] = k[x-0]$$

$$\ln\frac{I}{I_0} = -kx$$

or

$$\frac{I}{I_0} = e^{-kx}$$

or

$$I = I_0\, e^{-kx} \qquad ...(4)$$

where I_0 is the intensity of incident light, I is the intensity of transmitted light, k is a constant which depends upon the wavelength (λ) of light used and nature of the absorbing medium used.

Equation (4) shows how the intensity of incident light I_0 is reduced to intensity I after passing through a medium of thickness x. The difference between I_0 and I gives the intensity of light absorbed.

$$\therefore \qquad I_a = I_0 - I$$

or

$$I_a = I_0 - I_0\, e^{-kx} \qquad \ldots(5)$$

Equation (4) can be written in another form, which is derived as follows :

On changing equation (3) in terms of logarithm, we get :

$$2.303 \log \frac{I}{I_0} = -kx$$

or

$$\log \frac{I}{I_0} = \frac{-kx}{2.303} = -Kx \qquad \ldots(6)$$

where $K = \frac{k}{2.303}$; it is called the absorption coefficient (formerly called absorptivity or extinction coefficient). It has units of $[\text{length}]^{-1}$.

Equation (6) can be written as :

$$\log \frac{I}{I_0} = -Kx$$

or

$$\frac{I}{I_0} = 10^{-Kx}$$

$$I = I_0 \times 10^{-Kx} \qquad \ldots(7)$$

Lambert's law is very rigid and like Faraday's laws of electrolysis, it has no exception.

Physical significance of absorption coefficient 'K'

Equation (6) can be written as

$$K = -\frac{1}{x} \log \frac{I}{I_0}$$

$$= \frac{1}{x} \log \frac{I_0}{I}$$

If $\log \frac{I_0}{I} = 1$ then $K = \frac{1}{x}$

thus, $I = \frac{1}{10} I_0 \quad \left[\log \frac{I_0}{I} = 1, \text{ implies } \frac{I_0}{I} = 10 \text{ or } I = \frac{1}{10} I_0\right]$

According to Lambert's law, basic terminology of photo processes is given as follows :

(a) Transmittance. It is defined as the fraction of incident light transmitted by medium of thickness x. It is denoted by 'T'. Mathematically, the equation for transmittance can be given as

$$T = \frac{I}{I_0}$$

[where, I = Intensity of transmittted light

I_0 = Intensity of absorbed light.

(b) Absorbance. The ratio $-\left(\log\frac{I}{I_0}\right)$ is termed as absorbance of the medium. It is denoted A. Formerly absorbance was termed as optical density (D) or extinction (E).

$$A = \log\frac{I_0}{I} \qquad ...(9)$$

Optical density or absorbance is the logarithmic reciprocal of transmittance.

$$D = \log\frac{1}{T} = A \qquad ...(10)$$

2. BEER'S LAW

Lambert's law shows that there is a relationship between the transmittance 'T' and thickness of the medium. Beer observed that a similar relationship hold between transmittance and centration of a solution.

Beer's law states that, *"the intensity of beam of monochromatic light decreases exponentially h the increase in concentration of absorbing substance."*

Mathematically, Beer's law for a solution of concentration 'c' is written as;

$$-\frac{dI}{dx} \propto Ic$$

or

$$-\frac{dI}{dx} = k'\,Ic \qquad ...(1)$$

where k' is the constant of proportionality. Applying variable separable to equation (1), we ay write :

$$\frac{dI}{I} = -k'\,c\,dx \qquad ...(2)$$

On integrating the equation (2) between the limits $x = 0$ to x and $I = I_0$ to I, we have uation (3)

$$\int_{I_0}^{I}\frac{dI}{I} = -\int_0^x k'c\,dx \qquad ...(3)$$

$$-[\ln I]_{I_0}^{I} = k'\,[x]_0^x\,c$$

$$-[\ln I - \ln I_0] = k'\,[x-0]c$$

or

$$\ln\frac{I}{I_0} = -k'xc \qquad ...(4)$$

or

$$\frac{I}{I_0} = e^{-k'xc} \qquad ...(5)$$

or

$$I = I_0\,e^{-k'xc}$$

Equation (5) shows how the intensity of incident light (I_0) is reduced (to I) after passing rough a solution of concentration 'c' and thickness 'x'.

The difference between I_0 and I gives the intensity of the light absorbed

$$I_a = I_0 - I$$

or

$$I_a = I_0 - I_0\,e^{-k'xc}$$

Equation (4) can be written in another form, which can be derived by change in logarithmic ections as follows :

$$2.303 \log \frac{I}{I_0} = -k'xc$$

or $$\log \frac{I}{I_0} = \frac{-k'}{2.303} xc = -K'xc \qquad \text{...(6)}$$

where $K' = \frac{k'}{2.303}$; it is called molar absorption coefficient (formerly called molar extinction coefficient or molar absorptivity). Its units are [concentration] $[\text{length}]^{-1}$

Equation (6) can be written as

$$\log \frac{I}{I_0} = -K'xc$$

or $$\frac{I}{I_0} = 10^{-K'xc}$$

or $$I = I_0 \times 10^{-K'xc} \qquad \text{...(7)}$$

A plot of '$-\log \frac{I}{I_0}$' Vs 'c' is a straight line passing through origin, having slope $= K'x$.

It is clear from figure (3) that at higher concentration a dotted curve is obtained instead of a straight line. Thus, this curve shows the deviation of Beer's law at high concentration of the solution used.

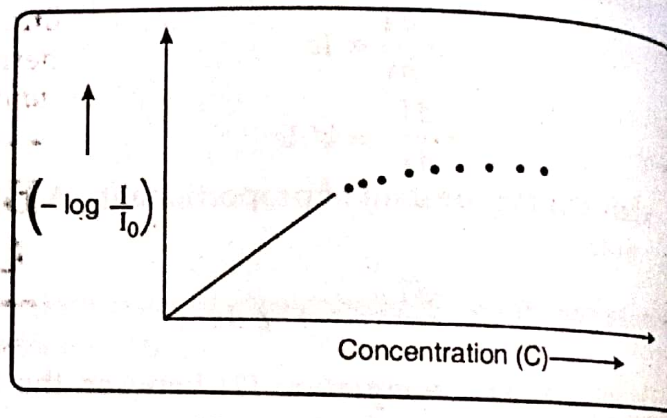


Fig. 3. Plot of absorbance Vs. concentration of solution.

Limitations of Beer's law

1. This law holds good only for light of single wavelength (i.e., monochromatic radiation).

2. The law is applicable to dilute solutions only as deviations are observed for solutions of high concentration.

Physical significance of Molar Absorption coefficient 'K'

The formal equation of Lambert-Beer's law can be given as :

$$\log \frac{I}{I_0} = -K'xc$$

or $$K' = -\frac{1}{xc} \log \frac{I}{I_0} \quad \text{or} \quad K' = \frac{1}{xc} \log \frac{I}{I_0}$$

If $\log \frac{I_0}{I} = 1$ and concentration, $c = 1$ M

$$\text{Then } K' = \frac{1}{x}$$

Also, $$\log \frac{I_0}{I} = 1 \text{ implies } \frac{I_0}{I} = 10$$

or $$I = \frac{1}{10} I_0$$

Therefore the **molar absorption coefficient** may be defined as, *"the reciprocal of the thickness solution of one molar concentration which is required to reduce the light of* $\frac{1}{10}$*th of its intensity."*

According to Lambert-Beer's law :

(a) **Transmittance 'T'** is given as :

$$T = \frac{I}{I_0} \qquad ...(8)$$

(b) **Absorbance 'A'** is given as :

$$A = K'cx = -\log\frac{I}{I_0} = -\log T \qquad ...(9)$$

Equation (9) may also be written as :

$$K' = \frac{A}{cx}$$

If $c = 1M$ and $x = 1$ cm, then $\mathbf{K' = A}$ ...(10)

From equation (10) it follows that the molar absorption coefficient is the specific absorption coefficient for a concentration of one mole per litre and a path length of one centimeter.

Hence, **specific absorption coefficient** (formerly called specific extinction coefficient) is defined as, *"the absorbance per unit thickness and unit concentration."*

3.3. LAWS OF PHOTOCHEMISTRY

There are basically two laws that govern the effect of radiation on a particular chemical reaction. These laws are : (1) Grothus-Draper law.
(2) Law of photochemical equivalence.

1. **Grothus-Draper law.** This law is also said to be **"the first law of photochemistry."** It was theoretically given by Grothos in 1818 and proved experimentally by Draper in 1841. It is stated as follows :

"When light falls on any substance, only that fraction of incident light which is **absorbed** *by the substance can bring about a chemical change; reflected and transmitted light do not produce any such ffect."*

It is important to note that all the absorbed radiation may not necessarily bring about a photochemical reaction.

When conditions are not favourable for a reaction, the absorbed light is converted into heat. While in some cases, the absorbed light is re-emitted as radiation of same or different frequency. Grothus-Draper law is purely qualitative. It does not give any relationship between the amount of light absorbed by a system and the number of reacting molecules.

2. **Law of photochemical Equivalence.** This law states that, *"Each molecule which takes part in a chemical reaction absorbs one photon of light which causes the reaction."* It is also called, **"the second law of photochemistry."**

It must be recalled here that one photon (or one quantum) of light has energy equal to $h\nu$.

$$E = h\nu$$

where h is the Planck's constant and ν is the frequency of radiation

$$\underset{\text{(Reactant molecule)}}{AB} + h\nu \longrightarrow \underset{\text{(Activated reactant molecule)}}{AB^*} \qquad \text{...(1)}$$

Thus, in the primary process each molecule absorbs one photon. The energy 'E' absorbed by 1 mole of substance is given by the equation

$$E = Nh\nu = \frac{Nhc}{\lambda} \quad [\text{N = Avogadro's number}] \qquad \text{...(2)}$$

"The quantity of energy 'E' absorbed per mole of reacting substance is called an **einstein."**

According to equation (2) the value of E is inversely proportional to the wavelength of light bsorbed, *i.e.* ;

$$E \propto \frac{1}{\lambda}$$

Thus, longer the wavelength, lesser is the energy of einstein and vice-versa.

Substituting the values of N, h and C in equation (2), we get, $E = \frac{2{\cdot}86 \times 10^5}{\lambda(\text{Å})}$ k cal/mol

VALUE OF EINSTEIN (IN S.I. UNITS)

In S.I. system, $N = 6.023 \times 10^{23}\ \text{mol}^{-1}$
$h = 6.206 \times 10^{-34}$ Js
$c = 3 \times 10^{8}\ ms^{-1}$

Substituting these values in equation; $E = Nh\frac{c}{\lambda}$; we get

$$E = \frac{0.1197}{\lambda} \text{ Joule/mole} \quad [\lambda \text{ is expressed in metres}]$$
$$= 11.97 \times 10^{-5}\ \text{kJ mol}^{-1}$$

In photochemistry, energy is usually expressed in electron volts [eV]

[1ev = 96.48 k J mole^{-1}]

3.5. QUANTUM YIELD OR QUANTUM EFFICIENCY

Quantum yield (ϕ) is defined as, "*the number of molecules observed to undergo chemical reaction per photon of light absorbed.*"

Mathematically, the quantum yield is given as follows :

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

or $$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of einsteins absorbed in same time}}$$

or $$\phi = \frac{\text{Rate of chemical reaction}}{\text{Number of Einsteins absorbed}}$$

As predicted by *Stark-Einstein law* the quantum yield of a photochemical reaction should be equal to one as there is 1 : 1 relationship between the number of photons absorbed and the number of reacting molecules. However, the quantum yield of a photochemical reaction is observed to vary from 10^6 to a very small fraction of unity (0·4).

Unexpectedly, high and low values of Quantum yield is described as being in most cases, a molecule activated in the primary step of a photochemical reaction initiates a series of thermal reactions called secondary reactions. Under such conditions, there is no 1 : 1 relationship between number of photons absorbed and the number of reacting molecules. Sometimes a molecule activated in primary step may undergo deactivation, thus less than one molecule may react for absorption of every photon. Hence quantum yield is less than one. The concept of quantum yield helps us to understand the nature of secondary processes.

Note. The quantum yield is dependent on the intensity of incident light.

3.5.1 PRIMARY AND SECONDARY PROCESSES

Photochemical resctions generally involve two processes. These are known as primary process and secondary process. These can be detailed as follows :

1. Primary processes. This step of photochemical reaction follows the law of photochemical equivalance. In this step one molecule absorbs one photon of light and gets excited to a higher energy state. This can be schematically given as follows :

$$A + h\nu \longrightarrow \underset{\text{(Activated molecule)}}{[A]}$$

The activated molecule may undergo a chemical change, it may associate or dissociate itself to atoms or free radicals, it may lose its energy by collisons with other moelcules or it may undergo *phosphorescence* or *flourescence*.

2. Secondary processes. The species (atoms, molecules or free radicals) formed in the primary process may undergo further reactions which are called secondary processes.

The secondary processes may involve one or more than one step. Sometimes, the secondary process initiates a chain reaction. Such reaction may result in very high or very low quantum yields. Both the primary and secondary processes can be shown in the following example:

$$2HI \xrightarrow{\text{light}} H_2 + I_2$$

Primary Process. $HI \xrightarrow{h\nu} H + I$

Secondary Processes. $\left.\begin{array}{l} H + HI \longrightarrow H_2 + I \\ I + I \longrightarrow I_2 \end{array}\right\}$

3.6. REASONS FOR LOW AND HIGH QUANTUM YIELD

As we already know that varying quantum yields are shown by different photochemical reactions. The reason for low and high quantum yields registered can be given as follows :—

Low quantum yields. The primary photochemical processes follow Stark-Einstein law. According to this law, the quantum efficiency of primary process should be one. But in some reactions the quantum yields are reported to be low because the excited molecule may deactivate itself by any of the following ways :

(1) The activatated molecule may simply emit the absorbed radiation.

(2) The excited molecule may collide with surrounding molecules and lose energy in the form of heat.

(3) *The excited molecule may emit energy in the form of flourescence or phosphorescence.*

(4) *Excited molecule may react with other molecules producing unwanted products.*

(5) *The atoms/radicals formed in the primary step may recombine to form the original* *cules.*

(6) *The secondary process may involve a reaction which forms reactant as one of the* *ducts.*

(7) *The primary process may be reversible.*

High Quantum yields

High quantum yields are explained on the bases of reactions taking place in secondary esses. The atoms or free radicals formed in the primary process may initiate a series of in reactions. For example, a photochemical reaction between H_2 and Cl_2 to form HCl has h quantum yield of order 10^4 to 10^6.

3.7. SOME PHOTOCHEMICAL REACTIONS

A few photochemical reactions and their respective quantum yields are given in Table 1.

TABLE 1

Photochemical reactions with their quantum yields

Reaction	Wavelengths of light used (in nm)	Quantum yield (ϕ)
1. $H_2 + Br_2 \longrightarrow 2HBr$	510	0·01
2. $2NH_3 \longrightarrow N_2 + 3H_2$	210	0·25
3. $CH_3COCH_3 \longrightarrow CO + C_2H_6$	300	1
4. $2NO_2 \longrightarrow 2NO + O_2$	400	0·7
5. $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$	420	1
6. $H_2S \longrightarrow H_2 + S$	208	1
7. $2HI \longrightarrow H_2 + I_2$	207—282	2
8. $3O_2 \longrightarrow 2O_3$	170 — 190	3
9. $CO + Cl_2 \longrightarrow COCl_2$	400—436	10^3
10. $H_2 + Cl_2 \longrightarrow 2HCl$	400	$10^4 — 10^6$

It is clear from Table 1 above that very few photochemical reactions obey law of otochemical equivalance and Stark-Einstein law. Some of these reactions and their echanisms are discussed below :

1. Photolysis of Ammonia

$$2NH_3 \xrightarrow[500\text{ atm}]{160\text{-}200\text{ nm}} N_2 + 3H_2;\ \phi = 0{\cdot}25$$

Following mechanism has been suggested to explain the observed quantum yield of the ove reaction.

Primary process :

$$NH_3 + h\nu \longrightarrow NH_2 + H$$

Secondary processes :

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

(*ii*) $H + H \longrightarrow H_2$

(*iii*) $NH_2 + NH_2 \longrightarrow N_2H_4$

(*iv*) $N_2H_4 + H \longrightarrow NH_3 + NH_2$

(*v*) $NH_2 + NH_2 \longrightarrow N_2 + 3H_2$

The reactions (*ii*), (*iii*) and (*v*) occur only to a small extent.

It is clear from the steps (*i*) and (*iv*) of the secondary process that the products of secondary process (NH_2 & H) recombine to form ammonia (the starting reactant). Therefore a low quantum yield ($\phi = 0.25$) is observed for this reaction.

2. Decomposition of hydrogen iodide in the gaseous phase

$$2HI \xrightarrow{h\nu} H_2 + I_2 ; \phi = 2$$

Following mechanism has been proposed to explain the quantum yield observed i decomposition reaction of Hydrogen iodide.

Primary process. $HI \xrightarrow{h\nu} H + I$

Secondary processes

(*i*) $HI + H \longrightarrow H_2 + I$
(*ii*) $I + HI \longrightarrow I_2 + H$
(*iii*) $H + H \longrightarrow H_2$
(*iv*) $I + I \longrightarrow I_2$
(*v*) $I + H \longrightarrow HI$

In the above mentioned secondary processes, step (*iii*) and (*v*) are highly exothermic. The products formed in these steps undergo dissociation as soon as they are formed. Step (*ii*) reaction is endothermic and therefore takes place slowly. Steps (*ii*) and (*v*) contribute less towards desired product formation which leaves steps (*i*) and (*iv*) as important secondary processes.

The decomposition of HI can thus be written as :

Primary process :

$$HI \xrightarrow{h\nu} H + I$$

Secondary Process :

$$H + HI \longrightarrow H_2 + I$$
$$I + I \longrightarrow I_2$$

Adding the above three equation, we get the desired reaction as :

$$2HI \xrightarrow{h\nu} H_2 + I_2$$

Thus the absorption of one quantum of radiation leads to the decomposition of two hydrogen iodide molecules. This agrees with the observed quantum yield ($\phi = 2$).

3. The Hydrogen-Chlorine reaction

$$H_2(g) + Cl_2(g) \xrightarrow[400-460\ nm]{h\nu} 2HCl\ (g)$$

The quantum yield of this reaction is exceptionally high ($10^4 - 10^6$). Following mechanism has been proposed for this reaction.

Primary Process :

$$Cl_2 + h\nu \longrightarrow 2Cl$$

Secondary Process :

(*i*) $Cl + H_2 \longrightarrow HCl + H$ (exothermic)
(*ii*) $H + Cl_2 \longrightarrow HCl + Cl$
(*iii*) $Cl \longrightarrow \frac{1}{2}Cl_2$
(at the walls)

Reaction (*i*) takes place very *rapidly* because of its *exothermic nature*. Reaction (*ii*) depend on the ease of formation of H and hence quickly follows step (*ii*) of the secondary process

Once the reaction starts by absorption of one photon of light, a very large number hydrogen chloride molecules are formed as a result of the repitition of steps (*i*) and Therefore the quantum yield of reaction is exceptionally high (10^4 to 10^6). The chai terminated at the walls of the vessel.

The quantum yield of the reaction between hydrogen and chlorine can be reduced if small *traces of oxygen* is introduced into the reaction vessel. Oxygen reacts as :

$$O_2 + H \longrightarrow HO_2 \quad \text{...}(a)$$

$$O_2 + Cl + HCl \longrightarrow HO_2 + Cl_2 \quad \text{...}(b)$$

Thus the free radicals formed in primary and secondary processes react with oxygen causing chain termination, this way oxygen helps in reducing the quantum yield of hydrogen-chlorine reaction. *The substances which reduce the quantum yield of a photochemical reaction are called photo-inhibitors.*

4. Hydrogen-Bromine reaction

$$H_2(g) + Br_2(g) \xrightarrow{h\nu} 2HBr\ (g)\ ;\ \phi = 0{\cdot}01$$

Above reaction reports a very low quantum yield. For this following reaction mechanism is suggested.

Primary Process :

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

Secondary Process :

(*i*) $Br + H_2 \longrightarrow HBr + H$ [endothermic]
(*ii*) $H + Br_2 \longrightarrow HBr + Br$
(*iii*) $H + HBr \longrightarrow H_2 + Br$
(*iv*) $2Br \longrightarrow Br_2$

Reaction (*i*) is endothermic and thus takes place very slowly. Further, reactions (*ii*) and (*iii*) depend upon the ease of formation of 'H' in step (*i*). As reaction (*i*) is very slow therefore the following reactions (*ii*) and (*iii*) also take place slowly. Step (*iv*) of the secodnary process marks the recombining of Br-atoms to form Br_2 rather than HBr. As a result of all these secondary processes, the quantum yield of the reaction is very low at ordinary temperature. However, on increasing the temperature at which the reaction occurs, the quantum yield of reaction increases this is because at higher temperature the endothermic reaction (*i*) is favoured.

5. Dimerization of Anthracene in Benzene solution

3.8. EXPERIMENTAL DETERMINATION OF QUANTUM YIELDS

We know that; Quantum yield, $\phi = \dfrac{\text{Number of moles reacting}}{\text{Number of einsteins absorbed}}$

Therefore, experimental determination of quantum yield involves :

(*i*) Determining the number of moles of reacting substance in a given time, *i.e.*, the rate of chemical reaction.

(*ii*) Determining the number of einsteins of light absorbed by the substance in same time.

3.8.1. EXPERIMENTAL SETUP

The arrangement of apparatus used for the study of photochemical reactions is shown in figure 4 as below :

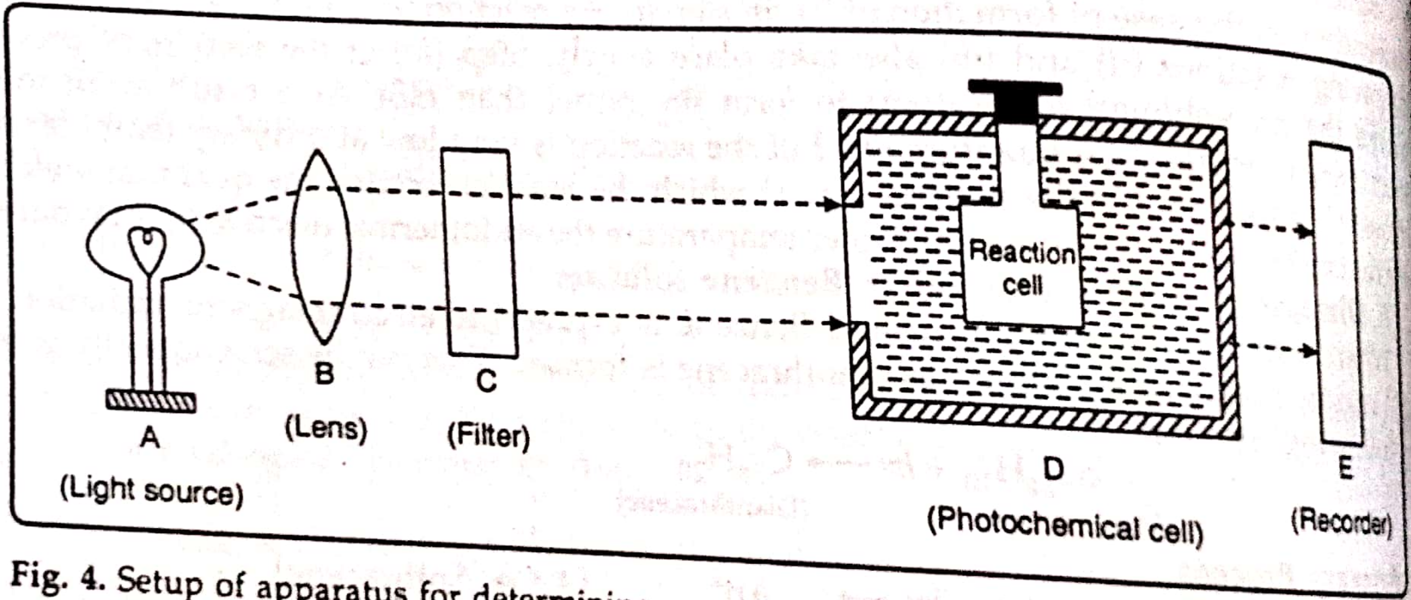


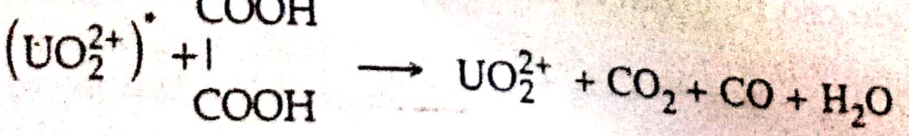
Fig. 4. Setup of apparatus for determining quantum yield of a photochemical reaction

3.8.2. DETERMINATION OF THE NUMBER OF EINSTEINS OF LIGHT ABSORBED

The number of einsteins absorbed are determined either by using a chemical actinometer or a thermopile. A **Chemical actinometer** is *used for measuring intensity of absorbed radiation for photochemical reactions of known quantum yield*. The most commonly used actinometer is uranyl oxalate actinometer. It consists of solution of 0·05 M oxalic acid and 0·01 M uranyl sulphate in water. *Uranyl Sulphate acts as a photosensitizer.*

The reaction involves decomposition of oxalic acid, sensitized by uranyl ion (UO_2^{2+}), this uranyl ion absorbs light and transfers the absorbed energy to oxalic acid. The rections involved in this process can be given as :

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



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

The amount of oxalic acid decomposed can be determined by titrating undecomposed oxalic acid against $KMnO_4$ solution.

A **thermopile** is a combination of thermocouples. It is made up of large number of junctions of two dissimilar metals (Ag and Bi) joined in series. One set of junctions is soldered to a metal strip blackened with lamp black. The other set of junctions is protected completely from the radiation by placing the system in a box. This can be described by the following figure :

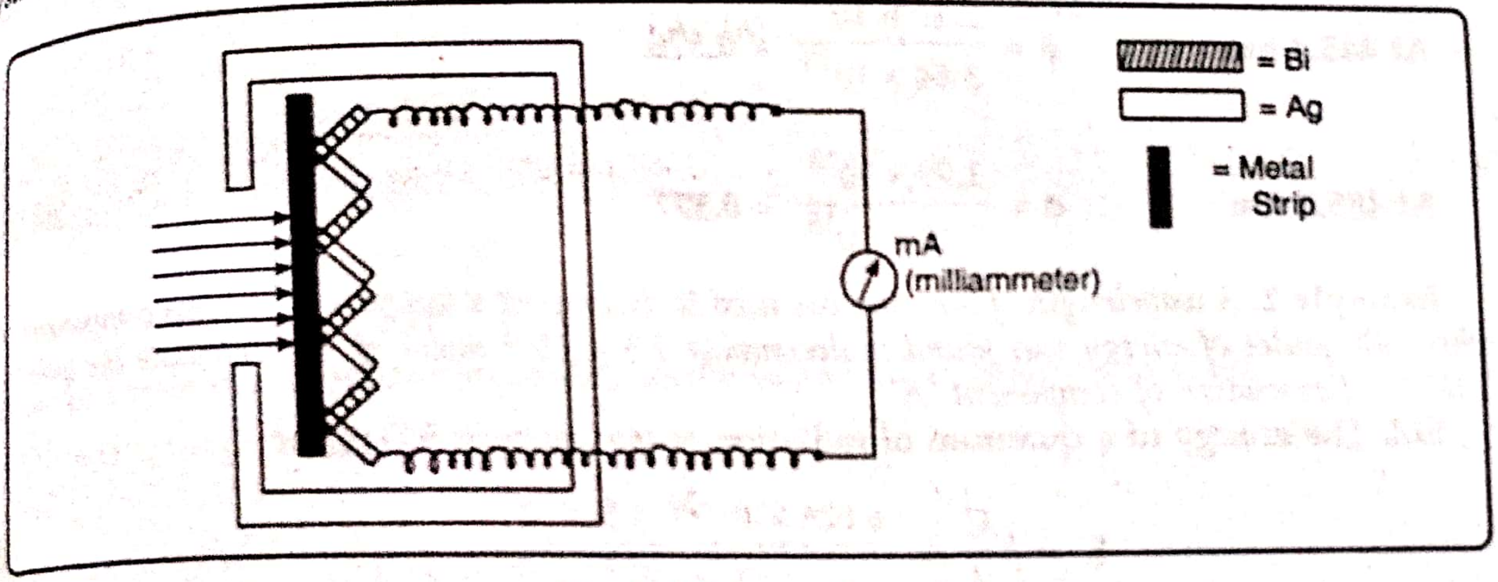


Fig. 5. A Thermopile

The radiation falling on the blackened strip are absorbed and the temperature of junction rises. The temperature difference between hot and cold ends of a junction generates a current. This current is measured by using a milliammeter (mA). The increase in the temperature is a measure of intensity of the electromagnetic radiation used. By callibrating the thermopile with radiations of known intensity, the intensity of desired radiation can be determined.

The procedure involves two basic measurements :

(*i*) **Measurement of intensity of light absorbed.** First of all the reaction cell is filled with pure solvent and is exposed to radiation. This gives the amount of energy incident on the system Then the cell is filled with the reaction mixture and is exposed to same radiation for same time. This indicates the amount of energy transmitted by the system. The difference between the incident energy and transmitted energy gives the total energy absorbed by the reaction mixture.

(*ii*) **Determining the rate of chemical reaction.** Chemical kinetics of a reaction are used to determine the number of moles reacting in a given time. To measure the rate of reaction, small samples of reaction mixture are taken out at definite intervals of time and analysed.

Sometimes, the rate is determined by measuring the change in some physical property like refractive index or optical rotation of the reaction mixture. The rate of reaction thus determined gives the number of moles of substance reacting per second. Thus we can calculate the quantum yield of reaction by knowing the rate of a reaction and the intensity of light absorbed.