

Photochemistry

Lambert-Beer's law, Its Applications and Quantum Yield:

1.1 Introduction: Photochemistry is concerned with reactions which are initiated by electronically excited molecules. Such molecules are produced by the absorption of suitable radiation in the visible and near ultraviolet region of the spectrum. Photochemistry is basic to the world we live in with sun as the central figure, the origin of life must have been a photochemical act. Simple gaseous molecules like methane, ammonia and carbon dioxide must have reacted photochemically to synthesize complex organic molecules like proteins and nucleic acids. Photobiology, the photochemistry of biological reactions, is a rapidly developing subject and helps in understanding the phenomenon of photosynthesis, photo-taxis, photoperiodism, vision and mutagenic effects of light.

The relevance of photochemistry also lies in its varied applications in science and technology. Synthetic organic photochemistry has provided methods for the manufacture of many chemicals which could not be produced by dark reactions. Some industrially viable photochemical syntheses include synthesis of vitamin D₂ from ergosterol isolated from yeast, synthesis of caprolactam which is the monomer for Nylon 6, manufacture of cleaning solvents and synthesis of some antioxidants.

Photoinitiated polymerization and photo-polymerisation are used in photography, litho-printing and manufacture of printed circuits for the electronic industry.

The photophysical phenomena of fluorescence and phosphorescence have found varied applications in fluorescent tube lights, TV screens, as luminescent dials for watches, as "optical brighteners" in white dress materials, as paints in advertisement hoardings and so on. Another revolutionary application of electronically excited molecular systems is laser technology. The two main processes, therefore, studied under photochemistry are:

1. Photophysical process

2. Photochemical process

1. **Photophysical process:** In this process, the absorption of light does not result into any chemical reaction.

2. **Photochemical process:** In this process, the light that is absorbed by a system results into chemical change.

1.2 Difference between thermal and photochemical reactions:

The main points of difference between thermal and photochemical reactions are as under:

Thermal Reactions	Photochemical Reactions
1. These reactions involve the absorption of heat	1. These reactions involve absorption of quantum of radiation. (UV/visible)
2. Temperature has significant effect on the rate of a thermal reaction.	2. Temperature has very little effect on the rate of a photochemical reaction. Instead, intensity of light has a marked effect on the rate of a photochemical reaction.
3. In these reactions, activation energy arises from the intermolecular collisions or it is supplied in the form of heat.	3. In these reactions, activation energy is acquired by absorption of quanta of radiation of suitable energy.
4. When a reaction mixture is exposed to heat radiation, all the reactant molecules absorb	4. When a reaction mixture is exposed to light radiation, the molecules of a single selected species can be promoted to an

<p>these radiations and get excited almost to the same extent i.e., there is no selectivity.</p> <p>5. All the thermal reactions are accompanied by a decrease in free energy i.e., ΔG is always negative.</p> <p>6. The presence of light is not necessary for the reaction to take place and can take place even in the dark.</p>	<p>excited state independent of the other species present in the mixture.</p> <p>5. There are various photochemical reactions such as photosynthesis of carbohydrates through chlorophyll and sunlight, polymerisation of anthracene, decomposition of ammonia etc. which are accompanied by increase in free energy.</p> <p>6. The presence of light is an essential requirement for the reaction to take place.</p>
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Laws of Governing Absorption of Light: We know that the light incident upon a system can be transmitted and absorbed. In photochemistry, we are concern with only a part of light which is absorbed.

When a beam of monochromatic light is allowed to pass through an absorbing medium, a part of the incident light is reflected, a part is absorbed by the medium and the rest is transmitted. If I_0 is the intensity of incident light, I_r , the intensity of reflected light, I_a the intensity of light absorbed and it the intensity of transmitted light then

$$I_0 = I_r + I_a + I_t$$

However, by using a comparison cell, I_r is very small (about 4%) and can be neglected for air-glass interfaces. Then,

$$I_0 = I_a + I_t$$

The decrease in intensity of light after passing through the medium is governed by two photophysical laws namely Lambert's law and Beer's law.

- (a) **Lamberts Law:** *It states that "when a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of incident radiation".*

Mathematically, the law is expressed as

$$-\frac{dI}{dx} \propto I \quad \text{or,} \quad -\frac{dI}{dx} = kI \quad \text{or,} \quad -\frac{dI}{I} = kdx \dots \dots \dots (1)$$

Where, dI = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness dx of the medium.

$\frac{dI}{dx}$ = Rate of decrease of intensity of radiation with thickness of the absorbing medium.

k = constants, called absorption coefficient of the medium for light of a particular wavelength.

$$-\frac{dI}{I} = kdx \dots \dots \dots (2)$$

If x is the total length of the medium (path length) and I_0 is the intensity of incident light at $x = 0$ then equation (2) can be integrated between the limits

$$x = 0; I = I_0$$

& $x = x$; $I = I_t$

as under:

$$\int_{I=I_0}^{I=I_t} \frac{dI}{I} = -k \int_{x=0}^{x=x} dx$$

$$\Rightarrow \left| \ln I \right|_{I=I_0}^{I=I_t} = -k \left| x \right|_{x=0}^{x=x}$$

$$\Rightarrow \ln I_t - \ln I_0 = -k(x - 0)$$

$$\Rightarrow \ln (I_t/I_0) = -k \cdot x \quad \dots\dots\dots (3)$$

$$\Rightarrow (I_t/I_0) = e^{-k \cdot x}$$

$$\Rightarrow I_t = I_0 \cdot e^{-k \cdot x}$$

If $I_{\text{abs.}}$ is the intensity of light absorbed, then

$$I_{\text{abs.}} = I_0 - I_t$$

$$\Rightarrow I_{\text{abs}} = I_0 - I_0 \cdot e^{-k \cdot x}$$

$$\Rightarrow I_{\text{abs}} = I_0 (1 - e^{-k \cdot x}) \quad \dots\dots\dots (4)$$

equation (3) can also be represented as

$$2.303 \log (I_0 / I_t) = k \cdot x$$

$$\Rightarrow \log \left(\frac{I_0}{I_t} \right) = k' \cdot x$$

where $k' = k / 2.303$

$$\text{thus, } k' = \frac{1}{x} \cdot \log \left(\frac{I_0}{I_t} \right) \quad \dots\dots\dots (5)$$

where k' is called absorption coefficient, absorptivity of the substance or extinction coefficient. Its value depends upon the nature of the absorbing medium and the wavelength of the light employed. According to equation (5)

$$k' = \frac{1}{x} \cdot \log \left(\frac{I_0}{I_t} \right)$$

$$\text{If } \log \left(\frac{I_0}{I_t} \right) = 1; \text{ then } \log \left(\frac{I_0}{I_t} \right) = \log 10$$

$$\Rightarrow \frac{I_0}{I_t} = 10 \quad \Rightarrow \quad I_t = (1/10) \cdot I_0$$

$$\therefore k' = 1/x$$

Thus, the extinction coefficient may be defined as the reciprocal of that thickness of the medium required to reduce the light to one-tenth of its intensity.

It may be noted that $\log(I_0/I_t)$ is called absorbance of the medium and the ratio (I_t/I_0) is called as transmittance.

while absorbance is denoted by A, the transmittance is denoted by T.

$$\begin{aligned} \text{Thus, } \log \left(\frac{I_0}{I_t} \right) &= k' \cdot x \\ \Rightarrow \quad A &= k' \cdot x \end{aligned}$$

$$\text{and } T = (I_t/I_0).$$

Absorbance (A) also called as optical density is related to transmittance by the following relation

$$A = \log \left(\frac{1}{T} \right)$$

$$\Rightarrow A = \log T^{-1} \quad \Rightarrow \quad A = -\log T \dots\dots\dots (6)$$

Physical significance of extinction coefficients(ϵ):

We know the relation $\log \frac{I}{I_0} = -k'x$

$$\text{Or } k' = -\frac{1}{x} \log \frac{I}{I_0} = \frac{1}{x} \log \frac{I_0}{I}$$

$$\text{If } \log \frac{I_0}{I} = 1, \quad k' = \frac{1}{x}$$

As $\log \frac{I_0}{I} = 1$, we say that $\frac{I_0}{I} = 10$ or $I = \frac{1}{10} I_0$

With this expression, **extinction coefficient** may be stated as follows:

Extinction coefficient is the reciprocal of that layer thickness (expressed in cm) at which the intensity of light falls to one tenth of the original value.

Lambert – Beer law: *When a beam of monochromatic radiation is passed through a solution, the decrease in intensity of light with thickness of the absorbing medium is directly*

proportional to the intensity of the incident radiation and also to the concentration “c” of the solution.

Mathematically

$$\begin{aligned}
 & - \frac{dI}{dx} \propto I \cdot C \\
 \Rightarrow & - \frac{dI}{dx} = \epsilon \cdot I \cdot C \\
 \Rightarrow & \frac{dI}{I} = - \epsilon \cdot C \cdot dx \quad \dots\dots\dots(1)
 \end{aligned}$$

where ϵ is a constant of proportionality. Integrating = n (1)

between the limits $x = 0, I = I_0$ and $x = x, I = I_t$

$$\text{We get} \quad \int_{I=I_0}^{I=I_t} \frac{dI}{I} = -\epsilon \cdot C \int_{x=0}^{x=x} dx$$

$$\Rightarrow \left| \ln I \right|_{I=I_0}^{I=I_t} = -\epsilon \cdot C \cdot \left| x \right|_{x=0}^{x=x}$$

$$\Rightarrow \ln (I_t / I_0) = -\epsilon \cdot C \cdot x \quad \dots\dots\dots (2)$$

$$\Rightarrow I_t / I_0 = e^{-\epsilon \cdot C \cdot x}$$

$$\Rightarrow I_t = I_0 \cdot e^{-\epsilon \cdot C \cdot X}$$

The intensity of the light absorbed by the solution when it passes through a length “x” of the solution is given by.

$$\begin{aligned} I_{\text{abs}} &= I_0 - I_t = I_0 - I_0 \cdot e^{-\epsilon \cdot C \cdot X} \\ &= I_0 (1 - e^{-\epsilon \cdot C \cdot X}) \end{aligned}$$

Equation (2) can be written as

$$\begin{aligned} 2.303 \log \left(\frac{I_t}{I_0} \right) &= -\epsilon \cdot C \cdot X \\ \Rightarrow \log \left(\frac{I_t}{I_0} \right) &= -(\epsilon / 2.303) \cdot C \cdot X \\ \Rightarrow \log \left(\frac{I_t}{I_0} \right) &= -\epsilon' \cdot C \cdot X \\ \Rightarrow \log \left(\frac{I_0}{I_t} \right) &= \epsilon' \cdot C \cdot X \quad \dots\dots\dots(3) \end{aligned}$$

where $\epsilon' = \epsilon / 2.303$ is called as molar absorption coefficient or molar absorptivity or molar extinction coefficient.

Since,
$$A = \log \left(\frac{I_0}{I_t} \right)$$

Therefore, eq(3) can be written as

$$A = \epsilon' \cdot C \cdot X \quad \dots\dots\dots(4)$$

or
$$\epsilon' = \frac{A}{CX} \Rightarrow \epsilon' = \frac{1}{CX} \cdot \log \left(\frac{I_0}{I_t} \right)$$

If $C = 1 \text{ M}$ & $\log \left(\frac{I_0}{I_t} \right) = 1$

Then $\epsilon' = \frac{1}{X}$; we know $\log \left(\frac{I_0}{I_t} \right) = 1$

means $I_t = \frac{1}{10} I_0$

Thus, molar extinction coefficient may be defined as the reciprocal of that 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.

Beer's law is thus an extension of Lambert's law applicable to solutions.

Units of molar absorption Coefficient: -

$$\epsilon' = \frac{1}{Cx} \log \frac{I_0}{I_t}$$

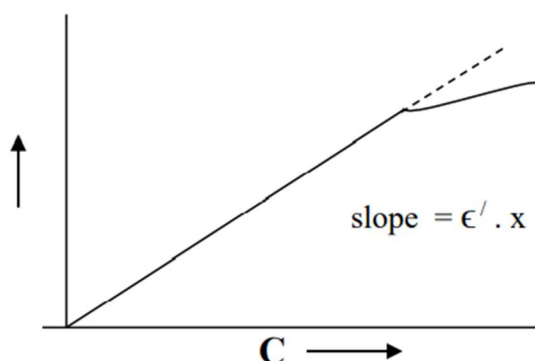
If concentration is expressed in mol L⁻¹ and length x in cm

Then unit of ϵ' is L mol⁻¹ cm⁻¹

& If concentration is expressed in mol dm⁻³ and x in m

Then unit of ϵ' is dm³ mol⁻¹ m⁻¹.

The plot of absorbance "A" versus concentration "C" is a straight line passing through origin. The value of ϵ' (molar extinction co-efficient) can be obtained from the slope.



Limitations of Lambert – Beer law:

1. The law holds good only for monochromatic radiation.
2. The law governs the absorption behaviour of dilute solutions only. At higher solute concentration, the ions of a solute in case it is an electrolyte, are close enough to disturb the charge distribution of their neighbours. The inter-ionic interaction drastically alters the ability of the solute to absorb a given wavelength of the incident radiation. Thus, the relationship between A and C is no longer linear. At higher concentrations, the refractive index (μ) of the solution also changes and it has been found that it is the quantity $[\mu/(\mu+2)^2]\epsilon'$, rather than ϵ' which remains constant. Thus when $[\mu/(\mu+2)^2]$ changes with change in concentration, the law shows deviation.
3. The temperature of the system should not be allowed to vary to a large extent. Too much rise in temperature shifts the absorption bands towards longer wavelength (bathochromic effect).

Physical Significance of Molar Extinction Coefficient (ϵ'):

We know the relation

$$\log \frac{I}{I_0} = -\epsilon' cx$$

$$\text{Or } \epsilon' = -\frac{1}{cx} \log \frac{I}{I_0} = \frac{1}{cx} \log \frac{I_0}{I}$$

$$\text{When } c=1\text{M and } \log \frac{I_0}{I} = 1,$$

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

But we know that when $\log \frac{I_0}{I} = 1$, then $\frac{I_0}{I} = 10$ or $I = \frac{1}{10} I_0$

With this expression, **molar extinction coefficient** may be stated as follows:

Molar extinction coefficient is the reciprocal of that thickness (expressed in cm) of the layer of 1 molar concentration which reduces the intensity of light passing through it to one tenth of the original value.

(b) **Beer's law (or Lambert's-Beer Law):** This law is applicable to solutions. It means that when the light absorbing substance is present in solution, the decrease in the intensity of light with thickness of solution is given by this law.

This law is stated as follows:

“When a beam of monochromatic radiation is passed through a solution, the decrease in intensity of light with thickness of the absorbing medium is directly proportional to the intensity of the incident radiation and also to the concentration “c” of the solution”.

1.5 Laws of photochemistry

There are two laws which govern the effect of radiation on chemical reactions. These laws are:

- 1. Grotthus–Drapper law:** - This law was enunciated by Grotthus and Drapper in the 19th century. They found that all the light that was incident on a sample was not effective in bringing about a chemical change. *According to this law, also called the principle of photochemical activation, only that part of the light which is absorbed by a system can bring about a chemical change.*

The law, however, does not imply that the absorbed light must always bring about a chemical change. The absorbed light may sometimes result in fluorescence and phosphorescence and in some cases, it may be converted into heat. The law is purely qualitative in nature and doesn't give any relationship between the amount of light absorbed by a system and the number of reacting molecules.

- 2. Stark-Einstein's law of Photochemical Equivalence:** - This law, also called the principle of quantum activation, was enunciated by Stark in 1908 and independently by Einstein in 1912. The two scientists applied the concept of energy quantum to photochemical reactions. According to this law, *one molecule is activated by the absorption of one quantum of radiation in the primary or first step of a photochemical reaction.* The law, however, does not imply that one molecule must react for each quantum of radiation absorbed.

If “v” is the frequency of the radiation absorbed, then the corresponding quantum of energy absorbed per molecule will be $h\nu$, where h is the planck's constant. The energy absorbed by one mole of the reacting molecules will then be given by

$$E = N_A \cdot h\nu = N_A \cdot \frac{hc}{\lambda}$$

where c is the velocity of light and λ its wavelength. The energy absorbed per mole of the reacting molecules is called one “Einstein”. Since E is inversely proportional to λ ; therefore, shorter the wavelength, the greater is the energy absorbed.

Numerical Value of Einstein in different units:

1) In CGS units:

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-27} \text{ erg s}$$

$$c = 3 \times 10^{10} \text{ cm s}^{-1}$$

& λ is in cm

$$\text{Then., } E = \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) (6.626 \times 10^{-27} \text{ erg s}) (3 \times 10^{10} \text{ cm s}^{-1})}{\lambda \text{ (cm)}}$$

$$= \frac{119.7 \times 10^6 \text{ erg mol}^{-1}}{\lambda \text{ (in cm)}}$$

$$= \frac{119.7 \times 10^6 \text{ cal mol}^{-1}}{4.184 \times 10^7 \lambda}$$

$$\begin{aligned}
 &= \frac{2.86 \text{ cal mol}^{-1}}{\lambda \text{ (in cm)}} \\
 &= \frac{2.86}{\lambda \text{ (in } \text{\AA})} \times 10^8 \text{ cal mol}^{-1} \\
 &= \frac{2.86}{\lambda \text{ (in } \text{\AA})} \times 10^5 \text{ K cal mol}^{-1}
 \end{aligned}$$

S. I. units:

$$\begin{aligned}
 N_A &= 6.022 \times 10^{23} \text{ mol}^{-1}, h = 6.626 \times 10^{-34} \text{ J s} \\
 c &= 3 \times 10^8 \text{ m s}^{-1} \\
 \lambda &= (\text{in m}) \\
 \text{then } E &= \frac{11.97 \times 10^{-5}}{\lambda \text{ (in m)}} \text{ KJ mol}^{-1}
 \end{aligned}$$

If λ is expressed in \AA , then the above relation is multiplied by 10^{10} . ($1\text{m}=10^{10}\text{\AA}$)

$$\begin{aligned}
 E &= \frac{119.7 \times 10^{-3} \times 10^{10}}{\lambda} \text{ joule mol}^{-1} \\
 E &= \frac{11.97 \times 10^5}{\lambda} \text{ kJ mol}^{-1}
 \end{aligned}$$

It is seen from the above relation that shorter the wavelength, greater will be the energy absorbed. Einstein is bigger in magnitude for the ultraviolet light absorbed as compared to the one where infrared light is absorbed.

The shorter the wavelength of a radiation, greater is the energy of the **Einstein**. For example, different radiation has the following order of wavelengths.

X-rays < UV < visible < IR

Therefore, the energy per Einstein is:

X-rays > UV > visible > IR

Quantum Efficiency:

For a primary process, the number of molecules activated is equal to the number of quanta absorbed. The activated molecule may or may not react. On the other hand, an activated molecule may cause the reaction of many molecules through a chain mechanism. The law applies to the primary process in which the light is actually absorbed. The products of the primary process may take part in thermal or 'dark' reactions known as secondary reactions. Thus, the total number of moles reacting for each Einstein of radiation absorbed may differ from unity.

To relate the number of quanta absorbed with the number of reacting molecules, a term called quantum efficiency or "quantum yield" (ϕ) has been introduced. It is expressed as:

$$\begin{aligned}
 \phi &= \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quanta of light absorbed in the same time}} \\
 &= \frac{\text{No. of molecules reacting in a given time}}{\text{No. of Einsteins absorbed in the same time}}
 \end{aligned}$$

$$= \frac{\text{No. of molecules reacting per sec.}}{\text{Quanta of absorbed per sec.}}$$

$$= \frac{\text{Rate of chemical reaction}}{\text{Quanta of absorbed per sec.}}$$

Experimental Determination of Quantum Yield:

Measurement using Actinometer:

The quantum yield of any photochemical reaction is measured using an experimental set up as shown below.

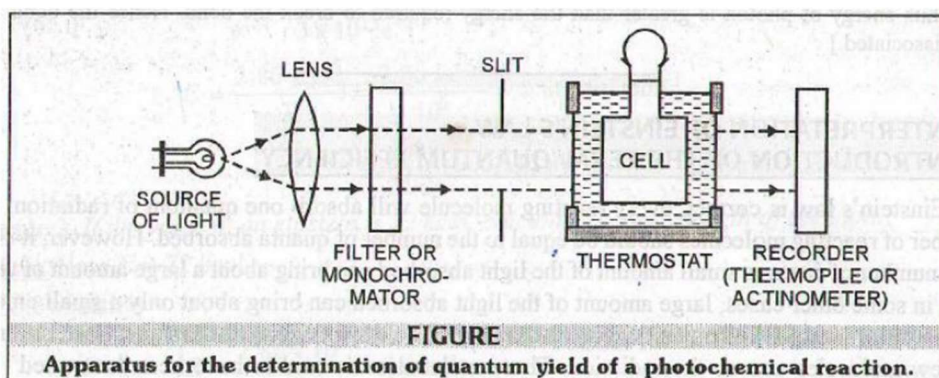
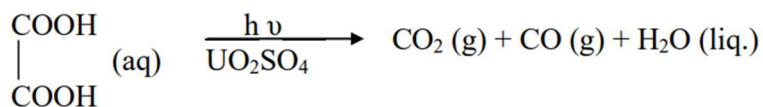


Fig. Apparatus for the determination of quantum yield of a photochemical reaction.

Various components of the apparatus are described as:

- (i) a **light source** which emits radiation of suitable intensity in the desired spectral range. The commonly used sources are filament lamps, carbon metal arcs and various gas discharge tubes.
- (ii) **lens** of suitable focal length.
- (iii) **monochromator** or filter which cuts off all radiations except the radiations of desired wavelength.
- (iv) slit to get a fine beam.
- (v) a **reaction cell** placed in thermostat and containing the reaction mixture. The reaction cell is made of glass or quartz and has optically plane windows for the entrance and exit of light. Glass is used only if the wavelength of light used lies in the visible range. For radiations below 350 nm, the cell completely made of quartz is used.
- (vi) A **detector or recorder** which is usually a thermopile or an actinometer is used to measure the intensity of light radiations.

Actinometer: The energy associated with radiation absorbed can also be measured by employing an *actinometer*. A *chemical actinometer* is a device in which gas mixture or solutions sensitive to light are used. The working of this device is based upon the fact that a definite amount of the radiation absorbed brings definite amount of a chemical reaction. The most commonly used is the *uranyl oxalate actinometer*. It consists of 0.05 M oxalic acid and 0.01 M uranyl sulphate (UO_2SO_4) solutions in water. When exposed to light the following reaction takes place.



UO_2SO_4 acts as a photosensitiser. The extent of reaction is measured by titrating the oxalic acid solution with KMnO_4 solution. The actinometer is first calibrated against a thermopile. This actinometer can be used for measuring only the intensity of the radiation lying in the range 250nm–500nm.

Procedure: The empty cell or the cell filled with solvent alone (in case of solutions) is placed in a thermostat. The monochromatic radiation is allowed to pass through the cell for a definite time. The reading is taken on the recorder. This gives the total energy incident at a given time. The cell is then filled with the reactants and again exposed to radiations for the definite time and the reading is taken again on the recorder. The difference between the two readings gives the total energy absorbed by the reactants in a given time. From this, the intensity of the radiation absorbed I_{abs} is calculated as follows:

$$I_{\text{abs}} = \frac{\text{Total energy absorbed}}{\text{Volume of the reaction mixture} \times \text{Time in sec.}}$$

The number of moles reacting in a given time (Rate of reaction) is determined by the usual analytical methods used in chemical kinetics. 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.

Example 1. Calculate the value of Einstein for the radiation having wavelength 600nm.

Solution: According to Stark-Einstein law

$$E = N_0 h \nu = N_0 h \frac{c}{\lambda} = \frac{6.02 \times 10^{23} \text{mol}^{-1} \times 6.626 \times 10^{-34} \text{Js} \times 3 \times 10^8 \text{ms}^{-1}}{600 \times 10^{-9} \text{m}} = 199 \text{kJmol}^{-1}$$

Example 2. A radiation having wavelength 400 nm is completely absorbed by a reaction mixture. How many moles of radiation are absorbed in 20 minutes if the intensity of radiation is 50W?

Solution: Energy absorbed by the reaction mixture in one second = 50W = 50Js⁻¹.

Energy absorbed in 20 minutes

$$= 50 \text{Js}^{-1} \times (20 \times 60 \text{s})$$

$$= 60000 \text{J}$$

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

$$\text{or, } 60000 \text{J} = n N_0 h \nu = n N_0 h \frac{c}{\lambda}$$

$$\therefore n = \frac{60000 \text{J} \times 400 \times 10^{-9} \text{m}}{(6.02 \times 10^{23} \text{mol}^{-1})(6.626 \times 10^{-34} \text{Js})(3 \times 10^8 \text{ms}^{-1})} = 0.200 \text{mol}$$

Example 3. A sample of acetone absorbs mono-chromatic radiation at the rate of 4.5×10^{20} quanta sec⁻¹. The number of moles of acetone decomposed in one second is 1.35×10^{-4} . Calculate the quantum yield of photolysis of acetone.

Solution: No. of moles of quanta absorbed

$$= \frac{4.4 \times 10^{20}}{6.023 \times 10^{23}} = 7.47 \times 10^{-4}$$

$$\text{No. of moles acetone decomposed} = 1.35 \times 10^{-4}$$

Quantum efficiency

$$= \frac{\text{No. of moles of acetone decomposed}}{\text{No. of moles of quanta absorbed}}$$

$$= \frac{1.35 \times 10^{-4}}{7.47 \times 10^{-4}} = \mathbf{0.18}$$

Example.4 Calculate the value of one Einstein of radiation whose wavelength is 2000A°.

Solution: We know that

$$E = hv = \frac{hc}{\lambda}$$

$$E = \frac{6.62 \times 10^{-34} Js \times 3 \times 10^8 ms^{-1}}{2000 \times 10^{10} m}$$

$$= \frac{19.86}{2} \times 10^{-16} J = \mathbf{9.93 \times 10^{-16} J}$$

It is the energy of one photon

One Einstein mean Avogadro number of photon

$$\therefore \text{Value of Einstein} = 9.93 \times 10^{-16} \times 6.02 \times 10^{23} J$$

$$= \frac{59.87 \times 10^7}{10^3} = \mathbf{59.87 \times 10^4 kJ}$$

Example.5 A certain system absorbs 3×10^{20} quanta of light per second. On irradiation of 20 minutes, 0.02 mole of the reactant was found to have reacted. Calculate the quantum yield of the reaction.

Solution: Number of photons absorbed per sec
 $= 3 \times 10^{20}$

No. of photons absorbed in 20 minutes

$$= 3 \times 10^{20} \times 20 \times 60$$

$$= 3.6 \times 10^{23} \text{ photons}$$

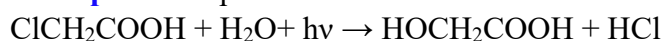
$$= \frac{3.6 \times 10^{23}}{6.023 \times 10^{23}}$$

=0.6 moles of photons

No. of moles of reactants decomposed=0.02 moles

$$\text{Quantum Yield} = \frac{0.02}{0.6} = \mathbf{0.033}$$

Example.6 In a photochemical reaction



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

Solution: Energy associated with a photon of wavelength 253.7 nm is given by

$$hv = h \cdot \frac{c}{\lambda} = \frac{(6.626 \times 10^{-34} Js)(3 \times 10^8 ms^{-1})}{(253.7 \times 10^{-9} m)} = 7.38 \times 10^{-19} J$$

Number of photons absorbed

$$= \frac{E}{hv} = \frac{34.36 J}{7.38 \times 10^{-19} J} = 4.39 \times 10^{19}$$

Number of moles of HCl formed=No. of moles of chloroacetic acid decomposed

$$= 2.296 \times 10^{-5} \text{ mol}$$

$$= 2.296 \times 10^{-5} \times 6.023 \times 10^{23} \text{ molecules}$$

$$= 1.38 \times 10^{19} \text{ molecules}$$

Quantum Yield (ϕ) of the reaction

$$= \frac{\text{No. of molecules of chloro acetic acid decomposed}}{\text{No. of photons (quanta) of light absorbed}}$$

$$= \frac{1.38 \times 10^{19}}{4.39 \times 10^{19}} = \mathbf{0.314}$$

Example 7. In a photochemical combination of $\text{H}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ a quantum efficiency of about 1.0×10^6 is obtained with a wavelength of 480 nm. What is the number of moles of $\text{HCl}(\text{g})$ produced if 1J of radiant energy is absorbed.

Solution: 1 Einstein corresponding to 480 nm

$$= N_0 h \cdot \frac{c}{\lambda} = \frac{(6.023 \times 10^{23} \text{ mol}^{-1})(6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{(480 \times 10^{-9} \text{ m})}$$

$$= 2.492 \times 10^5 \text{ J mol}^{-1}$$

Also, number of photons in 1J

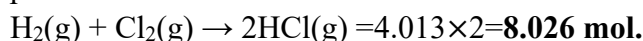
$$= \frac{1}{2.492 \times 10^5} = 4.013 \times 10^{-6} \text{ mol}$$

We know that $\phi = \frac{\text{Amount of substance reacted}}{\text{Amount of photons absorbed}}$ or, $10^6 = \frac{\text{Amount of } \text{Cl}_2(\text{H}_2) \text{ reacted}}{\text{Amount of photons absorbed}}$

Hence amount of $\text{H}_2(\text{g})$ or $\text{Cl}_2(\text{g})$ reacted

$$= 1 \times 10^6 \times 4.013 \times 10^{-6} = 4.013$$

In the photochemical combination of H_2 and Cl_2 , 1 mol of H_2 combines with 1 mol Cl_2 to produce 2 moles of HCl



High and low Quantum yield (ϕ): The various photochemical reactions can be divided into three categories:

- (i) Those in which the quantum yield is a small integer such as 1, 2, 3. Examples are combination between SO_2 and Cl_2 to give SO_2Cl_2 ($\phi = 1$), dissociation of HI and HBr ($\phi = 2$), ozonisation of O_2 ($\phi = 3$).
- (ii) Those in which the quantum yield is less than 1, examples are dissociation of NH_3 ($\phi = 0.25$) and combination between H_2 & Br_2 ($\phi = 0.01$)
- (iii) Those in which the quantum yield is very high, as for example combination of hydrogen and chlorine ($\phi = 10^6$) and combination between CO and Cl_2 ($\phi = 10^3$).

Reasons for high quantum yield:

1. The excited atoms or free radicals produced in the primary process initiate a series of chain reactions, as for example, in combination of H_2 and Cl_2 to give HCl , when the resulting quantum yields are of the order of 10^6 or more.
2. if the secondary reaction is exothermic, the heat of the reaction may activate molecules thereby causing them to react and thus result in a high quantum yield.

Reason for low quantum yield:

1. Excited molecules may get deactivated before they form products.
2. Collisions of excited molecules with non excited molecules may cause the former to lose energy.
3. The primary photochemical process may get reversed.

4. The dissociated fragments may recombine to form the original molecule.

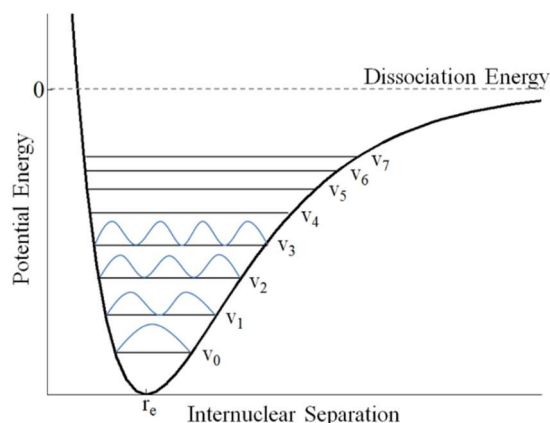
The law of photochemical equivalence can be applied only to primary process in which each molecule capable of entering into chemical reaction absorbs one quantum of radiation. The secondary processes take place of themselves quite independent of the light radiation.

It may also be noted that if reactions in the secondary processes that are responsible for the formation of products are endothermic in nature, their rate of occurrence is extremely slow at ordinary temperatures. The reactions immediately following the primary process fall into this category and the quantum yield of such reactions increases with temperature rise. Kuhn found that the quantum yield of photochemical decomposition of ammonia increase by about 15% for every 100% rise in temperature.

The quantum yield is also affected by the intensity of light. For instance, when radiation from a highly intense source, such as laser, falls on a molecule, the latter can even absorb two photons simultaneously. For such biphotonic and multiphotonic effects, the Stark-Einstein law needs to be modified.

Photochemical Processes:

Potential energy Curve:



Franck Condon Principle: Intensity distribution in the electronic spectrum can easily explained with the help of Franck-Condon. *According to this Principle, an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during transition.*

The principle is true to the first approximation since the electrons move so much faster than the nuclei that during the electronic transition the nuclei do not change their position. Time taken during electronic transition is 10^{-15} sec, whereas the vibrational period is only 10^{-12} sec, i.e., electronic transition is nearly 1000 times faster than the vibrational motion. Hence, an electronic transition may be represented by a vertical line on a plot of potential energy versus the internuclear distance.

Consider a diatomic molecule. Two potential energy curves are shown in figure for the molecule in the ground electronic state (E_0) and in the first electronic state (E_1). Since the bonding in the excited state is weaker than in the ground state, the minimum in the PE curve for the excited state occurs at a slightly greater internuclear distance than the corresponding minimum in the ground electronic state. Quantum mechanically, it is known that the molecule is in the centre of the ground vibrational level of the ground electronic state.

Consider in **Fig.3.1a**, where we have shown two potential energy curves for the molecules in the electronic state (E_0) and in the first electronic state (E_1). When an electronic transition occurs, the molecule is excited to the state represented by the upper curves. According to Franck-Condon principle the nuclei framework remains constant during the actual transition so the energy of the molecule rising on a vertical transition. The most probable bands in the absorption or emission spectrum depends on the relative horizontal separations of the potential energy curves of the ground and excited states of the molecules. According to quantum mechanics, the transition from the lowest vibrational level takes place at equilibrium internuclear distance. The relatively more probable electronic transitions are those which begin or end at the middle of the lowest vibrational level or at either extreme of any of the higher vibrational level.

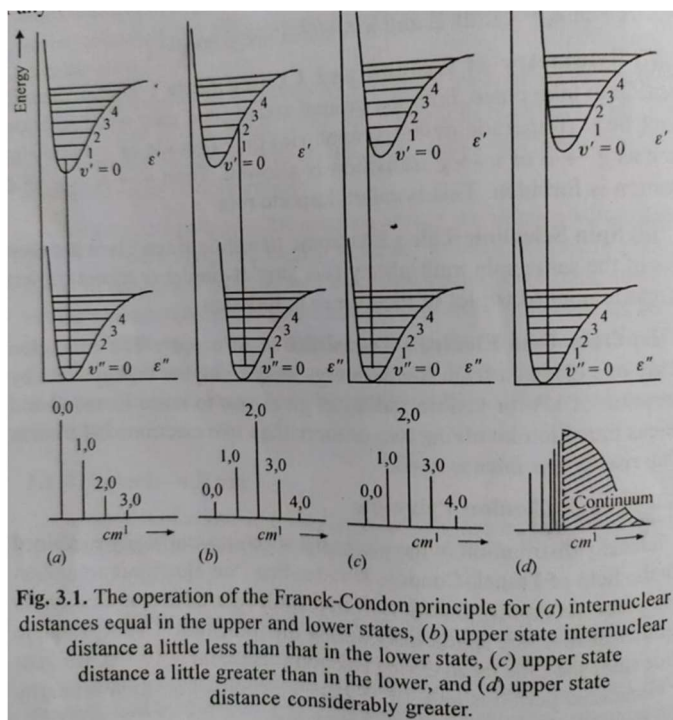


Fig.3.1b, the excited electronic state has a slightly smaller internuclear separation than the ground state. So, a vertical transition from $v''=0$ will occur into the upper vibrational level $v'=2$. In **Fig.3.1c**, the excited electronic state has a slightly larger internuclear distance, but the resulting transitions are similar with **Fig.3.1b**.

Fig.3.1d, the potential energy minima in two curves lies at a considerable internuclear distance. The transition point in the upper curve ϵ' lies asymptotic to the lower curve, therefore, corresponding to the continuous spectrum. This leads to dissociation of the molecule without any vibration.

Dissociation and Predissociation:

- (i) **Dissociation:** If excitation transfer a molecule in a state containing more energy than the separated components (atoms or molecules) dissociation take place. Above the dissociation limit the energy is not quantized and energy continuum appears instead of discrete energy levels. The dissociative state is not stable, which means that the molecule disassembled into the separated components very quickly. In Fig. the dashed line limits of Morse Curve represent the dissociation of the normal and excited molecule into atoms, the dissociation energies being D_0' and D_0'' from the $v=0$ state in each case. The total energy of the dissociation products from the upper state is greater by an amount called E_{ex} than that of the products of dissociation in the lower state. This energy is the excitation energy of one of the atoms produced of dissociation. The lower wave number limit of the continuum is

$$\bar{\nu}_{\text{continuum}} = D_0'' + E_x \text{ cm}^{-1}$$

In Figure, which illustrate the state of unstable upper electronic state or the continuous upper state. There is no minimum in the energy curve, as soon as a molecule is raised to the excited state, the molecule dissociates into products with total excitation energy E_{ex} . This dissociation product goes with kinetic energy $E_{kinetic}$.

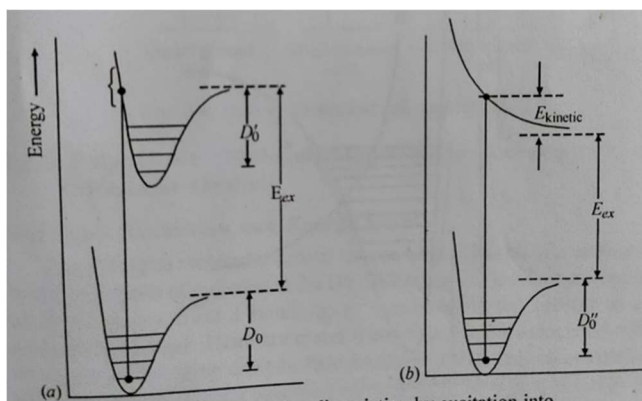
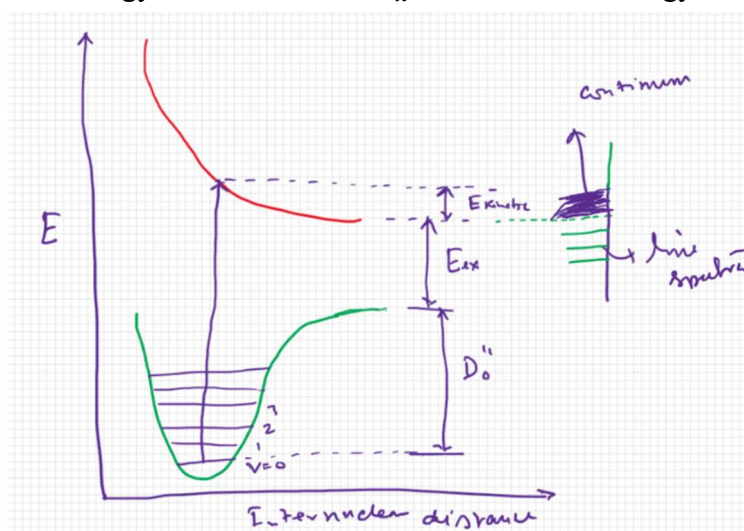


Fig. Showing Dissociation by excitation into (a) a stable upper and (b) a continuous upper state

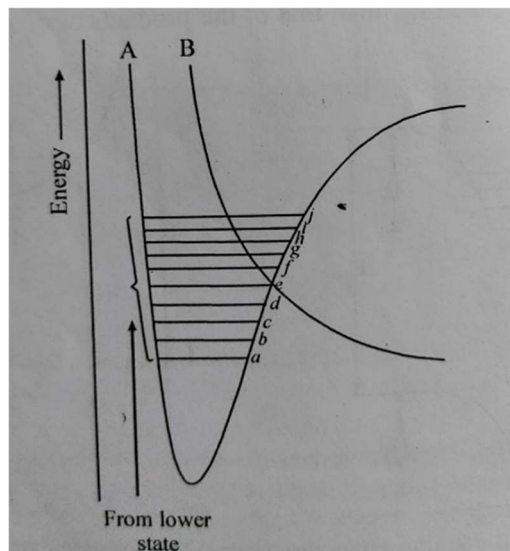
Measurement of D_0'' and E_x :

- We can measure D_0'' , the dissociation energy, if we know that E_x , the excitation energy of the product.
- excitation energy of atoms to various electronic state is readily measurable by atomic spectroscopy.
- The thermochemical studies can lead to measurement of approx. value of D_0'' and by spectroscopic methods we can measure the accurate value of $D_0'' + E_x$, we can measure approx. value of E_x .



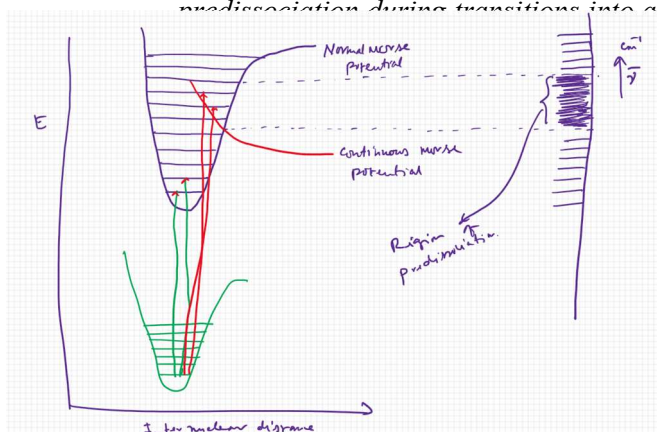
Dissociation limit: Dissociation limit can be determined accurately by spectroscopy i.e., $D_0'' + E_x$. If E_x can be found from a knowledge of the dissociation products, D_0'' can be measured with great accuracy.

- (ii) **Predissociation:** In some spectrum the discrete energy level structure disappears already for energies which are below the dissociation limit but reappears again at some higher energies. This phenomenon is called Predissociation. This can be usually explained as a result of internal conversion from an excited state A into a dissociative state B. We assume relationship between the vibrational states closely above the level of intersection and the translational motion during dissociation. These circumstances allow a separation of a molecule via state B without supplying the energy of dissociation for state A Fig.



Sometimes, predissociation is a result of some additional external factors. For example, we can imagine a molecule to be pushed from state A to state B due to collision with another atom, or molecule. Alternatively, an external electric or magnetic field can cause the predissociation of an initially stable molecule. Such cases are collision or field induced predissociation.

Fig. Showing the occurrence of predissociation during transitions into a



Decay of excited states by radiative and non-radiative paths: The radiative and non-radiative transition can be explained with the help of Jablonski diagram which photophysical processes occurring in electronic excited states.

A molecule which is photochemically excited to the higher energy state must return to the ground state. Promotions S_2 and higher singlet states take place but in liquids and solids, these higher states drop very rapidly to S_1 state (about 10^{-13} to 10^{-11} sec). The energy lost when an electron drops from S_2 to S_1 is given up to the environments by collisions with the neighbouring molecules. Such a process is called an energy cascade. It has been found that the lowest

vibrational level of the S_1 state is the only important excited singlet state.

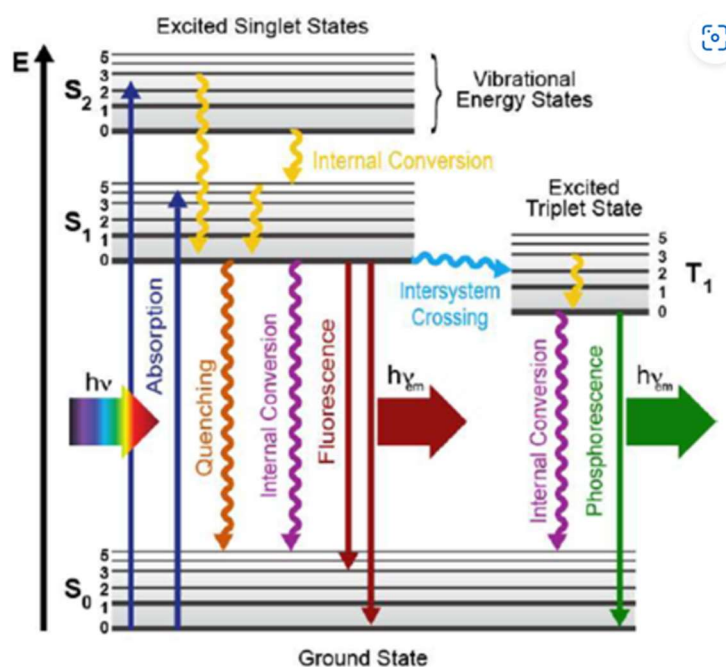


Figure 1. Jablonski energy diagram of electronic and vibrational energy levels of an excited molecule.

This state can undergo various physical and chemical processes. The various physical pathways open to the molecules in the S_1 and excited triplet state are described below.

- | | | |
|--------|---|---|
| (i) | $S_0 + h\nu \rightarrow S_1^0$ | Excitation |
| (ii) | $S_1^0 \rightarrow S_1 + \text{heat}$ | Vibrational relaxation |
| (iii) | $S_1 \rightarrow S_0 + h\nu$ | Fluorescence |
| (iv) | $S_1 \rightarrow S_0 + \text{heat}$ | Internal Conversion |
| (v) | $S_1 \rightarrow T_1^0$ | Intersystem crossing |
| (vi) | $T_1^0 \rightarrow T_1 + \text{heat}$ | Vibrational relaxation |
| (vii) | $T_1 \rightarrow S_0 + h\nu$ | Phosphorescence |
| (viii) | $T_1 \rightarrow S_0 + \text{heat}$ | Intersystem crossing |
| (ix) | $S_1 + A(S_0) \rightarrow S_0 + A(S_1)$ | Singlet-singlet transfer (photosensitization) |
| (x) | $T_1 + A(S_0) \rightarrow S_0 + A(T_1)$ | Triplet-Triplet transfer (photosensitization) |

It is important to note that an activated molecule returns to the ground state by dissipating its energy through the following processes.

(a) Radiative Transitions: In this type, the activated molecule returns from the singlet excited state S_1 to triplet excited state T_1 to the ground S_0 . Such transitions are accompanied by the emission of radiation. The transition $S_1 \rightarrow S_0$ is allowed transition and occurs in about 10^{-8} sec. the emission in this radiation is called **Fluorescence**. But the transition, T_1 to S_0 is forbidden transition. The emission of this radiation is called **Phosphorescence**. Since this transition involves spin inversion, its life time is greater and 10^{-3} second. Fluorescent and phosphorescent frequencies are shorter because a part of energy absorbs by the molecule is lost in the form of heat in such transitions.

(b) Non radiative Transition: in this type of transition, the activated molecule returns from higher excited state (S_3 , S_2 , to T_3 , T_2) to the first excited state (S_1 to T_1). Such transition does not involve the emission of any radiation and are thus, called non-radiative transitions. The energy of the activated molecule is dissipated in the form of heat through molecular collisions. The process is called **internal conversion (IC)** and occurs in less than 10^{-11} sec. Another way of losing energy by activated molecule is **intersystem crossing (I.S.C)**. it involves transitions between states of different spins. Example of such transition include $S_2 \rightarrow T_2$ or $S_1 \rightarrow T_1$. These radiations are non-radiative. Since these transitions are forbidden, they occur through relatively slow rates.

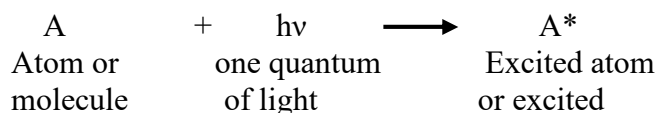
Rate of Photochemical Processes:

Photochemical Reactions: We know that according to Einsteins law of photochemical equivalence, every reacting molecule absorbs one quantum of radiation and clearly, the number of reacting molecules should be equal to the number of quanta absorbed. But it is not fully true and, in many cases, it has been observed that

- (i) a small amount of light absorbed can brings about only a large amount of reaction.
- (ii) a large amount of light absorbed brings about only a small amount reaction.

This anomaly is explained on the basis of the fact that a photochemical reaction consists of two processes. M. Bodenstein proposed that photochemical processes involve two distinct processes.

1. Primary Process: Primary processes are those processes in which quantum of energy ($h\nu$) is absorbed by a molecule, resulting in the excitation of the molecule. Thus,



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

- (i) **In Type I**, the energy absorbed raises the molecule to 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 spectrum.
- (ii) **In Type II**, the electronic transition 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 band 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 lower level to a stable upper level. During the course of vibration, the molecule may shift from the stable state 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 predissociation, the rotational lines are absent and the rotational bands have a diffuse appearance.

The molecule which absorbs light may get dissociated yielding excited state atoms or free radicals. The primary process may also involve loss of vibrational energy of excited molecules by collision with other molecules as well as by fluorescence and phosphorescence.

2. Secondary Process: The excited molecule during the primary process may undergo one of the following changes to complete the reaction.

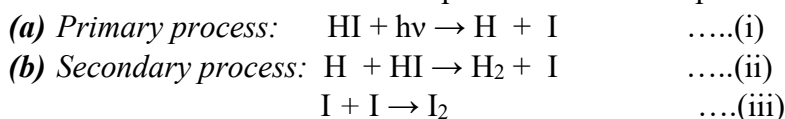
- (i) It may react to form the final product.
- (ii) It can be partly or fully deactivated and no more reaction occurs.
- (iii) It may start a chain reaction.

As the law of photochemical equivalence is applicable to primary processes, light radiations are essential only for the primary process. It is important to note that the secondary process may take place in the dark provided the products of primary reactions are available.

Secondary photochemical processes. 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 the different frequency. These processes are known as secondary processes.

In the light of above discussion, mechanism of some important photochemical reaction is given below:

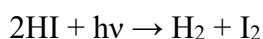
1. **Photochemical decomposition of hydrogen iodide in the gaseous phase (Photolysis of hydrogen iodide):** on the exposure to radiations having wavelength in the range 207-252 nm, the decomposition of hydrogen iodide takes place. The quantum yield of the reaction is 2. This has been explained with the help of mechanism given below.:



Possibility of other secondary processes such as



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

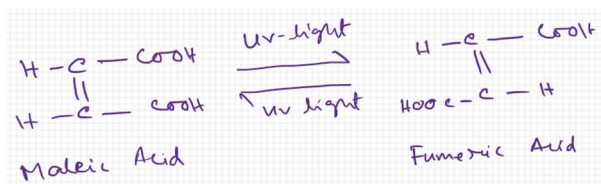


Thus, for every one quantum of light absorbed, two molecules of HI are decomposed. Hence, the quantum yields of reaction is 2. It may be noted that while adding the equations (i), (ii), and (iii), no distinction has been made between the excited iodine atom and normal iodine atom.

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.

Photo-chemical Equilibrium:

It has been found that in certain cases, a photochemical reaction is followed by another photochemical reaction or thermal reaction in the backward direction. The rate of photochemical reaction is proportional to the intensity of light radiation but the rate of thermal reaction is proportional to the concentration of photochemical product. Consider the following reactions in equilibrium.



Equilibrium Constant: Contrary to ordinary chemical reaction, the equilibrium constant of a photochemical reaction is different. The reason is that rate of forward reaction depends, upon the intensity of light absorbed instead of the concentration of reaction. Consider a reaction in equilibrium.



Rate of forward reaction in $(r_f) = k_1 I_{\text{abs}}$ (i)

Where, k_1 = rate constant of photochemical reaction:

I_{abs} = Intensity of absorbed radiation:

Rate of backward reaction: $(r_b) = k_2 [B]$ (ii)

Where, k_2 = rate constant of thermal reaction:

$[B]$ = concentration of photochemical product.

At equilibrium $r_f = r_b$. Thus, from (i) and (ii)

$$k_1 I_{\text{abs}} = k_2 [B] \text{ or } \frac{k_2}{k_1} = \frac{I_{\text{abs}}}{[B]} \text{ or, } K = \frac{I_{\text{abs}}}{[B]} \quad (K = \text{Equilibrium Constant})$$

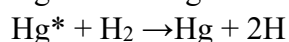
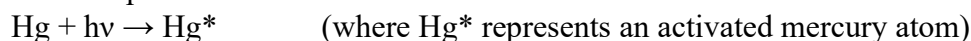
$$\text{Also, } [B] = \frac{k_1}{k_2} I_{\text{abs}}$$

From this, we say that concentration of B formed at their state of equilibrium is directly proportional to the intensity of light absorbed.

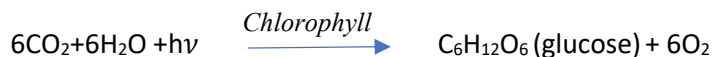
Photosensitization and Photosensitized Reactions: In some photochemical processes, the reactant molecules do not absorb the radiation to which they are exposed and no reaction occurs. However, if a suitable foreign substance that absorbs radiation is added to the reaction mixture, the reaction takes place. The atoms of foreign substance absorb the radiation and pass it on to the reacting molecule and thereby initiate 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 **photosensitization**.* Thus, a photosensitizer act as carrier of energy. Commonly used photosensitizer are cadmium and mercury vapour. Some important examples of photosensitized reactions are described below.

1. Dissociation of hydrogen molecule in presence of mercury vapour. A hydrogen molecule is unstable to absorb the radiation of wavelength of 2537\AA that is emitted when an electrical discharge is passed through a 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 and can be represented as:

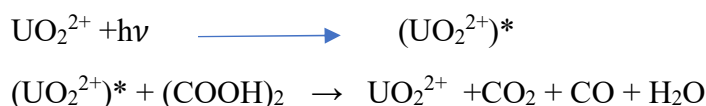


2. Photosynthesis of Carbohydrates in plants: *Photosynthesis is a process in which carbon dioxide and water vapour present in air combine in presence of chlorophyll (the green colouring matter of plants) and sunlight to form carbohydrates.*



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 (650-700nm) regions. Although, the exact mechanism of the reaction is not certain, it is believed that the chlorophyll passed 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 ion UO_2^{2+} :** As already discussed, the decomposition of oxalic acid into CO_2 and CO in presence of UO_2^{2+} ions form the basis of the actinometer used to measure the intensity of radiation. The process occurring are excitation of the coloured UO_2^{2+} ion followed by transfer of energy to the colourless oxalic acid resulting in its decomposition. Thus,

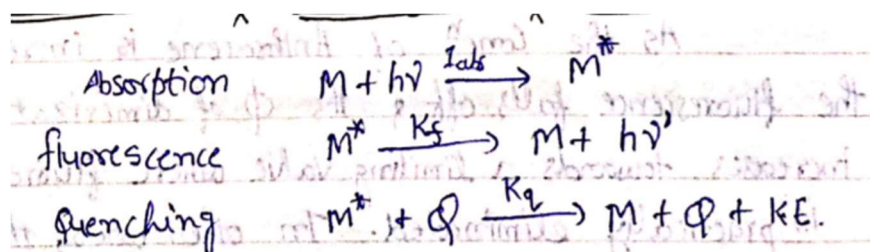


Thus, uranyl ions, UO_2^{2+} act as photosensitizer and are used over and over again.

4. **Application of photosensitizer 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 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 plates to the red light while neocyanine sensitizes the photographic plates even to the near infra-red radiations. Photographic emulsion which are sensitive to the near infra-red radiations have made night photography possible.

Quenching of Fluorescence: It has been found that 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 called **quenching of fluorescence**.

The substances responsible for stopping fluorescence are termed as quenchers (symbol Q for quencher). Following factors are responsible for quenching of fluorescence,



- Concentration of fluorescent atom and also of quenching substance.
- High pressure. The fluorescence of gases and vapours is quenched. The fluorescence of gases/vapours is usually quenched when the total gas pressure becomes even slightly

more than that at which collision between excited molecules and other molecules take place at time intervals shorter than 10^{-8} sec.

- (iii) In liquid medium, quenching occurs due to frequent collision.

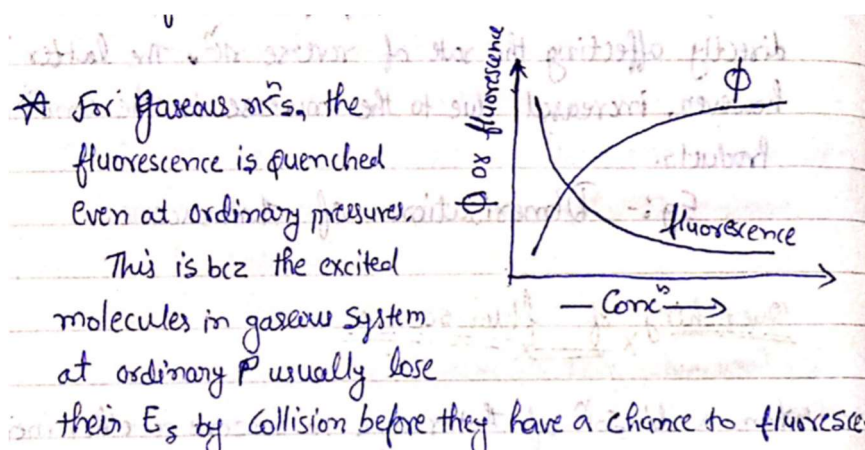
Example,

When a dil. solⁿ of Anthracene in benzene or other inert solvent, is exposed to UV light, the system exhibits fluorescence with a small ϕ of dimerisation etc².

As the concⁿ of Anthracene is increased, the fluorescence falls off, the ϕ of dimerization increases towards a limiting value where fluorescence is practically eliminated. In other words, the fluorescence is said to be quenched as the concⁿ of light absorbing substance is increased.

Explanation :- The natural life-time of an excited state in a molecule undisturbed by collisions is about 10^{-8} sec. At higher concⁿs, a molecule experience a large no. of collisions in 10^{-8} sec. Consequently, the excited molecule loses its E by collisions with other molecules before it has a chance to exhibit fluorescence.

As the concⁿ is decreased, the collision frequency decreases & the chance for the fluorescence is increased.

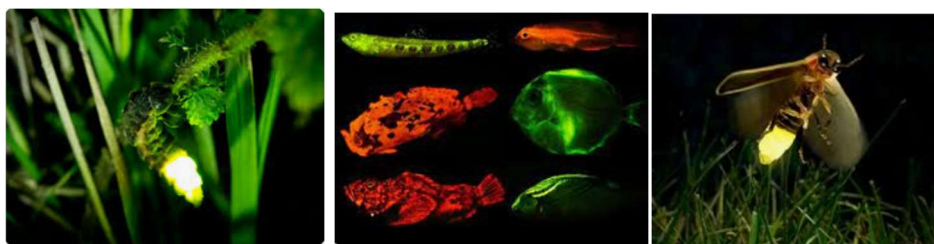


Role of photochemical reaction in the biochemical process:

- **Photochemical reactions** are chemical reactions that take place in the presence of light energy.
- **Biochemical processes** are chemical processes that take place in living organisms.
- There are some biochemical processes that need light energy and, in such cases, photochemical reactions are necessary for the successful completion of the biochemical process.
- Photosynthesis is one such biochemical process in which photochemical reactions take place.
- Photoreceptor Cell.

Chemiluminescence:

Energy can be transferred into (and out of) matter in many different ways, as heat, light, or by chemical reactions. When energy is released by matter in the form of light it is referred to as luminescence. It is defined "When energy in the form of light is released from matter because of a chemical reaction the process is called **chemiluminescence**". Or it can be defined "Some chemical reactions are accompanied by the emission of light, and the phenomenon is that of **chemiluminescence**". It is because one of the products formed is in the electronically excited which emits radiation of approximate wavelength in the visible region of spectrum. Several natural chemiluminescent phenomena are well known, among them *the light of glow worms* and *the light of the firefly*, *the glow of rotting fish*, the light emitted by some micro-



organisms in the course of metabolism.

Chemiluminescent emission may correspond to emission from the reactant or from products. Lucigenin may be oxidised by alkaline H_2O_2 under mild conditions to give a green chemiluminescence which is identical with fluorescent emission from lucigenin; the reaction is acting as a catalyst for decomposition of H_2O_2 , although the mechanism of electronic transition is not certain. A most remarkable chemiluminescent substance has recently been developed for possible commercial applications. Tetrakis (dimethyl amino) ethylene oxidises spontaneously in air to produce a very bright and long duration green chemiluminescence. Emission appears to be from excited molecules of the parent substance, how they obtain their energy is not clear. The material has been proposed for use, incorporated in a rope, as a safety light (e.g., for night time traffic accidents) which will become illuminated when an evacuated covering is torn off.

A better example of a chemiluminescent reaction is between nitrogen monoxide (symbol NO) and ozone (O_3). This reaction is routinely used to determine either ozone (using excess NO) or NO (using excess O_3). The reaction is shown in the following equations:

