→ Photochemistry :→

→ Introduction:→

- Photochemistry is the branch of chemistry which deals with the rates and mechanism of reactions resulting from the exposure of reactants to light radiations.

OR

Photochemistry deals with the study of chemical reactions which are caused by the absorption of light radiations (photons).

- Photochemistry includes reactions produced by all radiations of wavelengths ranging from γ-rays to radiowaves. But for practical purpose, the light radiations of the visible and ultraviolet regions lying between 800 nm to 200 nm wavelengths bring about such reactions. These reactions are called photochemical reactions.

→ Units and dimensions :→

- According to the modern convention, measurable quantities are expressed in SI units (System Internationalé) and replace the centimeter-gram-second (cgs) system.
- In SI system, unit of length is meter (m), the unit of mass is kilogram (kg) and the unit of time is second (s). All the other units derived from it.
- The unit of thermal energy, calorie, is replaced by joule ($1\,J = 10^7$ erg) to rationalize the definition of thermal energy. Thus, Planck's constant –

$$h = 6.62 \times 10^{-34}\ J\,s$$

- Velocity of light $c = 3.00 \times 10^8\ m\,s^{-1}$

- The wavelength of radiation λ is expressed in nanometers ($1\,nm = 10^{-9}\,m$). Therefore quantum energy of photon at 365 wavelength in SI unit can be expressed as -

$$E_{365} = h\nu \text{ or } \frac{hc}{\lambda} \quad \because \nu = \frac{c}{\lambda}$$

$$E_{365} = \frac{6.62 \times 10^{-34}\,Js \times 3.00 \times 10^{8}\,m\,s^{-1}}{365 \times 10^{-9}\,m}$$

$$E_{365} = 5.44 \times 10^{-19}\,J\,photon^{-1}$$

- An Avogadro number of photons is called an einstein. The amount of energy absorbed to promote one mole of anthracene molecules to the first excited state will be:

$$E_{365} = 5.44 \times 10^{-19}\,J\,photon^{-1} \times 6.02 \times 10^{23}\,photon\,mol^{-1}$$

$$= 3.27 \times 10^{5}\,J\,mol^{-1}$$

$$E_{365} = 327\,KJ\,mol^{-1}$$

This amount of energy is contained in one mole or one einstein of photons of wavelength 365 nm.

- The energy of an einstein of radiation of wavelength λ (in nm) can be calculated from the simplified expression

$$\boxed{\frac{1.196 \times 10^{8}}{\lambda}\,KJ\,einstein^{-1}}$$

- Rate of absorption is expressed in einstein per unit area per second.

$$\boxed{I_a = \frac{1.196 \times 10^8}{\lambda} \text{ einstein } m^{-2}\ s^{-1}}$$

- The energy of radiation is often expressed in terms of kilo-calorie per mole (kcal/mole). (1 calorie = 4.186 J).
- Sometimes, cm^{-1}, the unit of wavenumber is used to express energy. The proportionality constant hc, is implied, therein.
- The unit of electron-volt (eV) is used for single atom or molecule. A chemical potential of one volt signifies an energy of one electron volt per molecule.
- The intensity of incident flux from light source is in general defined in terms of power, i.e. watt per unit cross section (watt = Js^{-1}).

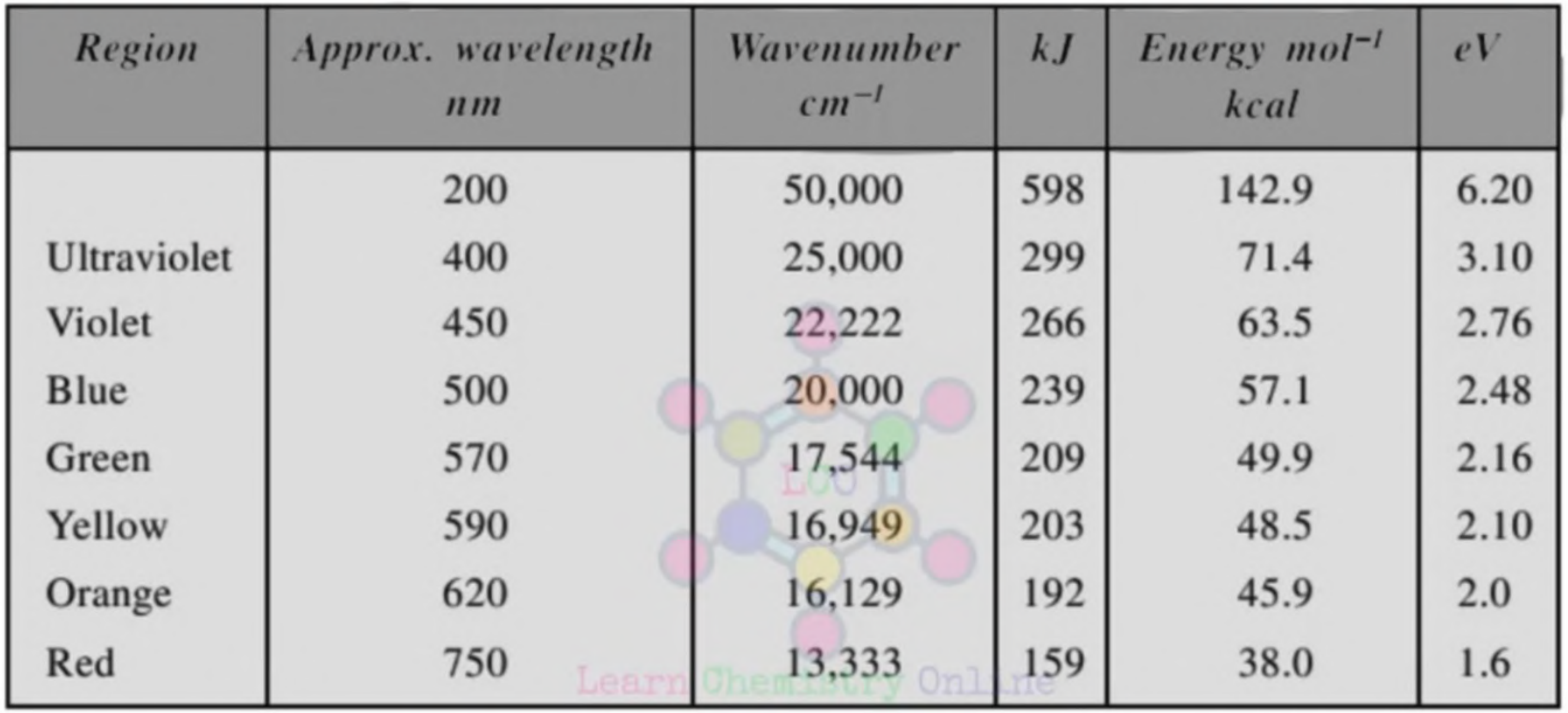
$$\boxed{\text{Power} = \frac{\text{watt}}{m^2} = \frac{J}{m^2 s}} \quad (\because \text{watt} = J s^{-1})$$

- Since power is energy per unit time and each photon has energy associated with it, intensity I can be expressed in number of quanta $m^{-2}\ s^{-1}$.

$$\boxed{I = \frac{n}{m^2 s}}$$

Also $$\boxed{I = \frac{\text{einstein}}{m^2 s}}$$

Table:- Energy of electromagnetic photon in the visible and UV region expressed in different units.



Region	*Approx. wavelength nm*	*Wavenumber cm^{-1}*	*kJ*	*Energy mol^{-1} kcal*	*eV*
	200	50,000	598	142.9	6.20
Ultraviolet	400	25,000	299	71.4	3.10
Violet	450	22,222	266	63.5	2.76
Blue	500	20,000	239	57.1	2.48
Green	570	17,544	209	49.9	2.16
Yellow	590	16,949	203	48.5	2.10
Orange	620	16,129	192	45.9	2.0
Red	750	13,333	159	38.0	1.6

→

$\lambda(nm) = \frac{c}{\nu} = \frac{1}{\nu}\ cm^{-1} = 10^{-9}\ m$

$1\ Cal = 4{\cdot}186\ J$

$1\ eV = 1{\cdot}6 \times 10^{-19}\ J$

$1\ cm^{-1}\ mol^{-1} = 2{\cdot}859\ Cal\ mol^{-1} = 0{\cdot}0135\ KJ\ mol^{-1}$

$1\ eV\ mol^{-1} = 23{\cdot}06\ Kcal\ mol^{-1} = 96{\cdot}39\ KJ\ mol^{-1}$

→ Interaction of radiation with matter:→

- The interaction between light and matter is the basis of all life in this world. Even our knowledge of physical world is based on such interactions, because to understand matter we have to make use of light, and to understand light we must involve matter.
- Light means the complete spectrum of the electromagnetic radiation from radioactive rays to radio waves. hence light and radiation have been used synonymously.
- For example, we use x-Ray to determine the structure of molecules in their crystalline state, and we use various spectroscopic method to understand architecture of atoms or molecules. on the other hand, we study the nature of light by falling it on surface of matter. Matter reflects, trasmits, scatters or absorbs it and allowing us to understand its behaviour.
- A beam of light in dark room will not be visible to us unless it is scattered by dust floating in air. A microscope will view a particle only when incident light is scattered by particle. All light measuring devices are based on such interactions.
- In some of these interactions, light behave as particle and in some others its behaviour like wave. Therefore, to obtain basic understanding of the interaction of light with matter, we must first understand the nature of radiation and nature of matter.

① Wave nature of radiation:→

- According to Maxwell's theory of electromagnetic radiation, light travels in space in the form of oscillating electric field. This field is generated by the accelaration or deceleration of charged particle which acts as the source of the radiation.

- An oscillating electric field generates a magnetic field at right angle to itself as well as to the direction of propagation.
- The magnetic field oscillates in phase with the electric field and the magnetic vector is directed perpendicular to the electric vector.
- The electic vector is directed along the displacement direction of the wave called the direction of polarisation. The plane containing the displacement vector is the plane of polarisation. A plane polarised light is oscillates only in one plane.

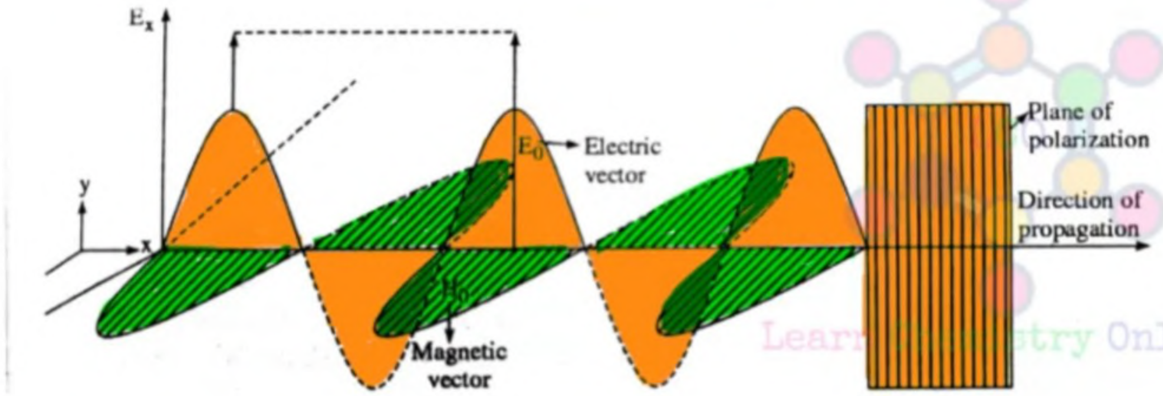


Fig:- Nature and propagation of plane polarised electromagnetic radiation.

② Particle nature of radiation:→

- The idea that light travels as photons was originated by Einstein in 1905.
- A particle is defined by its mass m and its momentum p or energy E. The particle nature of light is visualised in the form of a wave packet or a quantum of radiation whose energy is given by the relation $E = h\nu$.

- One quantum of radiation is called photon. The energy of photon is given by Einstein's equation, $E = mc^2$. where m = mass of a photon and c is the velocity of light in vacuum.
- Combining both the equation, we obtain.

$$mc^2 = h\nu$$

$$\boxed{mc = \frac{h\nu}{c} = \text{momentum of photon}}$$

③ Dual nature of matter:→

- In 1924, de Broglie emphasised the dual nature of matter and obtain an expression similar to that of the light wave in which de Broglie's wavelength λ for the electron wave is related to the momentum p of the particle by planck's constant.

$$\boxed{\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(E-V)}}}$$

E = Total energy V = Potential energy

- An expression for describing such a wave motion was obtained by Schrodinger in 1925.

$$\boxed{\frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m(E-V)}{h^2}\psi = 0}$$

where :- x, y, z → three coordinates
ψ → wave function.
h = Planck's constant

→ Difference between thermal and photochemical processes :→

Thermochemical reactions/process	Photochemical reactions/process
1. These involve either the absorption or evolution of heat.	1. These involve absorption of light.
2. In these reactions, the molecules even after aquiring activation energy, remain in the ground state.	2. In these reactions, an individual molecule is raised to first electronically excited state.
3. The rate of reaction depends upon temperature.	3. The rate of reaction depends upon intensity of light absorbed.
4. For these reactions ΔG (free energy change) is always negative.	4. ΔG (free energy change) may not always be nagative.
5. These reactions generally give *stable products*.	5. These reactions often yield highly strained and thermodynamically *unstable products*.
6. The rates of these reactions are usually accelerated by the *catalyst*.	6. Some photochemical reactions are initiated by the *photosensitizers*.
7. The product formed depends upon the chemistry of ground state molecules, e.g., *trans*, *trans*-2, 4-hexadiene on heating gives *trans*-3, 4-dimethylcyclobutene.	7. The product formed depends upon the chemistry of excited state molecules, e.g. *trans*, *trans*-2, 4-hexadiene on irradiation gives *cis*-3, 4-dimethylcyclobutene.

→ Laws of photochemistry:→

1. Grotthus – Draper law:→

- This is first law of photochemistry.
- This law is also called principle of photochemical activation.
- This law was discoverd by Grotthus in 1818 and proved by J.W. Draper in 1841 on the basis of photochemical reaction between hydrogen and chlorine.
- According to this law, " When light falls on any substance, only the 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 effect."

OR

" Only that light which is absorbed by a system can cause chemical change."

- All light radiations which are absorbed by reacting system are not effective in producing desired chemical reactions. When conditions are not favourable for the molecules to react, some portion or the whole light absorbed by reacting substances is converted into heat in some cases. While in other cases, the absorbed light is re-emitted as radiations of the same or another frequency.
- Grotthus – Draper law is purely qualitative. It does not give any relationship between the amount of light absorbed by a system and the number of molecules which have reacted.

2. Stark – Einstein law:→

- It is also called law of photochemical equivalence.

- According to quantum theory of light, energy is absorbed or emitted only in small packets of quanta. Energy of one quanta is

$$\boxed{E = h\nu}$$

where h = Planck's constant
ν = Frequency of light

- In 1905, Einstein applied quantum theory to photochemical reactions and discovered the law of photochemical equivalence which states that –

  "When an atom or molecule absorb light of a given frequency, it absorbs one quantum only."

- The photochemical importance of the above law emphasised in 1909 by Stark and other.
- In 1913, Einstein considered the work of Stark and restated his law as–

  "Each molecule which takes part in a chemical reaction absorbs one quantum of light which induces the reaction." or briefly "one molecule one quantum."

- The term one photon (or one quantum) means energy equal to $h\nu$.

$$AB + h\nu \longrightarrow AB^*$$

Thus in the primary process, the number of molecules that are activated is equal to the number of quanta absorbed. Therefore amount of energy F, for activation of 1 mole will be

$$\boxed{E = Nh\nu}$$

where N = Avogadro number

✱ This quantity of energy 'E' absorbed per mole of the substance is called an Einstein.

→ Jablonski diagram:→

→ Terminology:→

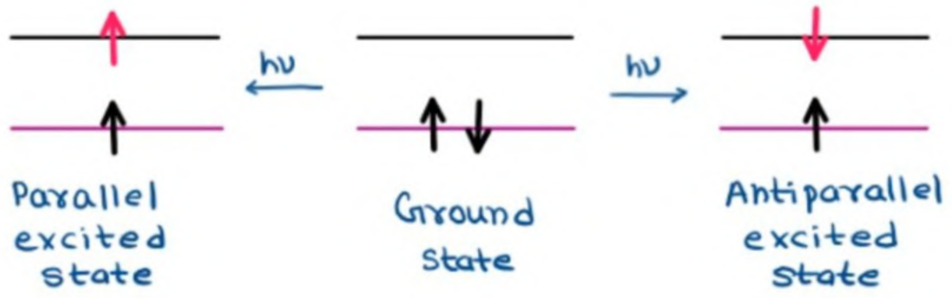
- Most molecules have an even number of electrons and thus in ground state, all the electrons are spin paired.
- The quantity 2S+1 is known as spin multiplicity of a state. where S is total electron spin.
- When the spins are paired (↑↓), the upward orientation of the electron spin is cancelled by the downward orientation so that S=0

$$s_1 = +\frac{1}{2} \; ; \; s_2 = -\frac{1}{2} \text{ so that } S = s_1 + s_2 = \frac{1}{2} - \frac{1}{2} = 0$$

$$\text{Hence} \quad 2S+1 = 2\times 0 + 1 = 1$$

Thus, the spin multiplicity of the molecule 1. i.e. the molecule is in singlet ground state.

- When by the absorption of a photon of a suitable energy hν, one of the paired electrons goes to a higher energy level (excited state), the spin orientations of the two single electrons may be either parallel ↑↑ or antiparallel ↑↓



- If the spins are parallel, then

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

Thus, the spin multiplicity of the molecule is 3. i.e. the molecule is in the triplet excited state.

- If the spins are antiparallel, then

$$S = s_1 + s_2 = \frac{1}{2} - \frac{1}{2} = 0 \text{ so that } 2S+1 = 2 \times 0 + 1 = 1$$

Thus, the spin multiplicity of the molecule is 1. i.e. the molecule is in the singlet excited state.

- Since the electron can jump to any of the higher electronic states depending upon the energy of the photon absorbed. We get a series of singlet excited states and triplet excited states.

S_n where $n = 1, 2, 3, 4 \ldots$; $S_1, S_2, S_3, S_4 \ldots$; First singlet excited state ------

T_n where $n = 1, 2, 3, 4 \ldots$; $T_1, T_2, T_3, T_4 \ldots$; First Triplet excited state ----

✯ (The symbol S in S_n should not be confused with S used for denoting the total spin)

- It has been shown quantum mechanically that a singlet excited state has higher energy than the corresponding triplet excited state.

$$E_{S_1} > E_{T_1} \quad ; \quad E_{S_2} > E_{T_2} \quad ; \quad E_{S_3} > E_{T_3} \text{ and so on}$$

→ Jablonski diagram :→

- Jablonski diagram explains about the consequences of excited molecules. i.e. This diagram is pictorial illustration of different energy states.
- When a molecule absorbs ultra violet light radiations, it gets excited, and promotes from ground state (S_0) to excited singlet state, S_1 or S_2 or higher singlet state, S_3.

In the above state, the molecule collides with neighbouring molecules, and after about 10^{-13} to 10^{-11} second it comes back rapidly to the S_1 state and releases energy to the environment. This entire process is called "energy cascade".

- The lifetime of singlet excited state, S_1 is relatively long, therefore this state can undergo different physical and chemical processes, like–

(a) Fluorescence

(b) Internal conversion (IC).

(c) Triplet state

(d) Inter system crossing (ISC).

(e) Phosphorescence etc.

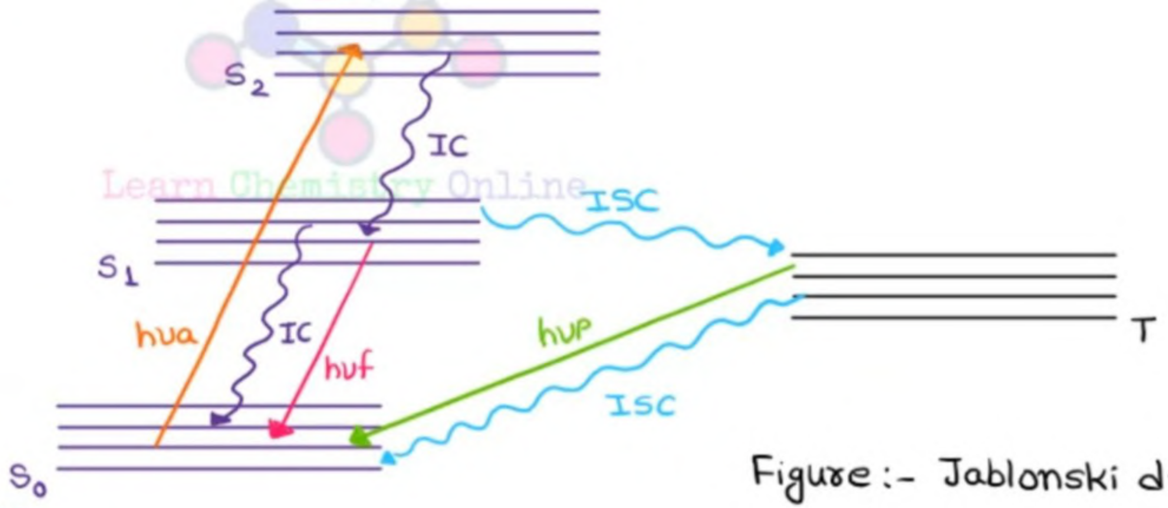


Figure :- Jablonski diagram

where :-

S_0 = Singlet ground state
S_1 & S_2 = Excited singlet states
T = Triplet state
$h\nu_a$ = Energy absorbed
$h\nu_f$ = Energy lost as fluorescent light
$h\nu_p$ = Energy lost as phosphorescent light

1. A molecule returs to its ground state (S_0) from its excited state (S_1) or (S_2) by giving up its energy as heat. This process in known as internal conversion (IC).
2. A molecule returs to its ground state (S_0) from its excited state (S_1) or (S_2) by emitting off energy in the form of light radiation within 10-9 seconds. This process is known as fluorescence.

   The process is relatively slow, hence it is not very common pathway in most of the compounds. Smaller molecules (e.g. diatomic) and the rigid molecules (e.g. aromatic compounds) are main examples of this process.

   The emitted fluorescent light is of slightly lower energy than absorbed light. hence has longer wavelength.
3. The energy of excitation is transfered to another molecule, which is therefore raised to an excited singlet state.
4. Some molecules from S_1 state may drop to triplet state (T_1). This transition is radiationless. This process is called intersystem crossing (ISC).

   The first excited triplet state (T_1) is more stable, because it has lower energy than the first excited singlet state. Hence ISC process is an energetically down hill process.
5. After sometime, i.e. 10^{-4} to several minutes, the triplet state also drops to the ground state (S_0) by emitting a photon of light. The wavelength of emitted light is longer than that of absorbed light radiation. This process is called phosphoresence.

The decay of excited triplet state to the ground state is due to collision of neighbouring molecules, or with the vessel walls.

6. In some cases, the excited molecules dissociates instead of vibrating.
7. As triplet state is more stable than singlet state, therefore triplet state can undergo chemical reaction more rapidly than singlet state. Hence photo-chemistry is largely the chemistry of triplet state.

- The following physical processes occur by excited molecules:-

States	Physical Process
$S_0 + h\nu \rightarrow S_1$	Excitation singlet state
$S_1 \rightarrow S_2 + \text{heat}$	Vibrational relaxation
$S_1 \rightarrow S_0 + h\nu$	Fluorescence
$S_1 \rightarrow S_0 + \text{heat}$	Internal conversion(IC)
$S_1 \rightarrow T$	Intersystem crossing(ISC)
$T \rightarrow T + \text{heat}$	Vibration relaxation
$T \rightarrow S_0 + \text{heat}$	ISC
$T \rightarrow S_0 + h\nu$	Phosphorescence

→ Non-radiative and radiative processes :→

1 Non-radiative processes or transitions :→

- These transitions involve the return of activated molecule from the higher excited states (S_3, S_2 or T_3, T_2) to the first excited state (S_1 or T_1). These transitions do not involve the emission of any radiations and are thus referred to as non-radiative or radiationless transitions.

Example :- Internal conversion (IC) and Inter System Crossing (ISC).

2. Radiative processes or transitions :→

- These transitions involve the return of activated molecule from the singlet excited state S_1 and triplet excited state T_1 to the ground state S_0. These transitions involve the emission of radiations and are thus referred to as radiative processes or transistions.

Example :- Fluorescence and Phosphorescence

→ Fluorescence :→

- When the light radiation is absorbed by a compound, its electron goes to higher energy level from lower energy level. From this level, electron returns to normal position either directly or in steps with the emission of light energy. When this emission of is instantaneous (10^{-8} sec.) the phenomenon is known as fluorescence.
- When a beam of light is incident on certain substances, they emit visible light or radiation and they stop emitting light or radiation as soon as the incident light is cutoff. This phenomenon is known as fluorescence. Such substances are called fluorescent substances.

→ Characteristics of fluorescence :→

- This phenomenon is instantaneous and starts immediately after the absorption of light and stops as soon as the incident light is cut off.
- Fluorescence is stimulated by light of the visible or ultravoilet regions of the spectrum. Line, band and continuous spectra of emitted light of fluorescence are observed. The character of spectrum depends of substance.
- It is general pheomenon and is exhibited by gases, liquids and solids. No fluorescence will be observed in gases, unless the pressure is low.
- Different substance fluoresce with light of different wavelengths. Thus fluorspar fluoresces with blue light, chlorophyll with red light, uranium glass with green light and so on.
- The fluorescent light from solution is polarised and degree of polarisation depends in some cases upon the concentration of solution.
- The extent of fluorescence depends upon the nature of the solvent and the presence of certain anion such as thiocyanate, iodide and bromide ion in solution.

- According to Stoke's law, during fluorescence, light is absorbed at certain wavelength and should be emitted at a greator wavelength.
- Fluorescence may be regarded as secondary effect resulting from the primary process of a quantum of light by a atom or molecule.

→ Types of fluorescence :→

1. Resonance fluorescence :→

- In resonance fluorescence, wavelengths of emitted and incident light are same.

  Example :→ Mercury

2. Senstized fluorescence :→

- When the fluorescence of some compounds and metal reagents is enhanced by adding some other foreign matter, the resulting fluorescence is known as senstized fluorescence.

  Example :→ Zn, Cd, Th or alkali metals added with Hg vapour.

3. Slow fluorescence :→

- When the emission of radiation occurs after some time, then it is called slow fluorescence.

  Example:- solid compounds.

→ Fluorescence producing compounds :→

- Fluorine, petroleum, uranium salts, Anthracene, Napthalene, Eosein, fluorescein, chlorophyll, Vinyl sulphate, sodium, mercury, acetone, vapours of iodine solution, aniline, azophenanthrene, acridine derivative, vitamin A, fluorite (The name fluorescence orignate from it), nitrogen peroxide etc.

→ Factors affecting fluorescence :→

- Only such compounds show this phenomena which are able to absorb ultra violet or visible radiation.
- Absorption of light radiation ∝ intensity of fluorescence.
- Compounds containing conjugated double bonds show fluorescence.
- Electron-donating groups like $-NH_2$ and $-OH$ often enhance fluorescence. Groups like $-SO_3H$, $-NH_4^+$ and alkyl groups do not have much effect on fluorescence.
- Electron-withdrawing groups like $-COOH$, $-NO_2$, $-N=N-$ and halides decrease or even destroy fluorescence.
- If a high atomic number atom is introduced into a π-electron system. it decrease fluorescence.
- The pH shows a marked effect on the fluorescence. For example, the neutral or alkaline solution of aniline shows fluorescence in the visible region. But if the solution is acidified, the visible fluorescence disappears (aniline shows fluorescence in the ultraviolet region regardless of pH).

→ Measurement :→ By using fluorometer ond fluorophotometer.

→ Applications of fluorescence :→

- Detection of uranium in salts.
- Detection of some inorganic ions such as ruthenium ion, Al^{+3}.
- Detection of B, Cd, Ca etc.
- Determination of vitamin B_1 and B_2 in food stuffs

- For detection of ringworms in animal body.
- Analysis of Drugs, dyes, medicine, fuels, chemical etc. and in paper industry, textile industry, bacteriology.
- In lamps and as fluorescent indicators.
- In qualitative and quantitative analysis.

→ Phosphorescence :→

- When the light is absorbed by a compound, the electron goes to a higher energy level from the lower energy level. From this level, the electron returns to the normal position by emitting the light energy. When this emission of light observed after some time (10^{-3} sec.), It is known as phosphorescence.
- Phosphorescence is also termed as slow fluorescence. It is mainly shown by solid compounds.
- When light radiation is incident on certain substances, they emit light continuosly even after the incident light is cut off. This type of delayed fluorescence is called phosphorescence and the substances are called phosphorescent substances.

→ Characteristics of phosphorescence :→

- The life-time of phosphorescence is much longer than fluorescence.
- The phenomenon of phosphorescence is caused by ultraviolent and visible region of spectrum.
- Phosphorescence is mainly shown by solid compounds.
- The magnetic and dielectric properties of phosphorescent substances are different before and after illumination.
- The time for which the light is emitted from phosphorescent substance depends upon the nature of substance and somtimes on temperature changes.

→ Phosphorescence producing compounds :→

- Sulphides of calcium, barium and strontium.
- Minerals, e.g. ruby and emerald.
- Many organic compound containing conjugated ring system.

→ **Facturs affecting phosphorescence :→**

- Only such molecules show phosphorescence which are able to absorb ultraviolet or visible radiations.
- Electron-donating groups like $-SO_3H$, $-NH_4^+$ and alkyl groups do not have much effect on phosphorescence.
- If a high atomic number atom is introduced into a π-electron system, it enhances phosphorescence.
- Temperature also affects phosphorescence, but good phosphorescence is obtained at room temperature.

→ **Measurement :→** Measured by phosphoremeter.

→ **Applications of phosphorescence :→**

- Determination of aspirin in blood serum.
- Determination of low concentrations of procaine, cocaine, phenobarbital and chloropramazine in blood serum.
- Determination of cocaine and atropine in urine.
- Phosphorimetry has been employed in combination with thin layer and paper chromatography.

→ Quantum yield :→

- The efficiency of a photochemical reaction is expressed in terms of quantum yield or quantum efficiency. It is denoted by ϕ.
- It is defined as the number of molecules reacting per quantum of light absorbed.
- Quantum yield is a relationship between the number of photon absorbed and number of molecules taking part in a photochemical reaction.
- Mathematically, this quantity is defined as follows :-

$$\text{or} \quad \phi = \frac{\text{No. of molecules reacting in given time}}{\text{No. of quanta absorbed in same time}}$$

$$\text{or} \quad \phi = \frac{\text{No. of moles reacting in given time}}{\text{No. of Einsteins absorbed in same time}}$$

$$\text{or} \quad \phi = \frac{\text{Rate of chemical reaction}}{\text{No. of Einsteins absorbed}}$$

- The concept of quantum yield or quantum efficiency was introduced by Einstein.
- If Stark-Einstein law is correct, the value of ϕ should always be unity. However, later on, it was realised that the law of photochemical equivalence (Stark-Einstein law) is applicable to only primary processes.

→ High quantum yield and Low quantum yield :→

- For several photochemical reactions, the high quantum yield is 10^6 and low quantum yield is 10^{-2}.

→ Reason for low quantum yield :→

- The excited molecules may get deactivated before they form product.
- The primary photochemical process may get reversed.
- Collision of excited molecules with non-excited molecules takes place during the reaction. In this process, the excited molecules may lose their energy and cause low quantum yield
- The dissociated fragments of reacting molecules may recombine to form original molecule.

→ Reason for high quantum yield :→

- The primary process of absorption of radiation produces excited free radicals which gives chain reaction, it causes high quantum yield.
- With the formation of excited free radicals in the primary process, they undergo secondary process. Each secondary process again generates excited free radicals. Thus by absorbing only one quantum of radiation, several reactant molecules undergo chemical reaction. Therefore, quantum yield will be higher than unity.

→ Measurement of quantum yield :→

- Quantum yield or quantum efficiency is an important quantity in photochemistry. It provides essential information regarding nature & mechanism of photochemical reaction. Hence, it is important to measure quantum yield in the study of photochemical reactions.

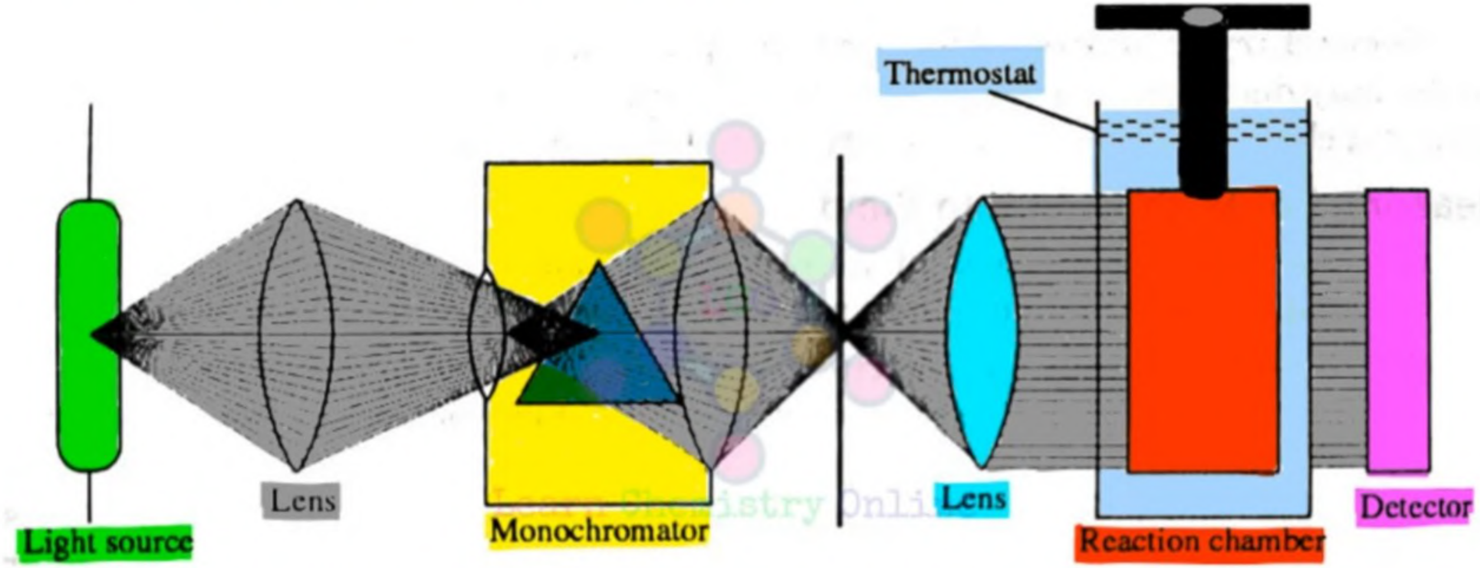


Fig:- Measurement of quantum yield.

- The experimental setup used for the measurement of quantum yield of a photochemical reaction consists of the following parts:-

(1) Light source
(2) A Monochromator
(3) Reaction chamber
(4) Detecter

(1) Light source :→

- A suitable light source such as, sun light, mercury vapour lamp or tungsten lamp etc. is used to provide radiation of required wavelength.
- If visible light is used, then high intensity xenon arc lamp or tungsten lamp is preferred.
- For ultra violet radiation, medium or low pressure mercury lamps are used.

(2) Monochromator :→

- Measurement of quantum yield of a photochemical reaction requires light of a constant wavelength, i.e. monochromatic light. As all light sources emit light of various wavelengths, which are mixed together, therefore, it becomes necessary to use filter or monochromator, which can provid light of a single wavelength.
- The monochromator used for this purpose, are generally prisms or filters.

(3) Reaction chamber :→

- For visible radiation, glass reaction chambers are used.
- For UV radiation, quartz reaction chamber are used.
- The temperature of reaction chamber is maintained constant with the help of thermostat.
- For the measurement of a rate of reaction, a suitable device is attached with reaction chamber.

(4) Detecter :→

- Detecter is used to measure intensity of transmitted light (light coming out from reaction chamber). Following devices are used for detection of the intensity of transmitted light :-

(a) Photoelectric cell:→

- Photoelectric cells are based on photoelectric effect and convert transmitted light energy into electrical energy.
- The electric current proudced by a photoelectric cell is proportional to the intensity of radiation to which it is exposed.
- The photoelectric cell consist of a piece of lithium, which is attached to electrometer.

(b) Radio- micrometer:→

- It consists of a couple of two unlike metals e.g. Bi and Ag. connected in a rectangular loop, suspended between the poles of an electromagnet.
- When transmitted light is fall on metal couple, it heated and induce a current to flow in a rectangular circuit.
- The current flowing in the circuit produces a magnetic field which interacts with the field of electromagnet. As a result of this, the rectangular loop gets deflected by a certain angle which is proportional to the intensity of light falling on the couple. The angle of deflection is measured by lamp and scale arrangement.

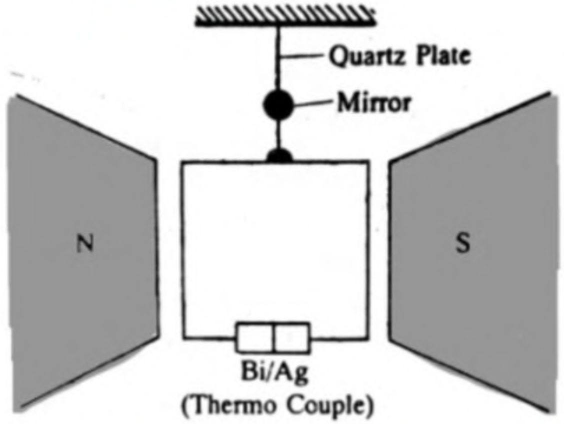


Fig:- Radio micrometer

(c) Thermoplile:→

- This device measures intensity of transmitted light to a high degree of accuracy.

- This device consists of a large number of junctions of two unlike metals i.e. thermopile, connected to a electrometer.
- when radiations fall on the junctions, they are converted into heat and a current is produced which is proportional to the intensity of incident light. The electric current is measured by a electrometer or by some other suitable devices.

→ Procedure:→

- The monochromatic light is first passed througth the empty reaction chamber from the source, and the intensity of light is measured by the detector.
- Now the reactants are taken into the chamber and same light is again passed through the chamber. The reactants absorb radiation and a photochemical reaction is induced in the reaction chamber. The rate of reaction is measured by a suitable technique. The intensity of light coming out of the reaction chamber is again measured. The difference of the two intensities gives the intensity of absorbed radiation.
- By knowing the rate of reaction, wavelength of light and intensity of absorbed radiation quantum yield of the reaction can be calculated using following formula:-

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

$$\boxed{\phi = \frac{dx/dt}{I_a}}$$

→ Photosensitised reaction - energy transfer processes :→

- Certain reactions are known which are not sensitive to light. These reactions can be sensitive by adding a small amount of foreign material which can absorb light and stimulate the reaction without itself taking part in the reaction. Such an added material is known as photosensitiser and the phenomenon as photosensitisation.
- Atomic photosensitiser are mercury, cadmium and zinc.
- Molecular photosensitiser are benzophenone and sulphur dioxide.
- The photosensitiser absorbs light and becomes excited and then pass on this energy to one of the reactants and thereby activate them for reaction, without itself taking part in the reaction. Thus, a photosensitiser acts as carrier of energy.
- The reaction depicting photosensitisation may be represented as:-

$$D + h\nu \longrightarrow {}^{1}D$$

$${}^{1}D \xrightarrow{ISC} {}^{3}D$$

$${}^{3}D + A \longrightarrow D + {}^{3}A$$

$${}^{3}A \rightarrow \text{product (photosensitisation)}$$

Where D = photosensitiser

A = Reactant

- It may be noted that the triplet excited state of the sensitiser must be higher in energy than the triplet excited state of the reactant so that the energy available is enough to raise the reactant molecule to its triplet excited state.
- Photosensitisation was discovered by Franck and Cario in 1922.

→ Examples of photosensitised reactions :→

1. Photosynthesis in plants :→

- Photosensitiser → Chlorophyll

$$CO_2 + H_2O + light \longrightarrow \frac{1}{n}(CH_2O)_n + O_2$$

2. Dissociation of H_2 molecule :→

- Photosensitiser → Mercury

$$Hg + h\nu \longrightarrow Hg^*$$
$$Hg^* + H_2 \longrightarrow H_2^* + Hg$$
$$H_2^* \longrightarrow 2H$$

3. Dissociation of Ethylene :→

- Photosensitiser → Mercury

$$Hg + h\nu \longrightarrow Hg^*$$
$$Hg^* + C_2H_4 \rightarrow C_2H_4^* + Hg$$
$$C_2H_4^* \longrightarrow C_2H_2 + H_2$$

4. Decomposition of Diazomethone :→

- Phosensitiser → Benzophenone (Bz)

$$Bz + h\nu \longrightarrow Bz^*$$
$$Bz^* + CH_2N_2 \longrightarrow CH_2N_2^* + Bz$$
$$CH_2N_2^* \longrightarrow CH_2 + N_2$$

5. Isomerisation of 2-Butene :→

- Photosensitiser → SO_2

$$SO_2 + h\nu \longrightarrow SO_2^*$$

$$SO_2^* + \text{Cis 2-Butene} \longrightarrow \text{Cis 2-Butene}^* + SO_2$$

$$\text{Cis 2-Butene}^* \longrightarrow \text{trans 2-Butene}$$