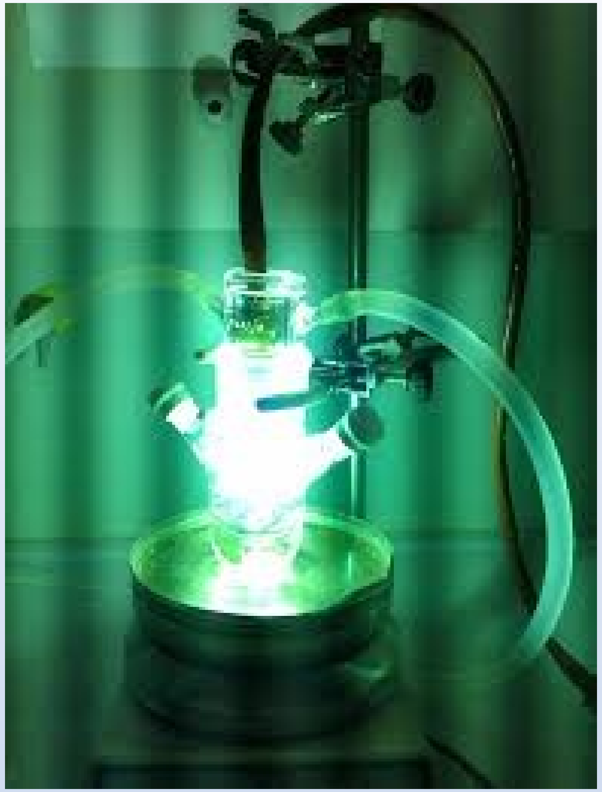
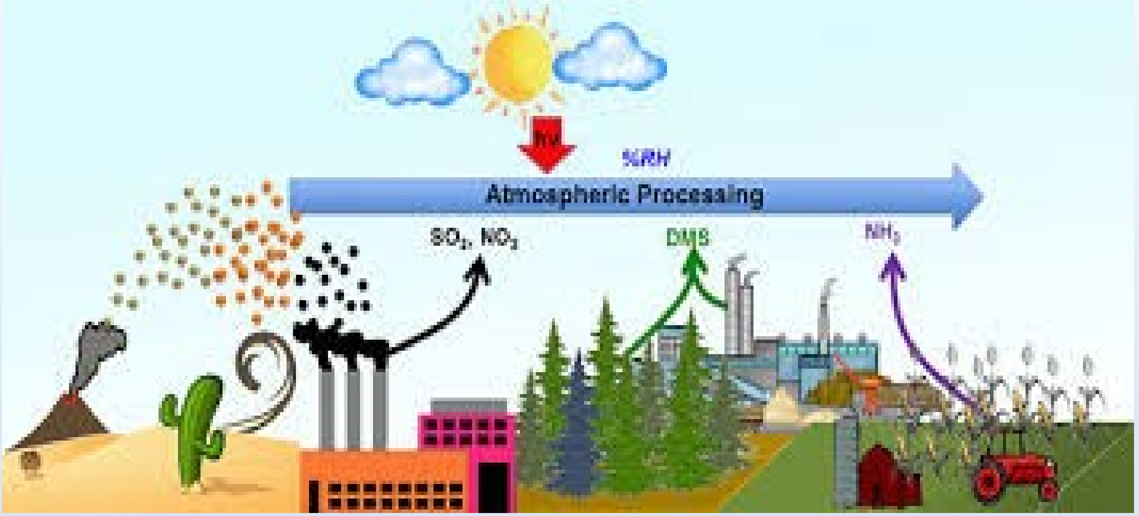
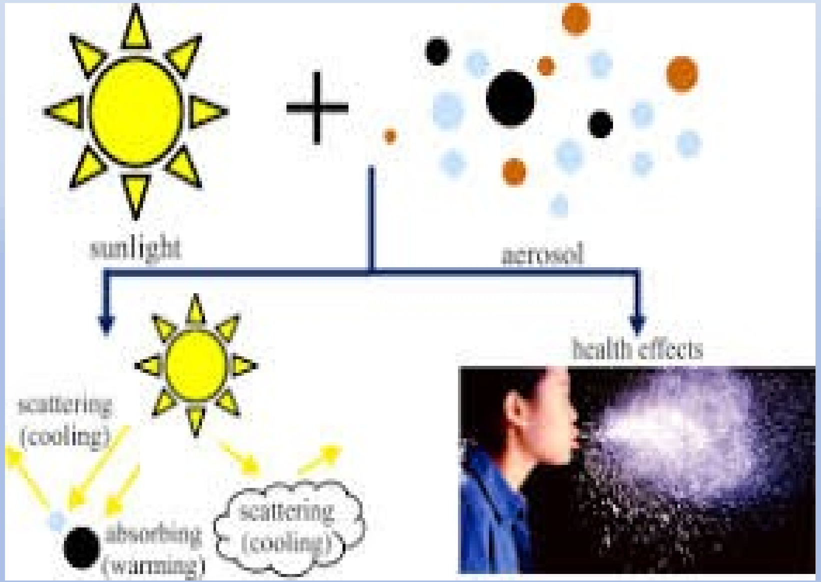
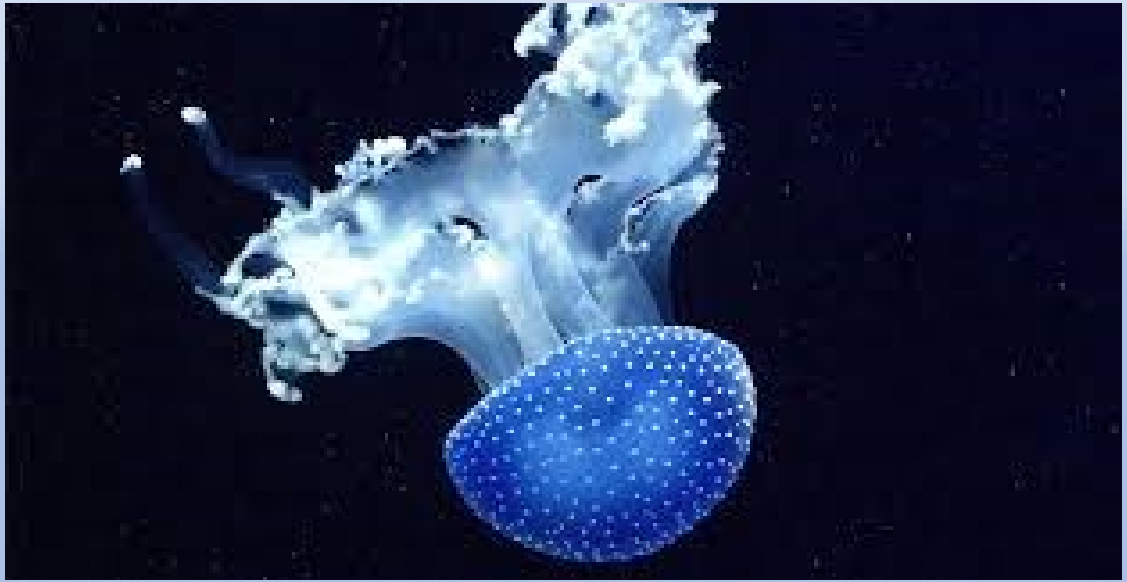




PHOTOCHEMISTRY

Dr. Sangeeta Kumar, Dept. of Chemistry





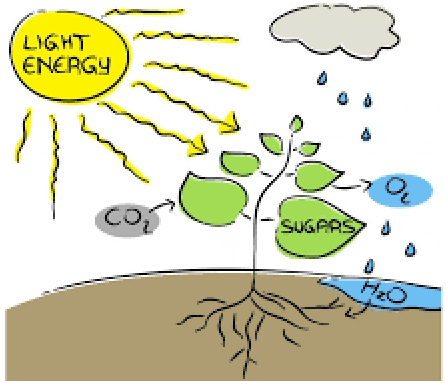
PHOTOCHEMISTRY

- Physical or chemical processes taking place in presence of light are called photochemical reactions. Usually such reactions take place in the region of 200nm to 800nm.

A few examples of photochemical reactions are:

1) Photosynthesis.

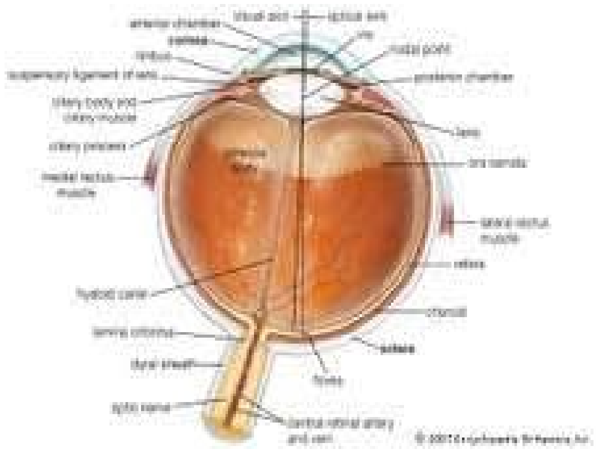
The most important process which sustains life.



2)Perhaps life on earth started due to photochemical reactions. With sun as the central figure, simple molecules like CH_4, NH_3, CO_2, H_2O etc must have undergone complex photochemical changes to form proteins and nucleic acids which is the basis for life.

PHOTOCHEMISTRY

3)We see because our eyes contain Rhodopsin, which is light sensitive.
Our eyes have rod cells and cone cells
which enable us to see. We perceive the light and
colours.

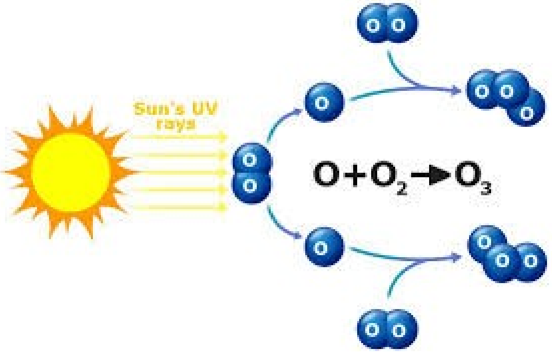


4)Many chemicals or compounds are produced photochemically which could not be produced from dark reactions:

a) Synthesis of antioxidants by photosulphonation.

b) Synthesis of vitamin D

c) Manufacture of cleansing solvents, insecticides and halogenated aromatics by photochlorination.



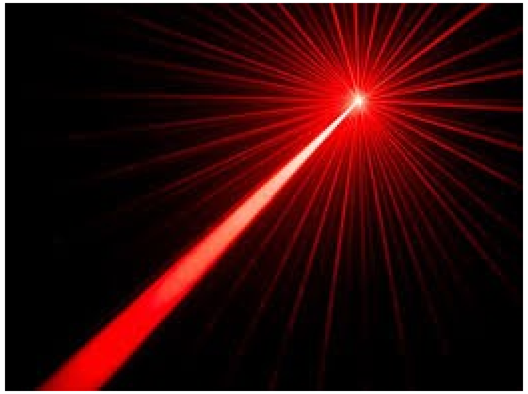
5) Formation of ozone from oxygen in stratosphere in sunlight. This ozone layer forms an umbrella which protects us from harmful UV radiation.

6) Formation of smog.

Photochemical smog is produced when sunlight reacts with nitrogen oxides and at least one volatile organic compound (VOC) in the atmosphere. Nitrogen oxides come from car exhaust, coal power plants, and factory emissions. VOCs are released from gasoline, paints, and many cleaning solvents. When sunlight hits these chemicals, they form airborne particles and ground-level ozone—or smog.

7) Fluorescence and phosphorescence find use in X-Ray and TV screens, fluorescent tube lights, CFLs, dials in watches….

8) LASERS are used in surgeries, in measuring distances between heavenly bodies etc



9) Solar panels and batteries are a boon as a renewal source of energy. The principle of photovoltaic difference is used to generate electricity.

10) Older cameras as well as digital cameras use the principle of absorption of light.

11) Photochromatic glasses use light to darken and become colourless when in dark.

The broad reaction is as follows:

$$\mathbf{Cu + Ag^{+} \xrightarrow{light} Cu^{+} + Ag}$$

12) Optical brighteners like Ujala, Neel and Tinopal are used to brighten white clothes.

13) Paints in advertising hoardings.

14) Decomposition of Ammonia in atmosphere to form nitrogen and hydrogen is a photochemical process.

What is interesting is that decomposition of ammonia, ozone formation and photosynthesis take place with increase in Gibb's Free Energy.

DIFFERENCE BETWEEN THERMOCHEMICAL AND PHOTOCHEMICAL REACTIONS

THERMOCHEMICAL REACTIONS	PHOTOCHEMICAL REACTIONS
1.These reactions involve absorption or evolution of heat.	These involve absorption of light radiations.
2. These reactions can take place in dark as well as in light.	The presence of light is the primary requirement for reactions to take place.
3. Temperature has a significant effect on the rate of a thermochemical reaction.	Temperature has a very little effect on the rate of photochemical reaction.
4. ΔG for thermochemical spontaneous reactions is always negative.	ΔG for photochemical reactions may be positive or negative
5. Thermochemical activation is not selective in nature. The energy needed is in the range of 10^4 to 10^5 cals per mole.	Photochemical activation is highly selective. The absorbed photon excites a particular atom or group of atoms which become site for the reaction. The energy of radiation of wavelength 200nm to 800nm varies from 23 to 230 kcals per mole.
6. They are simple in nature	They are complex in nature.

LAWS OF PHOTOCHEMISTRY

LAMBERT'S LAW

When a monochromatic beam of radiation is passed through a homogeneous medium, the decrease in the intensity of light with thickness of absorbing medium at any point X is proportional to the intensity of the incident light at the point X . Mathematically,

$$-dI/dx \propto I$$

$$\text{or, } -dI/dx = kI \qquad (1)$$

where dI is the is the small decrease in intensity of the light on passing through small thickness dx. The constant of proportionality k is called the ***Absorption coefficient,*** depending upon the nature of absorbing medium.

Equation (1) can be written as

$$dI/I = -kdx \qquad (2)$$

When $x=0$, $I=I_0$

$x=x$, $I=I$

Integrating equation (2) between the limits

$X=0$ and $x=x$ and $I=I_0$

$$\ln I/I_0 = -kx \qquad (3)$$

or, $I/I_0 = e^{-kx}$

or, $I = I_0 e^{-kx}$ (4)

This equation expresses how the original intensity I_0 is reduced to intensity I after passing through a thickness x of the medium .

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

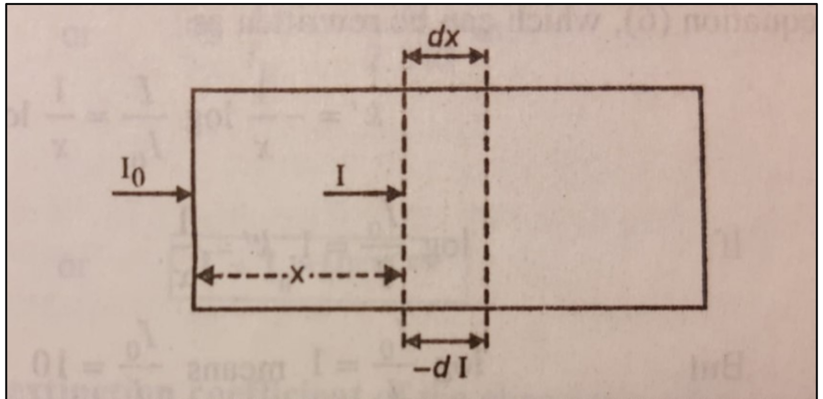


FIGURE 4.1.

Fall of intensity on passing through a medium.

Equation (3) can be rewritten as

$2.303 \log I/ I_0 = -kx$ or $\log I/ I_0 = -kx/2.303$

or $\log I/ I_0 = -k'x$ or $I/ I_0 = 10^{-k'x}$ (5)

$$\mathbf{I = I_0 x 10^{-k'x}} \qquad (6)$$

where $k' = k/2.303$ is called ***extinction coefficient*** of the substance.

BEER'S LAW

When a monochromatic light is passed through a solution, the decrease in intensity of light with the thickness of the solution is directly proportional to Intensity of the incident light and the concentration 'c' of the solution.

Mathematically, we have

$$-dI/dx \propto Ic \qquad (7)$$

$$-dI/dx = \epsilon Ic \qquad (8)$$

where Є is a constant of proportionality and is called ***molar absorption coefficient.*** Its value depends upon the nature of the absorbing solute and the wavelength of light used.

Equation (8) can be written as

$$dI/I = -\epsilon c dx$$

Integrating between x=0 to x and I between I_0 to I , we get

$$\ln I/ I_0 = -\epsilon cx \qquad (9)$$

or, $I/ I_0 = e^{-\epsilon cx}$

$$\mathbf{I=I_0 \times 10^{-\epsilon cx}} \qquad (10)$$

We can rewrite equation (9) as

$$2.303\log I/I_0 = -\epsilon cx \quad \text{or} \quad \log I/I_0 = -\epsilon cx/2.303$$

$$\text{or,} \qquad \log I/I_0 = -\epsilon' cx \qquad (11)$$

$$\text{or,} \qquad I/I_0 = 10^{-\epsilon' cx}$$

$$\mathbf{I=I_0 \times 10^{-\epsilon' cx}} \qquad (12)$$

where ϵ' is called the ***molar extinction coefficient.***

Units of molar extinction coefficient are **$\mathrm{Lmol^{-1}\ cm^{-1}}$**

BEER-LAMBERT'S LAW

The two laws have been combined together as Beer-Lambert's Law:

Writing equation (11), we have,

$$\log I/I_0 = -\epsilon' cx \qquad (11)$$

We can rearrange this equation to get ,

$$\log I_0/I = \epsilon' cx \qquad (13)$$

Now, $\log I_0/I$ is called ***Absorbance(A)****,or* ***Optical Density(OD)*** *or* ***Extinction(E).***

Equation (13) can thus be written as

$$\mathbf{A = \epsilon' cx} \qquad (14)$$

Equation (14) is the commonly used **Beer- Lambert's Law.**

Moreover, since Transmittance $T = I/I_0$,

Absorbance (A)=Extinction(E)=Optical Density(OD)=$\mathbf{\log 1/T = \log I_0/I}$

NUMERICAL 1

A monochromatic source of radiation is incident on a solution of 0.05 molar concentration of an absorbing substance. The intensity of the radiation is reduced to one fourth of the initial value after passing through 10 cm length of the solution. Calculate the molar extinction coefficient of the substance.

Solution:

Given:

$I/I_0 = 1/4 = 0.25$

i.e., $I_0/I = 100/25 = 4$

$x = 10$ cm

$c = 0.05$ M

$\log I_0/I = A = \epsilon c x$

$\log 100/25 = \epsilon \times 10\,\text{cm} \times 0.05\,\text{mol}\,\text{L}^{-1}$

$\log 4 = 2\log 2 = \epsilon \times 0.5$

$\epsilon = 2 \times 0.3010/0.5 = 4 \times 0.3010$

$= 1.204\,\text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$

Molar extinction coefficient is $1.204\,\text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$

NUMERICAL 2

A substance when dissolved in water at 10^{-3} molar concentration absorbs 10% of an incident radiation in a path of length 1 cm. What should be the concentration of the solution in order to absorb 90% of the same radiation?

Given:

First case:

Abs=10% so T=90%

$C_1 = 10^{-3}$ M

X=1cm

Second case

Abs=90% so T=10%

$C_2=?$

$\log I_0/I = A = Єcx$

Case 1

$\log 100/90 = Є \times 1\text{cm} \times 10^{-3}$ moles lit^{-1}

$Є=45.8$

Case 2

$\log 100/10 = 45.8 \times 1\text{cm} \times C_2$

$C_2 = 1/45.8 = 0.0218$ mol lit^{-1}

GROTTHUS- DRAPER LAW

This law was enunciated by the two scientists 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 ***Grotthus Draper Law***(Also called the Principle of Photochemical Activation), only that light which is ***absorbed*** by a system can bring about a Photochemical change.

This a common sense law.

STARK EINSTEIN LAW OF PHOTOCHEMICAL EQUIVALENCE

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 step of the photochemical reaction.**

Suppose ν is the frequency of the radiation absorbed. The corresponding energy absorbed by a molecule will be ν . **The energy E absorbed per mole of**

the reacting substance is given by

$$E=Nh\nu=Nhc/\lambda$$

The quantity E, the energy absorbed per mole of the reacting substance is called one Einstein.

VALUE OF EINSTEIN

The energy possessed by one mole of photons is called one Einstein.

Numerical value of Einstein in different units:

CGS Units:

$N=6.022X10^{23}$ mole^{-1}

$h=6.6X10^{-27}$ erg sec

$c=3X10^{10}$ cm/sec

$E= 6.022X10^{23}$ mole^{-1} X $6.6X10^{-27}$ erg sec x$3X10^{10}$ /$_{\lambda}$ cm/sec

$=119.7X10^{6}/ \lambda$(cm) ergs per mole

$= 119.7X10^{6} /4.184X10^{7} \lambda$(cm) cal per mole

$=2.86/ \lambda$(cm) cal per mole

$=2.86X10^{8}/\lambda(A^{0})$ cal per mole……. 1cm=10^{8} A^{0}

You have to remember that wavelength will be put in A^{0}

VALUE OF EINSTEIN

SI Units:

$N=6.022X10^{23}mole^{-1}$

$h=6.6X10^{-34}$ J.sec

$c=3X10^{8}$ m/sec

$E= 6.022X10^{23}$ $mole^{-1}$ X $6.6X10^{-34}$ J sec $x3X10^{8}$ $/\lambda(m)$ m/sec

$=0.1197/\lambda(m)$ Joules per mole

$=0.1197X10^{10}/\lambda(A^{0})$ joules per mole….. $1m=10^{10}$ A^{0}

$=11.97X10^{8}/\lambda(A^{0})$ Joules per mole

$=11.97X10^{5}/\lambda(A^{0})$ k Joules per mole

$=11.97X10^{4}/\lambda(nm)$ kJ per mole…………$1nm=10^{-9}$ m

It is very evident that the numerical value of Einstein varies inversely as the wavelength of light absorbed. The shorter the wavelength, greater is the energy absorbed.

Wavelength (A^0)	Colour Range	Values of Einstein $kJmol^{-1}$
2000	Ultraviolet	598.5
3000	Ultraviolet	399.0
4000	Violet	299.3
5000	Blue-green	239.4
6000	Yellow-green	199.5
7000	Red	171.0
8000	Near infrared	149.6

QUANTUM EFFICIENCY

The quantum efficiency or yield (Φ) of a photochemical process may be defined as:

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

or

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

If the law is correct, quantum yield of a photochemical process should be unity. Look at the table below to get an idea of quantum yields of various photochemical reactions.

EFFECTIVE WAVELENGTHS AND QUANTUM YIELDS OF PHOTOCHEMICAL REACTIONS

Reaction	Effective wavelength	Quantum Yield
1. $2NH_3 \rightarrow N_2+3H_2$	2100 A^0	0.2
2. $H_2+Cl_2 \rightarrow 2HCl$	4000 A^0	10^5
3. $CO+Cl_2 \rightarrow COCl_2$	4000-4360 A^0	10^3
4. $SO_2+Cl_2 \rightarrow SO_2Cl_2$	4200 A^0	1
5. $H_2+Br_2 \rightarrow 2HBr$	5100 A^0	0.01

WHY DIFFERENT QUANTUM YIELDS

The Law of Photochemical Equivalence is strictly valid for a very few reactions only.

The various reactions can be divided into three categories:

1. Those in which *quantum yield is a small integer.* Such as example 4.

2. Those in which quantum yield is less than 1. Such as example 1 and 5.

3. Those in which quantum yield is very high. Such as example 2 and 3.

WHY ARE QUANTUM YIELD VALUES SO DIFFERENT

In order to explain the above variations, Bodenstein suggested that photochemical reactions involve two distinct processes:

1. **Primary processes** in which light radiation is absorbed by an atom or molecule giving rise to the formation of an excited atom or excited molecule.

Thus, $A + h\nu \rightarrow A^*$

A^* is the excited state atom or molecule.

2. **Secondary Processes** which involve the excited atoms or molecules or free radicals produced in the primary step.

This step can lead to interesting possibilities, either high quantum yield or low quantum yield.

REASONS FOR HIGH QUANTUM YIELD

1. Atoms or free radicals produced in the primary process may initiate a series of chain reactions.
2. An intermediate product may be formed which acts as a catalyst.
3. The reaction involved may be exothermic with the result that the heat evolved may activate other molecules thereby causing them to react without absorption of additional quanta of radiation.
4. Collisions of activated molecules with other molecules may result in energy transfer so that more molecules may be activated.

REASONS 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 their energy.
3. The primary photochemical process may get reversed.
4. The dissociated fragments may recombine to form the original molecule.

WHAT DO WE INFER ABOUT APPLICABILITY OF LAW OF CHEMICAL EQUIVALENCE

- We conclude that Law of Photochemical equivalence can be applied only to primary processes.
- Each molecule capable of entering into chemical reaction absorbs one quantum of radiation.
- The secondary processes take place quite independent of light radiation
- As a result, the quantum efficiency of the reaction, as a whole, gives a distorted or misleading picture with regard to the applicability of the Law of Photochemical Equivalence.

  Let us take a few examples.

HYDROGEN BROMINE REACTION

The quantum yield of the reaction

$H_2(g)+Br_2(g) \rightarrow 2HBr(g)$ is extremely small, being 0.01

Bromine absorbs light in the green region of spectrum, at 5100 A^0

The primary process is dissociation of Bromine molecules into atoms:

(i) $Br_2 + h\nu \rightarrow 2Br$; Rate constant=$k_1$

The secondary reactions are the same as in thermal reactions. These are:

(ii) $Br + H_2 \rightarrow HBr + H$ Rate constant=k_2

(iii) $H + Br_2 \rightarrow HBr + Br$ Rate constant=k_3

(iv) $H + HBr \rightarrow H_2 + Br$ Rate constant=k_4

(v) $Br + Br \rightarrow Br_2$ Rate constant=k_5

continued.....

HYDROGEN BROMINE REACTION

- The Bromine atoms formed in the step (i) attack Hydrogen yielding Hydrogen Bromide and a Hydrogen atom.
- The latter then attacks Bromine forming another molecule of Hydrogen Bromide and Bromine atom.
- In this way, if steps (ii) and (iii) take place one after the other a very high quantum yield will be obtained. *But reaction (ii) is highly endothermic and requires very high energy of activation. This step is very slow at ordinary temperatures.*
- If it proceeds for a while, the reverse of it , which is, in fact step (iv) becomes increasingly important and the rate of formation of HBr decreases.
- As Bromine atoms accumulate, since these are not used in step (ii), the step (v) involving the recombination of Bromine atoms to form molecules takes place readily.
- Hence the quantum yield of the reaction is extremely low.

KINETICS OF THE HYDROGEN BROMINE REACTION

- The rate of formation of Bromine atoms in step (i) is photochemical. It depends on the intensity of the light used.
- The rate of formation of formation of Bromine atoms is given by the expression:

$$d[Br]/dt=k_1\,I_{abs} \quad \ldots\ldots\ldots \qquad (1)$$

where I_{abs} is the intensity of absorbed radiation.

- Hydrogen Bromide is formed in the steps (ii) and (iii) and is consumed in step (iv).Hence net rate of formation of HBr may be represented as:

$$d[HBr]/dt=k_2[Br][H_2]+k_3[H][Br_2]-k_4[H][HBr] \qquad (2)$$

- Bromine and Hydrogen atoms are merely *transitory intermediates* as these are used up in subsequent steps.

KINETICS OF THE HYDROGEN BROMINE REACTION

- It is assumed that the rate at which Hydrogen and Bromine atoms are formed is equal to the rate at which they disappear.
- This is known as *steady state approximation.*

- Thus, Hydrogen atoms are produced by reaction (ii) and removed by reactions (iii) and (iv). Hence,

$$k_2[H_2][Br]=k_3[H][Br_2]+k_4[H][HBr] \qquad (3)$$

- Similarly, Bromine atoms are produced by reactions (i), (iii) and (iv) and removed by reactions (ii) and (v). Hence.

$$k_1I_{abs}+k_3[H][Br_2]+k_4[H][HBr]=k_2[H_2][Br]+k_5[Br]^2 \qquad (4)$$

KINETICS OF THE HYDROGEN BROMINE REACTION

Subtracting (3) from (4), we get

$$k_1 I_{abs} = k_5[Br]^2 \qquad (5)$$

$$[Br] = \sqrt{\frac{k_1\, I_{abs}}{k_5}} \qquad = \{ k_1 I_{abs}/k_5\}^{1/2} \qquad (6)$$

Substituting this value of [Br] in equation (3), we have

$$[H] = \frac{k_2\,[H_2]\,\{ k_1 I_{abs}/k_5\}^{1/2}}{k_3[Br_2]+k_4\,[HBr]} \qquad (7)$$

Inserting the values of [H] and [Br] from equations (7) and (6),we have

$$d[HBr]/dt= \frac{2k_2k_3\,[Br_2]\{k_1/k_5\}^{1/2} \, X \, [H_2]\{I_{abs}\}^{1/2}}{k_3[Br_2]+k_4[HBr]}$$

$$=k\,\frac{\{I_{abs}\}^{1/2}\,[H_2][Br_2]}{[Br_2]+\ k'[HBr]} \qquad (8)$$

where k and k′ are new constants. This equation agreed with experimental results of Bodenstein. It also explained the observation that rate of the reaction varies as the square root of intensity of light.

THE HYDROGEN CHLORINE REACTION

This reaction is very interesting as , in total contrast to the Hydrogen Bromine reaction, its quantum yield is very high, varying between 10^4 to 10^6 in the absence of oxygen. The presence of oxygen slows down the rate of the reaction as well as the quantum yield also.

The extremely high quantum yield has been attributed to setting up of a chain. The primary process is the dissociation of one molecule of Chlorine into atoms as a result of absorption of radiation of energy.

THE HYDROGEN CHLORINE REACTION

Thus,

(i) $Cl_2 + h\nu \rightarrow 2Cl$ Rate constant=k_1

The following secondary processes then follow:

(ii) $Cl + H_2 \rightarrow HCl + H$ Rate constant=k_2

(iii) $H + Cl_2 \rightarrow HCl + Cl$ Rate constant=k_3

The regenerated Chlorine atom in equation (iii) reacts with another molecule of Hydrogen to form Hydrogen Chloride.

So, the steps alternate between reactions (ii) and (iii), forming a chain.

Thus, the chain set up by the dissociation of one molecule of Chlorine into atoms, on the absorption of one quantum of energy, is propagated.

THE HYDROGEN CHLORINE REACTION

Isn’t it strange that a similar reaction between Hydrogen and Bromine does not show a high quantum yield.

The reason is that the step immediately following the photochemical step is highly endothermic at room temperature and therefore very slow in the Hydrogen Bromine reaction.

The same step in Hydrogen Chlorine reaction is exothermic and takes place almost instantaneously.
The quantum yield would depend upon how many times steps (ii) and (iii) alternate before the termination of the chain.

THE HYDROGEN CHLORINE REACTION

The chain terminating reaction appears to be the recombination of Chlorine atoms to form molecules ***on the walls of the reaction vessel*** represented as

(iv) $Cl + Cl \rightarrow Cl_2$ Rate constant= k_4

In the presence of oxygen the chain may be terminated by the reaction

$H + O_2 \rightarrow HO_2$

HO_2 is called the perhydroxyl radical.

The quantum yield is consequently lower in the presence of oxygen.

KINETICS OF THE HYDROGEN CHLORINE REACTION

Since the chlorine atoms are formed in reactions (i) and (iii), and they disappear in reactions (ii) and (iv), we can write from the steady state approximation,

$$k_1 I_{abs} + k_3[H][Cl_2] = k_2[H_2][Cl] + k_4[Cl]^2 \qquad (1)$$

where I_{abs} is the intensity of absorbed radiation.

Since hydrogen atoms are formed in step (ii) and removed in step (iii), Hence at the stationary state,

$$k_2[H_2][Cl] = k_3[H][Cl_2] \qquad \mathbf{(2)}$$

Subtracting (2) from (1), we have

$$k_1 I_{abs} = k_4[Cl]^2 \qquad \mathbf{(3)}$$

KINETICS OF THE HYDROGEN CHLORINE REACTION

$$[Cl] = \{k_1 I_{abs}/k_4\}^{1/2} \qquad (4)$$

Hence, overall rate of formation of HCl is given by

$$d[HCl]/dt = k_2[H_2][Cl] + k_3[H][Cl_2]$$

$$= 2\,k_2[H_2][Cl] \qquad (5)$$

Since these two terms are equal from equation (2),

Substituting the value of [Cl] from equation (4) in equation (5),

$$d[HCl]/dt = 2\,k_2[H_2]\{k_1 I_{abs}/k_4\}^{1/2}$$

$$= k[H_2]\{I_{abs}\}^{1/2} \qquad (6)$$

where k is a new constant.

According to equation (6),the rate of reaction should vary directly as Square root of intensity of light as well as pressure of hydrogen. This has been verified by experiment.

PHOTOSENSITIZATION

Some of the photochemical reactions take place by the absorption of light by one of the non reactants which maybe present in the system. This is known as **Photosensitization.**

A very important example of photosensitization is the action of chlorophyll in combination of carbon dioxide and water in presence of sunlight to form carbohydrates in photosynthesis.

Carbon dioxide and water, being colourless, do not absorb any portion of visible light, but chlorophyll, the green colouring matter of plants, can do so.

PHOTOSENSITIZATION

It appears that the chlorophyll passes on the radiant energy absorbed by it to carbon dioxide and water molecules. These molecules then react together to form the product:

$$6CO_2 + 6H_2O + h\nu \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

Carbon dioxide and water, themselves being colourless, do not absorb any portion of visible light, but chlorophyll, the green colouring matter of the plants, can do so.

It appears that chlorophyll absorbs radiant energy and passes it on to carbon dioxide and water which then combine to form product.

PHOTOSENSITIZATION

There are several examples of Photosensitization.

1.Decomposition of Hydrogen molecules into hydrogen atoms when hydrogen gas, mixed with mercury vapour is exposed to ultraviolet light of wavelength 2537 A^0 coming from a mercury vapour lamp.

The energy associated with this radiation is 46.8 kJ per mole of photons. The energy required to dissociate hydrogen molecules into atoms is 435.1 kJ per mole.

In this case, ultraviolet light is absorbed by mercury vapour which is then made available to hydrogen for dissociation into atoms.

The reaction may be represented as:

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow Hg + 2H$$

Obviously, in this reaction, mercury acts as a *sensitizer*.

2. Irradiation of a mixture of ethylene and mercury vapour light of wavelength 2537 A^0 to yield acetylene.

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + C_2H_4 \rightarrow C_2H_4^*$$

$$C_2H_4^* \rightarrow C_2H_2 + H_2 + Hg$$

In this example also mercury acts as a photosensitizer.

3. The decomposition of diazomethane (CH_2N_2) by benzophenone which acts as a photosensitizer at 3200A^0.

$$Bz + h\nu \rightarrow Bz^*$$

$$Bz^* + CH_2N_2 \rightarrow Bz + CH_2N_2^*$$

$$CH_2N_2^* \rightarrow CH_2 + N_2$$

$$CH_2 + CH_2 \rightarrow C_2H_4$$

Mercury is widely used as a photosensitizer in several lighting applications. It is used in CFLs, tubelights etc.

Since mercury is a poison, the disposal of CFLs and tubelights should be done carefully.

CHEMILUMINESCENCE

The phenomenon of emission of light in a chemical reaction is called **Chemiluminescence.** So, it is the reverse of a photochemical reaction.

1. The glow of phosphorus and its trioxide is an example of chemiluminescence.
2. The oxidation of Grignard reagents by air or oxygen emits greenish blue luminescence.
3. On mixing a solution of strontium chloride with dilute sulphuric acid, feeble glow is emitted along with precipitation of strontium sulphate.

The emission of so called ‘cold light’ by glow worm is another example of chemiluminescence.

The chemical reaction involved is the oxidation of luciferin- a protein by atmospheric oxygen in the presence of an enzyme called ***luciferase.***

FLUORESCENCE

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence.

In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation.

FLUORESCENCE

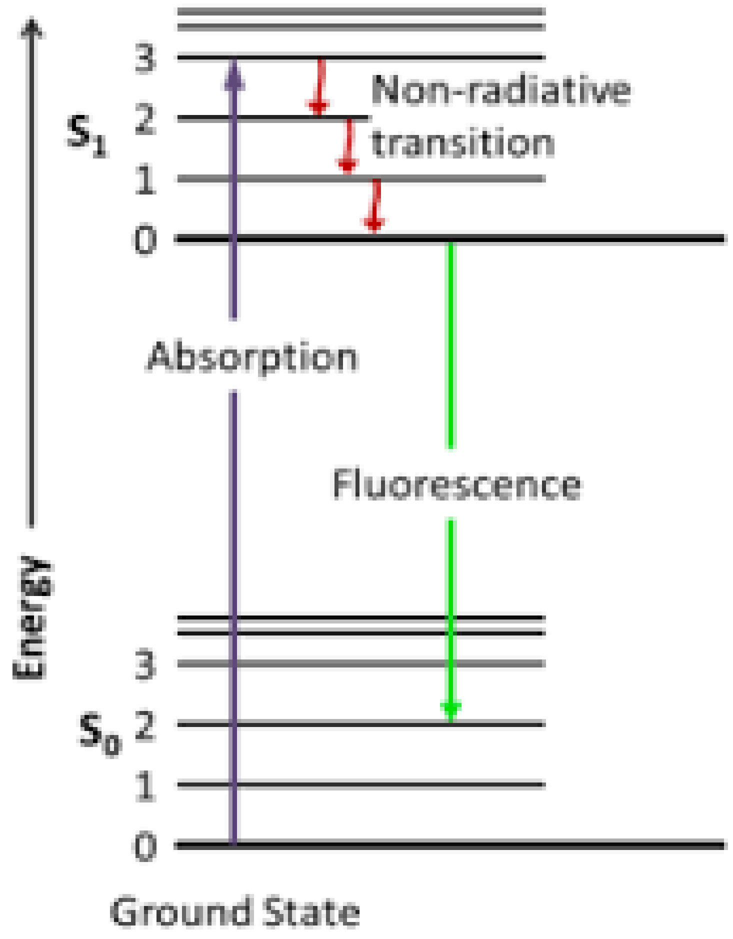
The most striking example of fluorescence occurs when the absorbed radiation is in the ultraviolet region of the spectrum, and thus invisible to the human eye, while the emitted light is in the visible region, which gives the fluorescent substance a distinct color that can be seen only when exposed to UV light.

Fluorescent materials cease to glow nearly immediately when the radiation source stops

FLUORESCENCE

Two rules govern the transition of molecule from one state to another.
The first one is the **Franck-Condon Principle.**

The transition or absorption of radiation is so fast that the bond length of the molecule does not change in that time period. In other words, there is a vertical transition.



JABLONSKII DIAGRAM

The second rule is of Spin Multiplicity.

Transition takes place between states of ‘like’ multiplicity.

That is , when a molecule absorbs radiation, it goes to the excited state which has the same spin multiplicity.

A singlet state will go to a singlet state.

A triplet state will absorb radiation and go to a triplet state.

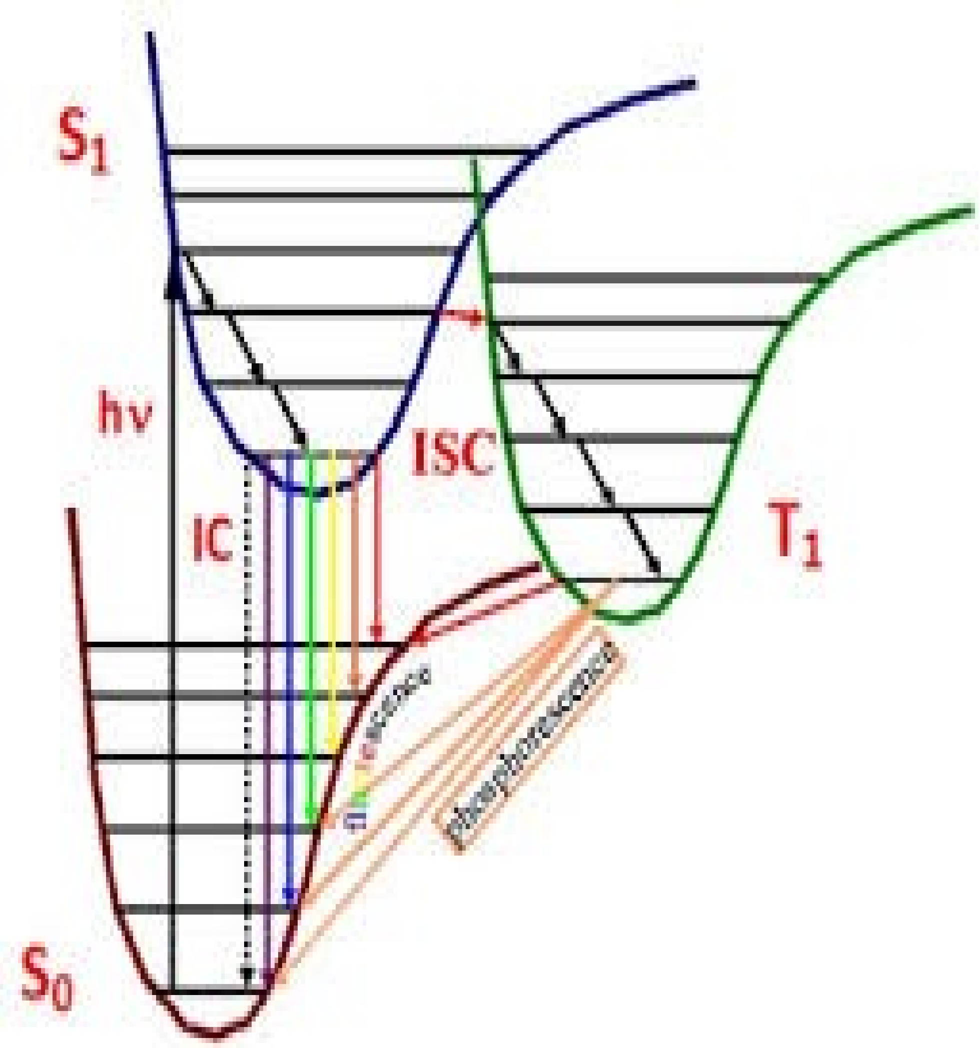
Absorption cannot take place from singlet to triplet, it is **forbidden**.

The mechanism of Fluorescence is as follows:

When a source of radiation is incident On a sample, it absorbs energy and goes from ground electronic state to excited electronic state in a vibrational energy level in accordance with

a) Franck Condon Principle
b) Transition between states of ‘like’ spin multiplicity.

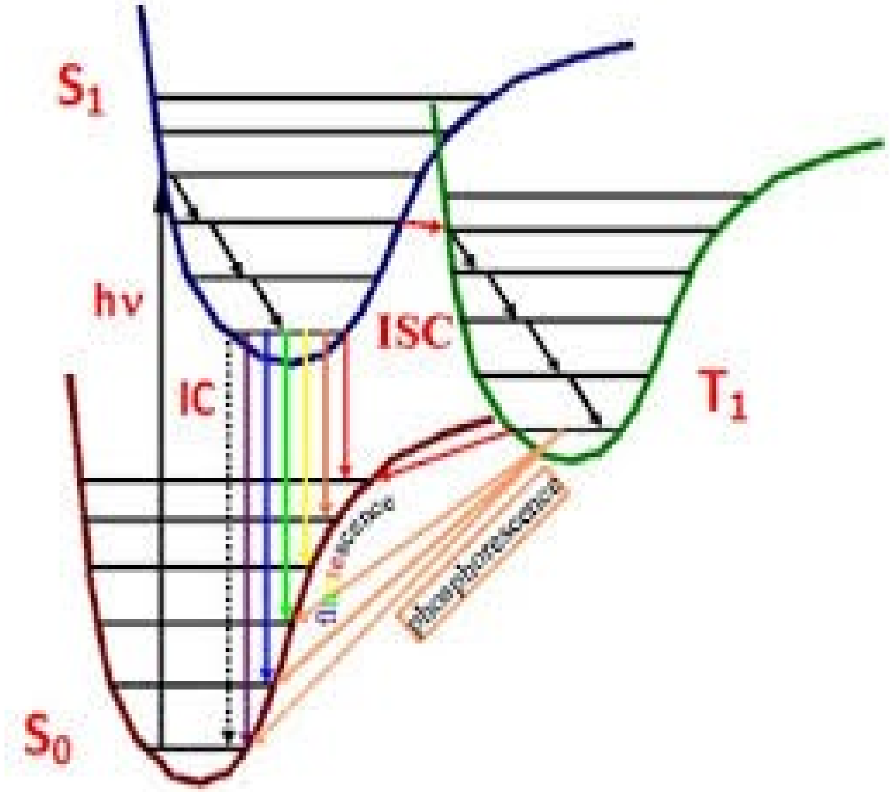
Once the excited state is reached and the source of radiation is withdrawn, the following takes place:



The molecule quickly loses energy in the excited electronic state via the vibrational energy levels and reaches the ground vibrational level of the excited state. This is called **nonradiative transition**. The energy is absorbed by the solvent.

Now the molecule returns to the ground electronic state in accordance with the two principles.

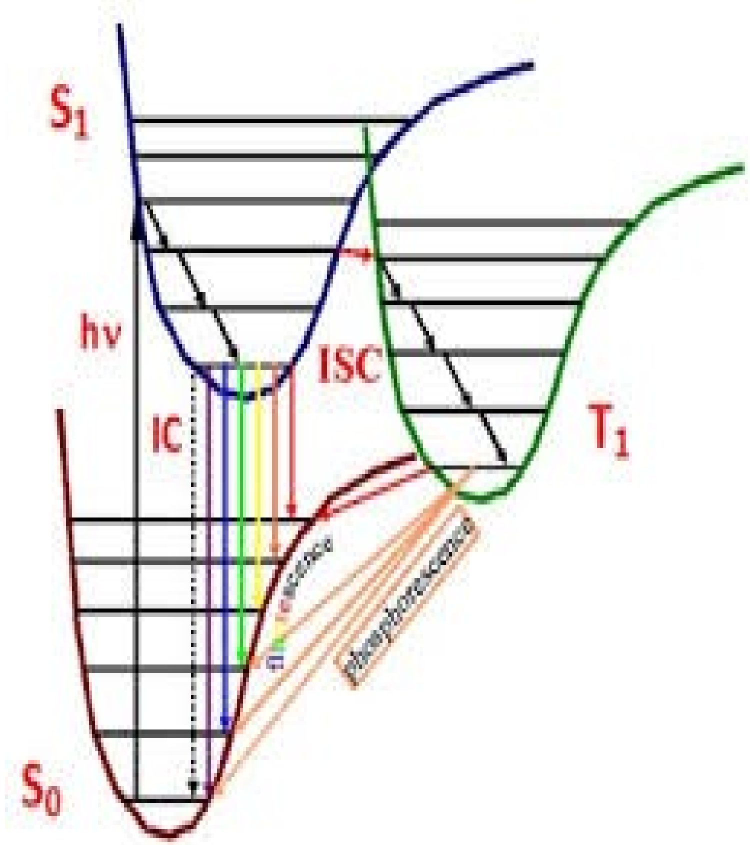
It is clear from the diagram that the energy absorbed is greater than the energy emitted. The emitted light is in the visible region and therefore it can be 'seen' and has a longer wavelength.



PHOSPHORESCENCE

Sometimes, there is a triplet state close to the excited singlet electronic state, and, in the process of losing energy of vibrational energy levels, it crosses over to the triplet state. This is called **Inter system crossing (ISC).**

It continues to lose energy in the triplet state till it reaches the ground vibrational state of the triplet state.



PHOSPHORESCENCE

Now the molecule is stuck in the triplet state.

Since triplet to singlet transition is forbidden, the molecule

Cannot return to ground singlet state.

Thus radiation ‘leaks’ from the excite state and it is visible

in the dark.

This phenomenon is called PHOSPHORESCENCE. It is also called **Delayed Fluorescence.**

This is a forbidden transition.

Phosphorescence finds use in paints, jewellery, illumination, stickers for decoration etc.