Branching chain Reactions :-

The chain reaction in which the mechanism have a definite pattern further distinguishing them from non-chain preach. The mechanism invariably involve an initiation step in which the chain carried are genarated and propagation step in which the products are formed and the intial chain carrier is regenarate and termination reaction in which the chain reaction undergoy secondary reaction resulting in the termination or shortening of chains. some type of chain reactions called brached chain reactions, i.e involving branching steps in which more chain carrig are produced than are consumed.

A reaction mechanism that involvy braching reactions is known as braching chain preach. The theory of such reaction way given by Semenoff and Hinshelwood.

consider a general gascous chain reaction in which A is the reactant. R is reactive chain carrier. P is product & α is the no of chain carries produced by one carrier in the propagation step.

chain initiation : $A \xrightarrow{K_1} R$

chain propagation : $R + A \underset{}{\overset{K_2}{\rightleftharpoons}} \alpha R + P$

chain Termination : $R \xrightarrow{K_3}$ destruction

The chain carrig may be destroyed by either collision against the wall of the vessel or with other molecule.

The chain carrier may be destroyed by either collision against the wall of the vessel or with other molecule.

The rate of formation of chain carriers is given by

$$\frac{d}{dt}[R] = K_1[A] - K_2[R][A] + K_2\alpha[R][A] - K_3[R]$$

Assuming steady approximation for the chain carrier

$$\frac{d}{dt}[R] = 0$$

$$K_1[A] - K_2[R][A] + \alpha K_2[R][A] - K_3[R] = 0$$

$$K_1[A] = [R]\{K_2[A] - \alpha K_2[A] + K_3\}$$

$$\therefore [R] = \frac{K_1[A]}{K_2[A] - \alpha K_2[A] + K_3}$$

$$[R] = \frac{K_1[A]}{K_2[A](1-\alpha) + (K_w + K_g)} \quad \text{---} (1)$$

where $K_3 = K_w + K_g$

K_w = wall reaction

K_g = gas phase reaction

case :1 when $\alpha = 1$

i.e Each propagation sequence of the reaction results in the formation of product molecule. with regenaration of only one chain carrier such chain reactions are called non-branched (or) stationary chain reactions.

Eg: pyrolysis of several organic compound.

case :2 when $\alpha >>> 1$

i.e a very large no of chain carriers are produced in the propagation sequence, the carrier concentration $[R]$ becomes almost infinite. As a result the rate of reaction also becomes almost infinite resulting in explosion

when $[R] \longrightarrow \infty$

$$\therefore K_2[A][(1-\alpha)] = -(K_w + K_g)$$

Case: III when $x > 1$

i.e more than one chain carriers are produced in the propagation sequence of the reaction such chains are called branched chains (or) non stationary chains.

Upper and lower Explosion limits

These limits were studied by Hinshelwood and Semenoff.

The reaction b/n hydrogen and oxygen proceeds at a measurable speed if the temperature is between 450c and 600c. Below this range, the reaction becomes slow but above this range, explosions take place.

The reaction has been shown to proceed according to the following mechanism.

$$H_2 \xrightarrow{\cdot\cdot} H^\cdot + H^\cdot \longrightarrow ①$$

$$H^\cdot + O_2 \longrightarrow OH^\cdot + O^\cdot \longrightarrow ②$$

$$O^\cdot + H_2 \longrightarrow OH^\cdot + H^\cdot \longrightarrow ③$$

$$H^\cdot + O_2 + M \longrightarrow HO_2 + M \longrightarrow ④$$

$$HO_2 + H_2 \longrightarrow H_2O + OH^\cdot \longrightarrow ⑤$$

$$OH^\cdot + H_2 \longrightarrow H_2O + H^\cdot \longrightarrow ⑥$$

The steps are that consider a mixture of O_2 & H_2 in the ratio of 1:2 which is maintained at 55oc and at pressure 2mm when the pressure is slowly increased, the rate of reaction also increases slowly at that certain critical pressure of 50mm or so the mixture explodes. The exact value of this critical pressure will depends upon the size and shape of vessel. The limit at which occurs at first explosion limit or lower explosion limit.

Now maintain the mixture of O_2 and H_2 at 200 mm pressure. Again the reaction proceeds at a steady rate. If pressure is reduced, the rate of reaction is also reduced. But about 100 mm, the reaction mixture explosively. Thus there is pressure region bln 50 and 100 mm with in which explosion take place. Above and below this pressure region, reaction proceeds at a normal rate. The pressure limit of 100 mm at which the explosion occurs is known as upper explosion limit (or) second limit.

From fig (i) there is third limit of explosions which is at still higher pressure. Here explosions are due to the rise in the temperature of the reaction system. Such explosions are known as thermal explosions. No explosion occurs pressure above 600°C and under any pressure conditions below 460°C. (from fig ii)

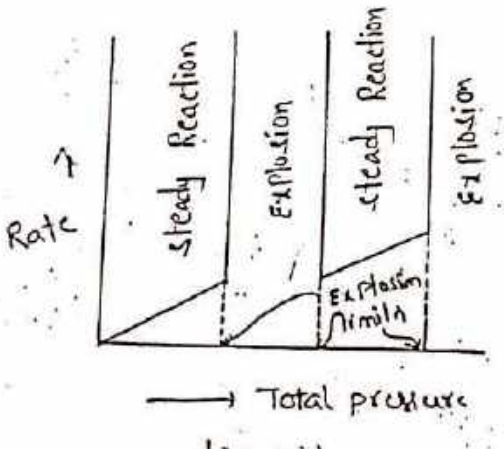


fig: (i)

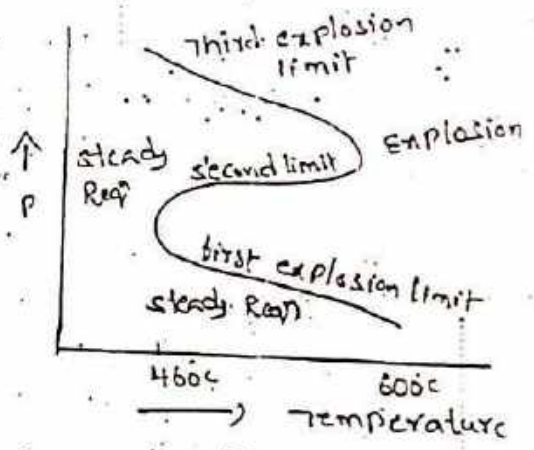


fig: II

Flow methods

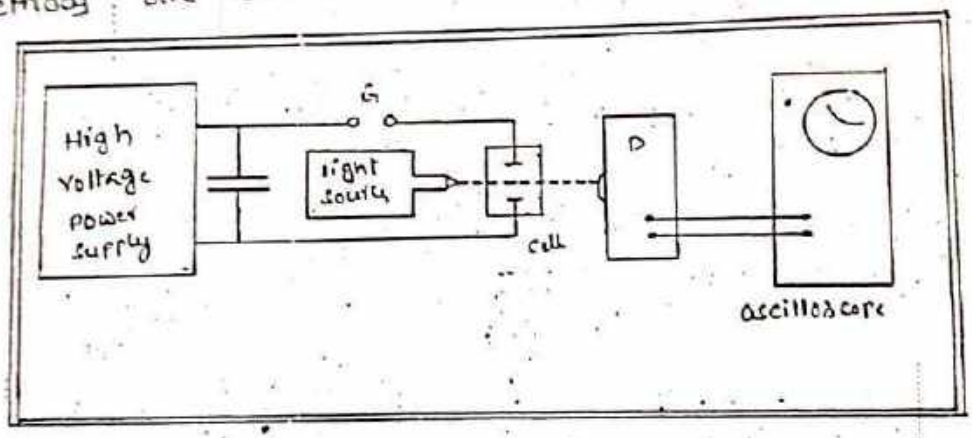
Kinetics of Fast Reactions :-

The reactions which go to equilibrium with in few seconds or less are said to be fast reactions. Kinetics of fast reactions cannot investigated by conventional methods. However in recent years, various methods have been developed to study fast reactions. In this section we will consider various methods one by one.

Relaxation methods:-

This method was developed by the German chemist manfred Eigen in 1950.

Relaxation method is used to investigate fast reactions in solutions. This is one of the perturbation method in which the reacting system in equilibrium is subjected to a sudden change in some physical parameters such as temperature, pressure and electric field on which the equilibrium constant of the reaction depends the system changes to new equilibrium state. The rate of this change is called Relaxation. Relaxation methods are carried out with parameters.



A high voltage power supply charges a capacitor 'C' when a certain voltage is reached, the spark gap G breaks down discharge the capacitor and sending a strong current through the cell containing a reactive system at equilibrium, in a conducting aqueous solution.

As the current passes, the temp of the system rises by about 10^{-6} in few seconds. In certain time interval, the concentration of the reacting species adjust to the new equilibrium value w.r.t temperature Jump. As a result the intensity of light beam leaving the cell and entering the detector is changed.

Derivation :-

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$$

If the displacement from the Equilibrium is very small, the rate of Relaxation i.e restoration of Equilibrium always follows first order Kinetics.

Consider a reversible first order reaction

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$$

If 'a' is the concentration of A+B, $a-x$ is concentration of B at any instant then

$$r = \frac{dx}{dt} = K_1(a-x) - K_{-1}(x) \quad \text{— ①}$$

If x_e is the equilibrium concentration, then

$$\Delta x = x - x_e \quad \text{— ②}$$

$$x = \Delta x + x_e$$

$$\frac{d}{dt}(\Delta x) = \frac{dx}{dt}$$

$$\frac{d}{dt}(\Delta x) = K_1(a - \Delta x - x_e) - K_{-1}(\Delta x + x_e) \quad \text{— ③}$$

At Equilibrium $\frac{dx}{dt} = 0$

$\Rightarrow x = x_e$

Hence Eq^n ① becomes $\frac{dx}{dt} = K_1(a-x_e) - K_{-1}(x_e) = 0$

$$K_1(a-x_e) = K_{-1}(x_e) \quad \text{— ④}$$

substitute this value in Eq^n ③

$$\frac{d}{dt}(\Delta x) = -K_1 \Delta x - K_{-1} \Delta x$$

$$= -\Delta x [K_1 + K_{-1}]$$

But $K_r = K_1 + K_{-1}$ where K_r is relaxation rate constant

$$\therefore \frac{d}{dt}(\Delta x) = -\Delta x K_r \quad \text{— ⑤}$$

integrating the above Eq^n to give Δx

$$\Delta x = \Delta x_0 e^{-K_r t}$$

The Reciprocal of K_r is

$$\frac{1}{K_r} = \frac{1}{K_1 + K_{-1}}$$ known as relaxation time.

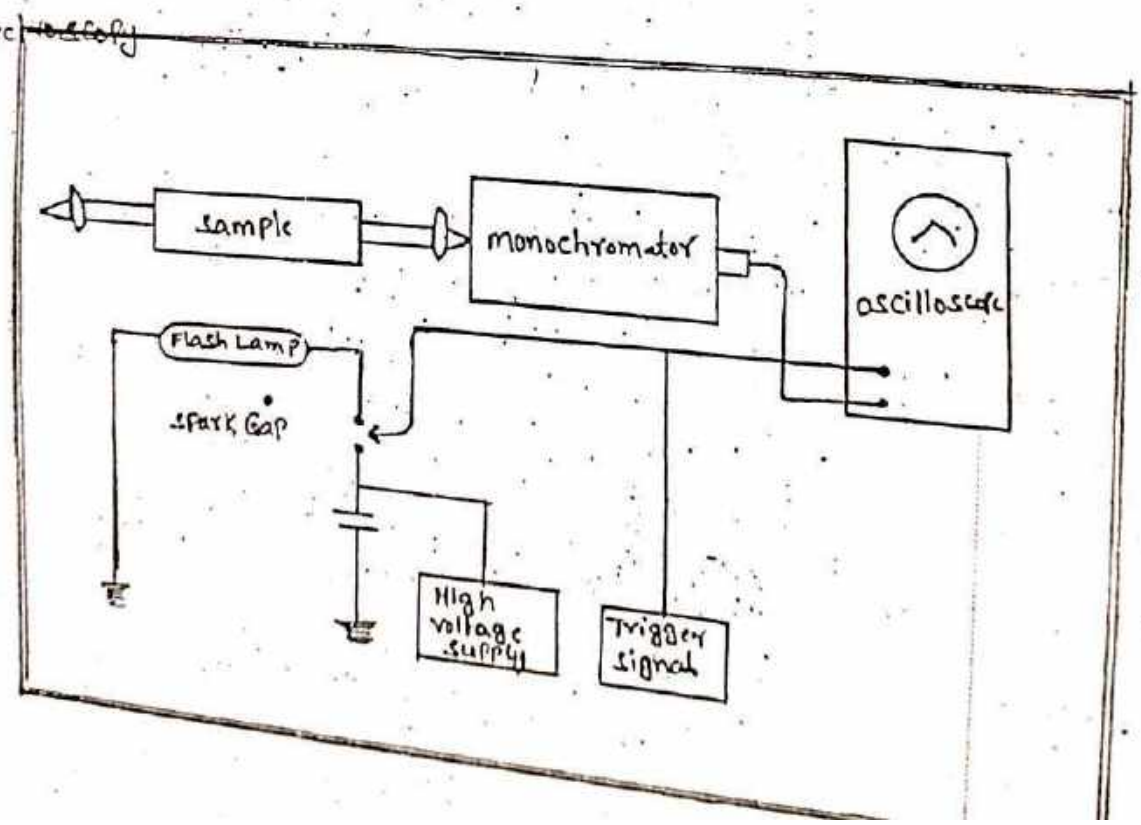
$$\therefore \boxed{T = \frac{1}{K_1 + K_{-1}}}$$

(ii) **Flash photolysis :-**

This method was introduced by R.G.W. Norrish and G. Porter in 1949. Eigen, Norrish and Porter shared the 1967. Noble prize for contribution to fast reaction kinetics.

This method is used to study the very fast reactions of both gas and liquid phase.

The procedure is to produce a light flash of very high intensity and in very short duration. i.e 10^{-6} sec. in the neighbourhood of the reaction vessel containing the sample under suitable conditions thus will produce atoms, free radicals and exited species in the reacting system. This method is known as Kinetic ~~spectroscopy~~



The sample is subjected to very powerful flash having energy of order of 10^{15} Joule and in a duration 10 μs.

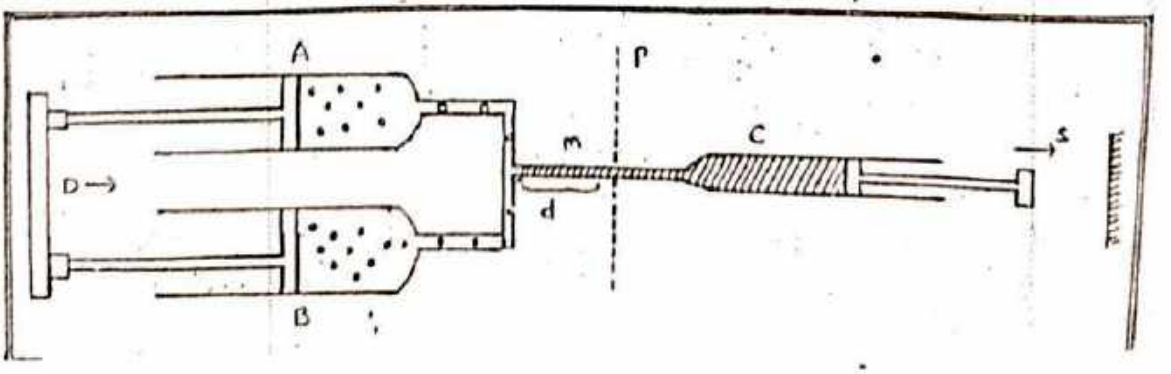
The flash is so intense that in some cases almost all the molecule dissociated into free radicals. 50 mega watts may be obtained in few micro seconds. The concentration of intermediate produced by Flash photolysis is followed as a function of time by absorption photometry.

A condenser of high microfarad capacity is charged to 10,000 volts by a high voltage supply. By means of trigger signal, a spark gap is produced which permits rapid passage of current through the discharge lamp. The condenser discharge in few micro seconds. The lasers can produce a flash of the duration of few nano seconds. After the capacitor discharge, a flash lamp which can produce analysing light is automatically trigged off.

" The rate of disappearance of excited molecule or free radicals is followed by the rate of increase in the monochromatic light as measured with an oscilloscope and photomultiplier.

Applications :- This method is used for determine the absorption spectra of free radicals such as $^{\cdot}NH_2$, $^{\cdot}CH_3$ and $^{\cdot}ClO$ whose concentration may be as small as 10^{-6} m

Stopped flow Technique: It is used by chang for reaⁿ in solution



The two solutions are forced through jets into a mixing chamber which is design that mixing is extremly rapid, mixing occurs with in 10^{-3} sec. The solution passing from mixing chamber into the vessel at once. But in some system mixing chamber and reacting vessel are one and the same. The flow is stopped suddenly and measurements are made usually spectrophotometrically, of concentration as a function of time since the reaction are rapid, the spectrophotometric reading must be recorded continuously using an oscilloscope the trace of which is photographed.

Eg: The reaction bln ethylene and bromine water.

Advantage :-

1) This method is not effected by the rate at which mixing and the character of the flow provided that mixing is satisfactory

2) A permanent record can be obtained of the progress of the reaction

3) The volume of the reagents used in small. This is particularly important when it is desired to work such of enzymy that are difficult to obtain large quantities

NOTE:- The continuous flow and quenched flow techniques are other flow methods. But they are less popular

Dis advantage :-

It is less sensitive than continuous flow method.

Catalyst :-

A catalyst is a substance that accelerates a reaction but it undergoes no net chemical change

(or)

A catalyst is any substance that alters the velocity of chemical reaction without appearing in the end product of reaction.

Homogeneous catalyst :-

A homogeneous catalyst is a catalyst in the same phase as the reaction mixture.

Heterogeneous catalyst :-

A heterogeneous catalyst is a catalyst in a different phases from the reaction mixture.

Substrate :-

A term used in enzymic reactions, the molecule on which the enzyme acts.

Mechanism of Homogeneous catalysis :-

In a simple catalysed reaction involving only one substrate, the substrate and the catalyst form a complex which subsequently decomposes with the formation of product and the regeneration of the catalyst, and this decomposition take place in a single stage. In complicated catalysis reactions the catalyst acts in different way and it gives free radicals are thus formed free radicals intiate chain process.

In case of a non-chain mechanism i.e involving a single substrate the following mechanism take place

(i) $C + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + Y$

2) $X + W \xrightarrow{k_2} P + Z$

Hence 'e' represent the catalyst, s is substrate, x is intermediate complex, and y some substance which is formed in addition to it. w is a molecule which reacts with complex to give the product p with elimination of molecule y.

Two possibility exist with regard to the stability of the intermediate complex x. The first place is that the complex may be one that is reconverted into the catalyst and the substrate at a rate that is significantly greater than the rate which it undergoes reaction and give the final product. In this case the overall rate of reaction can be calculated by knowing the concentration of x from the equilibrium alone and multiply this by $K_2[w]$. This type of catalysis is also known as Arhenius complex.

The second possibility is that the intermediate complex is much less stable specie, so that the rate of reaction (2) to give the final products is not small compared with the reverse rate of reaction (1). In this case in calculating the concentration of 'x' are also consider in rate of (2) along with equilibrium (1). In this case we use steady state treatment. A complex of this type is also known as Vanthoffs complex.

(i) **Steady – state Treatment :-**

In reaction (2) occurs sufficiently rapidly the concentration of [x] is small, so we can use steady-state treatment

The steady state expression for [x] is :

$$\frac{d}{dt}[x] = K_1[e][s] - K_{-1}[x][y] - K_2[x][w] = 0$$

substitute [e] with $[e]_0 - [x]$ and [s] with $[s]_0 - [x]$.

we get

$$K_1[[e]_0 - [x]]\,[[s]_0 - [x]] - K_{-1}[x][y] - K_2[x][w] = 0 \longrightarrow (1)$$

since [x] is small, the term $[x]^2$ can be neglected. so eqn ① becomes

$$[x] = \frac{K_1 [c]_0 [s]_0}{K_1 [c]_0 + K_1 [s]_0 + K_{-1} [Y] + K_2 [w]} \quad - ②$$

The rate of reaction is $K_2 [x] [w]$

$$-\frac{d}{dt}[s] = \frac{K_1 K_2 [c]_0 [s]_0 [w]}{K_1 \left[[c]_0 + [s]_0 \right] + K_{-1} [Y] + K_2 [w]} \quad - ③$$

This eqn indicates that at low concentrations of catalyst and of substrate, the rate vary linearly with the concentration of each of these, and at higher concentrations of either, the rate will become independent of concentration.

In catalysis by surface and by enzymes w and y are non existent. so eqn ③ becomes (or) rate law becomes

$$-\frac{d}{dt}[s] = \frac{K_1 K_2 [c]_0 [s]_0}{K_1 \left[[c]_0 + [s]_0 \right] + K_{-1} + K_2} \quad - ④$$

(ii) <u>Equilibrium Treatment</u> :-

If the rate of reaction ② can be neglected in calculating the concentration of complex x, the concentration of x, y, c and s are related by

$$\frac{[x][Y]}{[c][s]} = \frac{K_1}{K_{-1}} = K \quad \cdots (I)$$

where K is Equilibrium constant.

This expression give the concentration of 'x' in terms of concentrations [y], [c] and [s]. But later two concentrations do not correspond to the initial concentrations. since by hypothesis

The appreciable amounts of c and s have combined in the ① intermediate complex 'x'. If $[c]_0$ and $[s]_0$ are the initial concentrations of c and s then

$$[c] = [c]_0 - [x] \quad \text{—} ⑤$$

$$[s] = [s]_0 - [x] \quad \text{—} ⑥$$

∴ Eqn ③ becomes

$$\frac{[x][Y]}{([c]_0 - [x])([s]_0 - [x])} = K \quad \text{—} ⑦$$

this is a quadratic eqn in $[x]$ and can solved for $[x]$

<u>Case-1</u>

If the intial concentration of the substrate is much greater than that of the catalyst. i.e if $[s]_0 \gg [c]_0$

then eqn ⑦ changes to

$$\frac{[x][Y]}{([c]_0 - [x])[s]_0} = K$$

$$\therefore [x] = \frac{K[c]_0[s]_0}{K[s]_0 + [Y]} \quad \text{—} ⑧$$

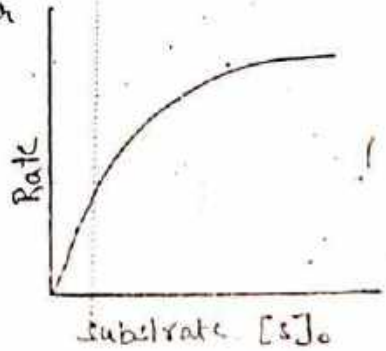
then rate of reqn $= K_2[x][w]$

$$\therefore -\frac{d}{dt}[s] = \frac{K_2 K[c]_0[s]_0[w]}{K[s]_0 + [Y]} \quad \text{—} ⑨$$

This rate eqn correspondy to a variation in rate If $K[s]_0 \ll [Y]$, the rate vary linear with $[s]_0$

This is shown in fig. where at higher substrate concentrations i.e when $K[s]_0 \gg [Y]$ then rate is independent of $[s]_0$

This condition we holdy as long as $[s]_0 \gg [c]_0$ otherwise the rate vary linear with $[c]_0$



Case-II

If the initial concentration of the catalyst is much greater than that of substrate i.e if $[c]_0 >> [s]_0$ then

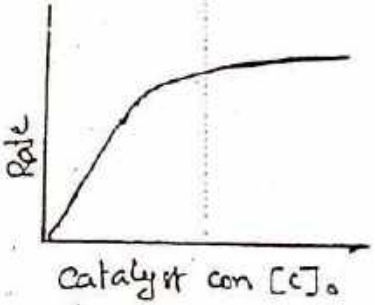
eqn (8) becomes $$\frac{[x][y]}{[c]_0[[s]_0 - [x]]} = K \quad -(10)$$

The rate of reaction in this case

$$-\frac{d}{dt}[s] = \frac{K_2 K [c]_0 [s]_0 [w]}{K[c]_0 + [y]}$$

The relationship b/n rate and $[c]_0$ shown in fig

At low catalyst con the rate is proportional to the catalyst conc, while at higher once, the rate is independent of $[c]_0$



Enzyme Catalysis: Michelis-Menten Kinetics.

Enzymes are homogenous biological catalysts. These obiquious compounds are special proteins (or) nucleic acids that contain an active site, which is responsible for binding the substrate, the reactant and processing into products. The products catalysed by enzymes are termed enzyme catalysis. Enzymes are complex organic compounds which are produced by living plants and animals.

Eg:- (i) $2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} n\,C_{12}H_{22}O_{11}$
maltose

(ii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{maltase}} 2\,C_6H_{12}O_6$
Glucose

(iii) $C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\,C_2H_5OH + 2CO_2$

(iv) $NH_2CONH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$

Mechanism and Kinetics of Enzyme catalysed Reaction:-

Biochemists michaelis and menten proposed a mechanism for the kinetics of enzyme - catalysed reaction which involves following steps.

step-1 the enzyme combines with Reactant (substrate) to form an enzyme substrate complex which remains in equilibrium with the enzyme and substrate

$$E + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} ES$$

where E is the enzyme, S is substrate and ES is an enzyme substrate complex.

step: 2

The enzyme substrate complex ES, can decompose to form products with simultaneous regeneration of enzyme

$$ES \xrightarrow{K_3} E + P \quad \text{--- (1)}$$

where P is product

In the overall reaction $S \longrightarrow P$ the enzyme is consumed in the step (1) and regenerated in step (2)

Here we can steady state approximation, Because in first step (1) true equilibrium is not achieved.

According to slow rate determining step

$$r = -\frac{d}{dt}[S] = \frac{d}{dt}[P] = -K_3[ES]$$

$$y = \frac{dP}{dt} = K_3[ES] \quad -(1)$$

using steady state approximation for [ES] we have

$$\frac{d}{dt}[ES] = K_1[E][S] - K_2[ES] - K_3[ES] = 0 \quad -(2)$$

The equilibrium bln free and bound enzyme is given by enzyme conservation equation.

$$[E]_0 = [E] + [ES] \quad -③$$

where $[E]_0$ is total Enzyme concentration

$[E]$ is free Enzyme concentration

$[ES]$ is react Enzyme concentration

from Eq^n ③ $[E] = [E]_0 - [ES]$ —④

substitute Eq^n ④ in Eq^n ② we get

$$\Rightarrow K_1\{[E]_0 - [ES]\}[S] - K_2[ES] - K_3[ES] = 0$$

$$\Rightarrow K_1[E]_0[S] - K_1[ES][S] - K_2[ES] - K_3[ES] = 0$$

$$\Rightarrow K_1[E]_0[S] = [K_1[S] + K_2 + K_3][ES]$$

$$\therefore \boxed{[ES] = \frac{K_1[E]_0[S]}{K_1[S] + K_2 + K_3}} \quad -⑤$$

substitute Eq^n ⑤ in Eq^n ①

$$\frac{dP}{dt} = K_3[ES]$$

$$\frac{dP}{dt} = \frac{K_3 \frac{K_1}{K_1}[E]_0[S]}{K_1[S] + K_2 + K_3} \quad -⑥$$

deviding the above Eq^n by K_1 we get.

$$\frac{dP}{dt} = \frac{K_3[E]_0[S]}{\left(\frac{K_2+K_3}{K_1}\right) + [S]}$$

$$\therefore \boxed{r = \frac{K_3[E]_0[S]}{[S] + K_m}} \quad -⑦$$

where $K_m = \frac{K_2 + K_3}{K_1}$

K_m is called michaelis constant above Eq^n known as michaelis – menten Eq^n for formation of Products.

When all the enzyme has reacted with the substrate at high concentrations, the reaction will be going on at maximum rate. No free Enzyme will remain so that $[E]_0 = [ES]$

then $r_{max} = V_{max} = k_3 [E]_0$ —/ (b)

where the notation V_{max} refers max rate in enzymology

then Eq^n (a) can be written as

$$r = \frac{V_{max}[S]}{K_m + [S]}$$

case-1 If $K_m \gg [S]$ then $[S]$ can neglected

$$\therefore r = \frac{V_{max}[S]}{K_m}$$

$$r = K'[S] \quad \left[\because K' = \frac{V_{max}}{K_m}\right]$$

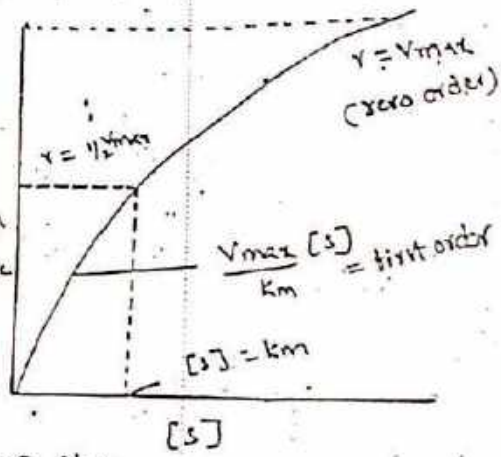
It is first order reaction

case-2 If $K_m \ll [S]$ then K_m can neglected

$$\therefore r = \frac{V_{max}[S]}{[S]}$$

$$\therefore r = V_{max} = \text{Constant}$$

It is zero order reaction



these two cases shown in fig.

If $K_m = [S]$ then $r = \frac{1}{2} V_{max}$

Hence michalis constant may be defined as equal to the conc. of S at which the rate of formation of product becomes half the maximum rate obtained by high conc. of S.

— o —

Acid – Base catalysis :-

Acid – base catalysis includy reactiony in solutiony which are catalysed by acidy or basy or both.

A reaction which is catalysed by H^+ ions but not by other Brownsted acid is said to specially proton catalysed.

Eg : 1) solvolysis of esters

2) Inversion of sugars.

A reaction which is catalysed by Brownsted acid is called general acid catalysis.

A reaction catalysed by $OH^\ominus$ ions is called specially base catalysed and Broanstead base is called general base catalysis.

Mechanism of Acid – Base catalysis :-

one step in reaction catalysed by an acid or a base is always the transfer of proton bln the substrate and the catalyst

The mechanism of catalysis is

$$C + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} X + Y$$

$$X + W \xrightarrow{K_3} P + Z$$

If 'C' is an acidic catalyst, which transfer a proton to the substrate then Y is the base conjugate to C. similarly if C is base Y is its conjugate acid. The specie W may either the solvent or a solute. If W is the solvent then the specie W may also be a basic substance present in solution.

Protolytic and prototropic mechanism :-

We know that the first stage in an acid catalysed reaction is a proton transfer to the substrate S, and the second proton transfer from the protonated substrate SH^+. In aqueous soln the intial proton transfer can be from a hydrogen ion H^+ or from some other acidic specie present in solution i.e BH^+. In second stage the proton transfer from SH^+ may be to water molecule (or) to some basic specie B present in the solution. It will be seen that the specie that transfer the proton to the substrate in the initial stage doy not have an important effect on the kinetic behaviour. The specie to which BH^+ transfer the proton in the second stage is important.

Protolytic Reaction :-

If the proton is transfered to the solvent molecule the mechanism is said to be protolytic

$$SH^+ + H_2O \longrightarrow S + H_3O^+$$

Prototropic process :-

The proton is transfered to a solute molecule generally in the second stage of mechanism called as prototropic

$$SH^+ + B \longrightarrow S + BH^+$$

Protolytic mechanism :-

The process are

$$S + AH^+ \underset{K_2}{\overset{K_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + H_2O \xrightarrow{K_3} P + H_3O^+$$

The rate of reaction $-\frac{d[P]}{dt} = + K_3 [SH^+] [H_2O]$

$$\frac{d[P]}{dt} = K_3 [SH^+] \quad [\because [H_2O] = 1]$$

In this proton is transfered from an acid (AH^+) to the substrate (S). The acid form of substrate then react with water molecule to form the product P.

Applying steady state approximation to $[SH^+]$

$$\frac{d}{dt}[SH^+] = K_1[S][AH^+] - K_2[SH^+][A^-] - K_3[SH^+][H_2O] = 0$$

i.e $$K_1[S][AH^+] = K_2[SH^+][A^-] + K_3[SH^+][H_2O]$$

$$= [SH^+]\left[K_2[A^-] + K_3[H_2O]\right]$$

$$\therefore [SH^+] = \frac{K_1[S][AH^+]}{K_2[A^-] + K_3[H_2O]}$$

But $[H_2O] = 1$

$$[SH^+] = \frac{K_1[S][AH^+]}{K_2[A^-] + K_3} \quad \text{— ①}$$

The rate of formation of products

i.e $$\frac{d}{dt}[P] = K_3[SH^+][H_2O]$$

$$= K_3[SH^+] \quad \text{— ②}$$

substitute eq^n ① in eq^n ②

$$\frac{d}{dt}[P] = \frac{K_3K_1[S][AH^+]}{K_2[A^-] + K_3}$$

<u>case-1</u> If $K_3 >> K_2[A]$

$$\frac{d}{dt}[P] = \frac{K_3K_1[S][AH^+]}{K_3}$$

$$= K_1[S][AH^+]$$

The reaction rate is depends upon substrate and acid concentration

The reaction is called as acid catalysed Reaction.

Case-II If $K_2[A^-] \gg K_3$ then

$$\frac{d}{dt}[P] = \frac{K_3 K_1 [S][AH^+]}{K_2 [A^-]}$$

Multiply the above Eqn with H^+ both num & dm

$$\frac{d}{dt}[P] = \frac{K_3 K_1 [S][AH^+][H^+]}{K_2 [A^-][H^+]}$$

We Know that $AH^+ \rightleftharpoons H^+ + A^-$

$$K = \frac{[H^+][A^-]}{[AH^+]}$$

$$1/K = \frac{[AH^+]}{[H^+][A^-]}$$

$$\frac{d}{dt}[P] = \frac{K_3 K_1}{K_2 K}[S][H^+]$$

It is also special type of H^+ ion catalysed Reaction.

Prototropic mechanism :-

$$S + AH^+ \underset{K_2}{\overset{K_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + A^- \xrightarrow{K_3} P + [AH^+]$$

The rate of reaction $\frac{d}{dt}[P] = K_3[SH^+][A^-]$ — ①

we assume that acid form of substrate to react with base instead of water molecule to form the products.

Apply steady state treatment for SH^+

$$\frac{d}{dt}[SH^+] = K_1[S][AH^+] - K_2[SH^+][A^-] - K_3[SH^+][A^-] = 0$$

$$K_1[S][AH^+] = K_2[SH^+][A^-] + K_3[SH^+][A^-]$$

$$= [SH^+]\left[K_2[A^-] + K_3[A^-]\right]$$

$$\therefore [SH^+] = \frac{K_1 [S] [AH^+]}{K_2 [A^-] + K_3 [A^-]} \quad -②$$

Substitute Eq^n ② in Eq^n ① we get

$$\frac{d}{dt}[P] = \frac{K_3 K_1 [S] [AH^+] [A^-]}{[K_2 + K_3] [A^-]}$$

$$\boxed{\frac{d}{dt}[P] = \frac{K_3 K_1 [S] [AH^+]}{K_2 + K_3}} \quad -③$$

Case-1 If $K_2 \gg K_3$ then Eq^n ③ becomes

$$\therefore \frac{d}{dt}[P] = \frac{K_1 K_3 [S] [AH^+]}{K_2}$$

This is an example for acid catalysed Reaction.

Case-2 If $K_3 \gg K_2$ then Eq^n ③ becomes

$$\frac{d}{dt}[P] = \frac{K_1 K_3 [S] [AH^+]}{K_3}$$

$$\frac{d}{dt}[P] = K_1 [S] [AH^+]$$

∴ this is also an acid catalysed Reaction.

Photochemistry

Introduction:-

The branch of chemistry which deals with the absorption of light and its effect on the substance is known as photochemistry. The light radiations important for photochemistry point of view are visible and UV regions. i.e. whole having wavelength b/n 4000 Å to 8000 Å

Laws of photochemistry :-

Grotthus - Draper law :-

When a 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 producing such effect.

Light of a particular wavelength and small range of wavelength is responsible for photochemical change.

White light ⟶ Alkaline cupric tartrate ⟶ cuprous oxide

The light absorbed undergoes the following changes

1. The absorbed light is converted into heat
   Eg:- Kinnow absorbs the light without any chemical change
2. The absorbed light is reemitted of light of different wave lengths
   Eg: Fluorescence and phosphorescence sequence
3. The absorbed light is absorbed to another substance which undergoes chemical change
   Eg. photosynthesis.

2. Law of photochemical Equivalence: (or) Stark-Einstein Law

In the photochemical reaction each atom (or) a molecule of a reacting substance absorbs one quantum of radiation

The energy of one quantum of radiation is photon. It given by

$$E = h\nu$$

The energy absorbed by one molecule of reacting substance is called Einstein

$$E = Nh\nu$$

N = Avagardo number = 6.023×10^{23}

h = plank's constant = 6.625×10^{-27} erg/sec

$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10}}{\lambda}$ → light velocity

$$\text{Einstein} = E = \frac{6.023 \times 10^{23} \times 6.625 \times 10^{-27} \times 3 \times 10^{10}}{\lambda \text{ in cm}} \text{ Erg/mole}$$

$$E = \frac{119.7 \times 10^{6}}{\lambda \text{ in cm}} \text{ Erg/mole}$$

(or)

$$E = \frac{119.7 \times 10^{6} \times 10^{-7}}{\lambda \text{ in cm}} \text{ Joule/mole}$$

(or)

$$E = \frac{119.7 \times 10^{6} \times 10^{-7}}{4.182 \times \lambda} \text{ Cal}$$

$$= \frac{2.86}{\lambda \text{ in cm}} \text{ Cal}$$

(or)

$$\therefore E = \frac{2.86 \times 10^{5}}{\lambda \text{ in A}^{\circ}} \text{ K. Cal}$$

Quantum yield (or) Quantum efficiency :-

The no of molecule reacted for photon of light absorbed is known as Quantum yield. It is denoted by ϕ

$$\phi = \frac{\text{No of molecule reacted}}{\text{No of photons absorbed}}$$

$$= \frac{\text{No. of mole reacted}}{\text{No of Einstein absorbed.}}$$

Normal Quantum yield :-

In some reaction in which the quantum efficiency is unity. It is agreement with Einstein law. This is called Normal quantum yield.

Eg: $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$

$\phi = 1$

Abnormal quantum yield :-

In some reactions the quantum efficiency is extremly high, or low. It is called abnormal quantum yield.

Eg: $H_2 + Cl_2 \longrightarrow 2HCl$ / $\phi = 10^4 - 10^6$

$H_2 + Br_2 \longrightarrow 2HBr$ $\phi = 0.01$

Based on the quantum yield the photochemical reactions are devided into three typs.

1. Reactions in which quantum efficiency is a simple Integer

Eg: Formation of ozone $3O_2 \longrightarrow 2O_3$

$2HI \longrightarrow H_2 + I_2$

2. Reactions in which quantum efficiency is extremely high.

Eg: Formation of phosgene & formation of HCl

$CO + Cl_2 \longrightarrow COCl_2$

$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl \quad \phi = 10^4 - 10^6$

3. Reactions in which quantum efficiency is extremely low

Eg: Formation of NH_3, HBr

$N_2 + 3H_2 \longrightarrow 2NH_3 \quad \phi = 0.2$

$H_2 + Br_2 \longrightarrow 2HBr \quad \phi = 0.01$

Mechanism of photochemical Reactions:

In order to explain the exceptions to Einstein law of photochemical equivalance, Bodenstein pointed out that photochemical reaction involve in two process

Primary process :-

In primary process each molecule absorbs one quantum of radiation. The absorbed energy may give rise to the formation of exited molecule

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

Secondary process :-

In this process a different no of molecule may undergo reaction by absorbing one quantum only. As a result the quantum efficiency of the reaction as whole will differ from unity.

Reasons for High Quantum yield

1. Each exited molecule in the primary process undergoes secondary process. Each secondary process give rise to some further

excited particle. This process continuous as a result a large no of reactant molecule undergo reaction. Hence the quantum yield is greater than unity.

3. In such reactions such as combination of H_2 & Cl_2 a chain is set up and quantum yield becomes about 10^6. These reactions are known as chain reactions.

$$Cl_2 + h\nu \longrightarrow 2Cl^{\cdot} \quad \text{chain initiation}$$

$$H_2 + Cl^{\cdot} \longrightarrow HCl + H^{\cdot}$$
$$H^{\cdot} + Cl_2 \longrightarrow HCl + Cl^{\cdot} \quad \Big\} \text{ chain propagation}$$

$$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2 \quad \text{chain termination}$$

$$\therefore \phi = 10^4 - 10^6$$

Reasons for low quantum yield :-

1) If the excited particle from the primary process are not react due to deactivation by collisions with other molecules. Hence quantum yield is extremely low.

2) The excited molecule produced in the primary may recombine to form the reactant to give low quantum yield.

3) Absorbed light is not sufficient to produce the activated molecule.

Eg:- Formation of HBr & NH_3

Bunsen and Roscoe law :-

The chemical action of light (expressed in the amount of product obtained) is directly proportional to product of light intensity (I) and duration of its action t.

Mathematically this law may be written as

$$n \propto It$$

$$n = KIt$$

n is no of photochemical change in time t sec and K is proportionality constant.

Q. 9

Experimental determination of quantum yield

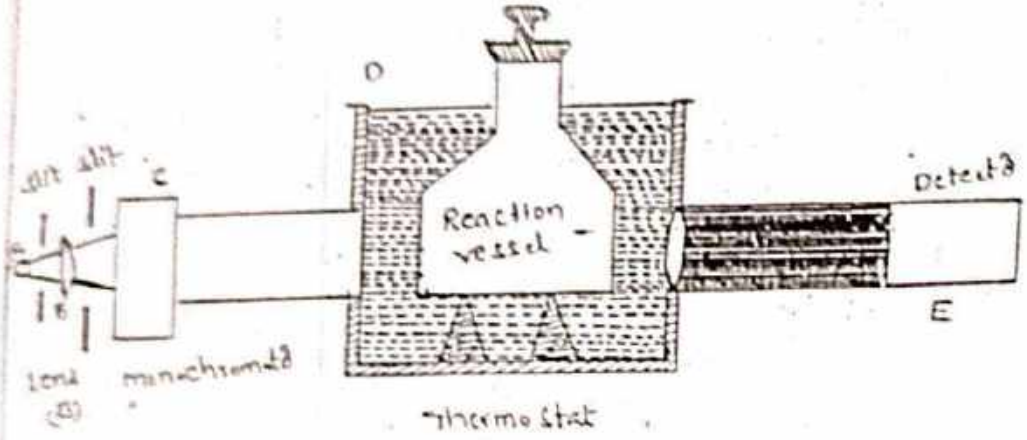
Knowledge of quantum efficiency of photo chemical rxn offers valuable information about the mechanism of photochemical reactions.

In order to determine the value of photochemical reaction it is essential to know

a) No. of moles reacting

b) No. of einsteins absorbed.

For this purpose an arrangement such as shown in fig.



i) Light Source :-

'A' is the source of light which may be sunlight lamp, mercury vapour lamp, discharge tube etc. For a quantitative type of work mercury vapour lamp is best suited source of ultra violet radiations, because it emits radiations of suitable intensity in desired spectral range. For visible or ultra violet the tungsten lamp is used.

ii) Monochromator :-

C is a monochromator or a filter. when light from source A is passed through the lens B and then allowed to pass through C, the monochromate 'C' will absorb the undesired wave length and transmit light of definite wavelength.

It has been observed that these colour filters transmit light with in certain range of wavelengths. monochromators generally made of gelatin or coloured glass of transparent plate with metd films of suitable thickness which absorb of undesired wavelength by interbac.

(iii) Radiation cell :-

The light from chromator enters a reaction cell D which contains the reaction mixture. The reaction cell is generally made of glass or quartz with optical plane windows for free exist and entrance of light radiation for visible special range, the reaction cell and other parts of instruments are generally made of glass. For ultra violet light all optical parts are made of quartz glass for solution; the cell is provide for stirring.

(iv) Detector :-

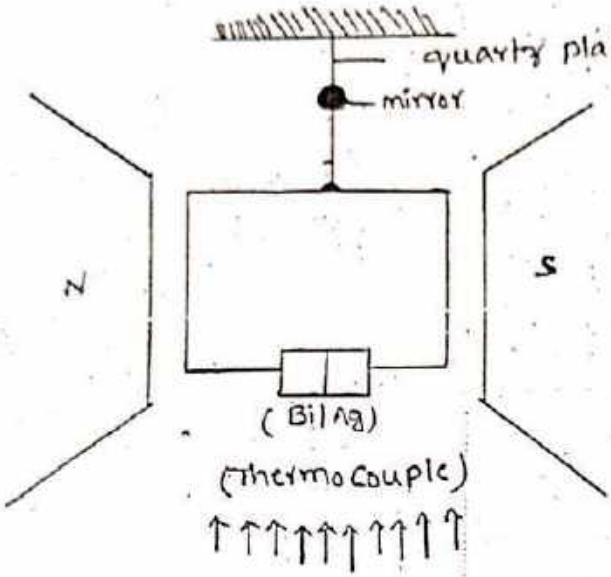
E is the detector which is used for deter-mine the intensity of light from a reaction cell. The intensity of light is measured with the reaction cell when empty and then with a reaction mixture. The difference bln two reacting will give the amount of energy absorbed by the reaction system under examination.

The intensity of light can be measured by the following detectors.

(i) Radio micrometer
(ii) photo electric cell
(iii) chemical actinometer
(iv) Geiger- muller counter
v) thermophile.

(i) Angle interferometer :-

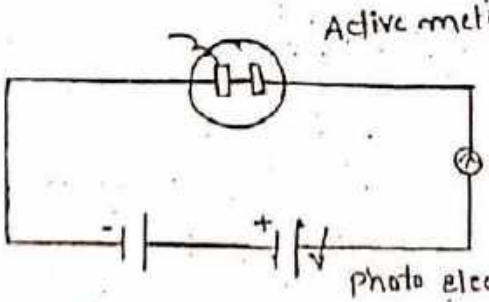
It consists of a coil (Thermo couple) which is suspend in the pole of an electro magnet. when the couple gets heated by light radiations, a current flows in the circuit and is deflected in the magnetic field.



The deflection can be measured by lamp and scale measurement. this deflection is proportional to intensity of light radiation.

(ii) Photo Electric cell :-

It is a device which converts the light energy into electrical energy. It is based on the principle of photo-electric effect, which state that electrons are effected from a metal plate when light of suitable wave length falls on it.



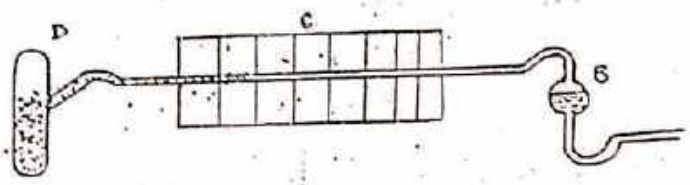
A photo electric cell consists of Li or Na metal which is enclosed in a vessel. this vessel is generally connected

upon the Li metal it loses electrons and develop +ve charge on itself. The current passing to the ammeter. The ammeter readings are noted current readings are directly proportional to the intensity of light radiation. photo electrically are generally used to measure very low intensity of light.

iii) **Chemical Actinometer :-**

A chemical actinometer can be used to measure the intensity of light radiation when extreme accuracy is not needed. A chemical actinometer generally consists of gas mixture of solutions which are sensitive to light. when light falls on the substance a chemical reaction will take place. The extent of chemical reaction is directly proportional to the energy absorbed, there are different types of actinometers given below

a) **Bunsen- Roscoe's Actinometer :-**



The bulb B contains mixture of H_2 and Cl_2 over water. The bulb D also contain water. The two bulbs B and D connected through a graduated tube C. when the light is incident on bulb B. some of the gases react to form HCl.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

This formed HCl is absorbed in water. This water is removed and water from bulb D is allowed to pass to bulb B through graduate tube C.

The motion of the water will proportional to the amount of HCl formed and also the intensity of light is absorbed.

b) J.m. Edeyk Actinometer:-

J.m. Eder utilized the following reaction to determine the absorbed radiation

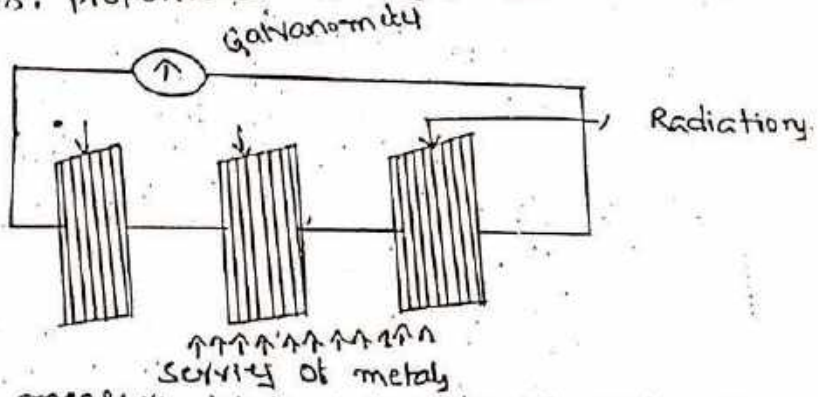
$$2HgCl_2 + (NH_4)_2C_2O_4 \longrightarrow 2NH_4Cl + 2CO_2\uparrow + Hg_2Cl_2\downarrow$$

when light falls on the system reaction takes place and the mercurous chloride formed in the reaction weighed and also the amount of CO_2 evolved is also estimated. From the weight of Hg_2Cl_2 or CO_2 the absorbed radiation may be determined quantitatively.

iv) Geiger - Muller counter :-

This is used for measuring very low intensities of radiations. The apparatus consists of ionisation chamber with a thick wire of steel or tungsten. when a charged particle enters the chamber the air present in it gets ionized and discharge is initiated in gas. A current then flows bln the Electrody is detected which is proportional to light radiation.

v) Thermophile:-



It is used to measure high intensity of light. It consists of series of unlike metals connected to a galvanometre. one end of it is coated with lamp black or platinum black and the other end is kept of such. The thermophile is kept in glass or quartz vessel. when a light from reaction cell is incident upon the black surface, it gets heated up results in the difference in the black and cold end. Thus a current flows in the circuit. The current produced is proportional to the intensity of light absorbed.

Procedure to determine the quantum yield :-

The apparatus is set up with the detector of the choice depending on the nature of the experiment. At first the intensity of light is determined by allowing the light through empty reaction cell the reaction cell is filled with reaction mixture and light is allowed to pass through it for known time and the intensity of light is measured after the reaction is over. The difference in the reaction gives the amount of Energy absorbed for the no of moles reacted can be known by different volumetric titrations or else the difference b/n the no of moles in initial mixture and the no of moles in the product formed gives the no of moles reacted. Now the quantum yield can be calculated by using the formula.

$$\text{Quantum yield } \phi = \frac{\text{No of moles reacted in given time}}{\text{No of photons absorbed in same time.}}$$

High quantum yield reactions :-

These are the photochemical reaction in which the quantum yield is greater than unity.

Eg:-

1) The quantum yield of the combination of carbon monoxide and chlorin by a light of wavelength 4000 – 4360 Å

$$CO + Cl_2 \longrightarrow COCl_2$$

2) Another example is photochemical decomposition of H_2O_2 by a wavelength of about 3100 Å. The quantum yield for this reaction more than 7.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Low quantum yield :-

This type include such photochemical reactions in which the quantum yield is less than unity.

Eg- 1) Combination of hydrogen and bromine to form HBr. This quantum yield of this reaction about 0.01

$$H_2 + Br_2 \longrightarrow 2HBr$$

2) photolysis of ammonia by a wavelength 2100 A°

$$2NH_3 \longrightarrow N_2 + 3H_2$$ 0.2

3) The quantum yield of concentration of malic acid into formic acid by light wave length range from 2000 to 1200 A° is 0.04

malic acid

formic acid

Photosensitization :-

It is frequently possible for a molecule in an exited state to transfer energy to another molecule raising the second molecule to an exited state while itself dropping down to the ground state. Transfer of energy in this way is called sensitisation.

certain reactions are known which are not sensitive to light these reactions can be made 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.

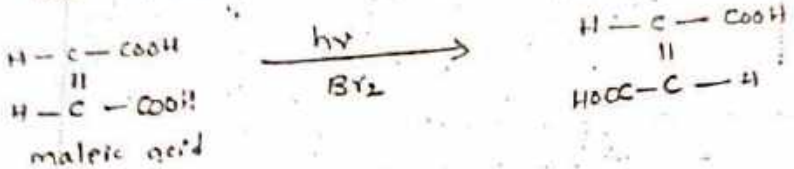
Formerly, it was thought that photosensitisation might be akin to catalysis. It has been conformed that photosensi-

Explanation (or) Role played by photo sensitiser :-

The formation of photosensitiser is to absorb light, become 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 act as carries energy.

Eg:-

(i) Bromine act as photosensitiser in the conversion of maleic acid into fumaric acid.



(ii) when a mixture of mercury vapour and hydrogen gas is illuminated by light of wavelength 2537 Å, the dissociation of molecular hydrogen into atomic hydrogen takes place.

$$Hg + H_2 \xrightarrow{h\nu} 2H + Hg$$

mechanism:-

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

$$Hg^* + H_2 \longrightarrow H_2^* + Hg$$

$$H_2^* \longrightarrow 2H$$

(iii) when the reaction is carried out bln hydrogen and oxygen in the presence of the influence of light radiations, the reaction leads to the formation of H_2O_2 and H_2O

$$3H_2 + 2O_2 \xrightarrow[h\nu]{Hg} 2H_2O + H_2O_2$$

iv) chlorine act as photosensitiser by decomposition of ozone gas in presence of chlorine under influence of u.v. light

$$2O_3 \xrightarrow[h\nu]{Cl_2} 3O_2$$

v) Cadimium vapour acts as photosensitiser for the polymerisation of ethylene for decomposition of Ethane

$$n\,CH_2=CH_2 \xrightarrow[h\nu]{Cd\ vapour} -(CH_2-CH_2)_n-$$

vi) chlorophyill act as photosensitiser in photosynthesis of carbohydrate from CO_2 and H_2O.

$$\text{chlorophyll} + h\nu \longrightarrow [\text{chlorophyll}]^*$$

$$6CO_2 + 6H_2O + [\text{chlorophyll}]^* \longrightarrow C_6H_{12}O_6 + 6O_2.$$

Exciplexes and Excimers :-

Eximer :-

It is an exited dimer molecule. It is formed as the combination of one atom in singlet state attached to the normal atom. when it gained energy and undergoes exited singlet state this state is known as eximer.

i.e $S + S^* \longrightarrow (SS)^*$

Exiplex :-

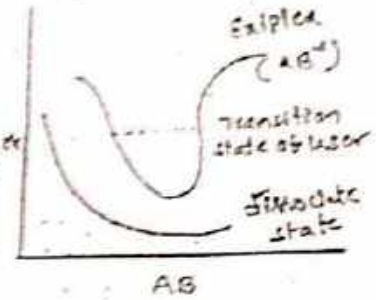
It is also an exited state of molecule. i.e A combination of two different atoms that exist as only in exited state. When an exiplex emits as a photon of electromagnatic radiation when it immediatly dissociate into atoms.

$$A^* + B \longrightarrow (AB)^*$$

By the combination of two atoms of molecule that survive only in an exited state which dissociates as soon as the exited energy has been discarded.

Eg :- mixture of xenon chloride and Ne. In which 'Ne'

The molecule of potential energy curve for an exciplex is shown in fig. The species can survives only as an excited state. Because on dissociating its energy it enters the ground state dissociated state, because only the upper state can exist.



Use:- This exiplex used in Laser Technique

Photochemical Equilibrium:- (or)

Photo stationary state:-

A state of photochemical equilibrium is said to exist in a reaction when the rate of two opposing reactions of which at least one is light sensitive, become equal under the influence of light radiation.

photo stationary state cases are fall into two categories.

a) In the first category:

only one reaction is light sensitive

$$A + B \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} C + D$$

Eg:-

b) Dissociation of NO_2:

when NO_2 vapour is exposed to light radiation of wavelength less than 3700 A°, it dissociates to form nitric oxide & oxygen. But the combination of these products is a dark reaction. Hence the equilibrium is

$$2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2NO + O_2$$

(ii) Dimerization of Anthracene:

In which formed from is light sensitive, but the backward reaction is a thermal or dark reaction. Its eqn is

$$2\ C_{14}H_{10} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} C_{28}H_{20}$$

b) In the second category :-

Both the reactions are light sensitive

$$A + B \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} C + D$$

Eg :-

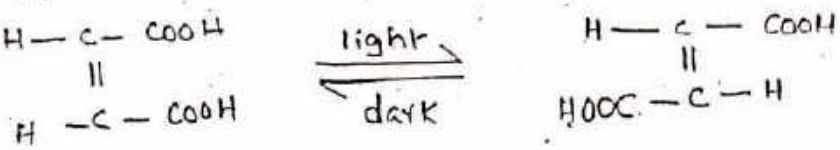
1) Formation of sulpher trioxide :-

It is an example of photostationary state. In which both forward and back ward process are light sensitive

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

2) Isomerisation of malic acid to Fumeric acid :

In which both forward and back ward reactions are light sensitive.



Applications :-

The concept of photostationary state has been used to explain the phenomenon of vision. when the light sensitive substance in eye called visual purple is exposed to light, the letter gets bleached to form visual yellow. Thus an Equilibrium is establish between visual purple and visual yellow. In dark the visual purple accumlaty and eye becomes sensitive when exposed to light further, it result in the phenomenon of dazzling.

Chemiluminscence:-

It may be defined as the emission of light radiation as a result of chemical reaction at temperatures when light rays are normally expected. The chemiluminscence is due to formation of products in exited state and when they return to ground state they emit light.

⇒ A classical example is that when atomic hydrogen comes into contact with mercury surface, blue luminscence appears with resonance line at 2537 Å. A characteristic of mercury along with band spectrum due to HgH. The process may be explained accedding to the following mechanism.

$$HgH + H + H \longrightarrow HgH^{*} + H_2$$

$$HgH + HgH^{*} \longrightarrow H_2 + Hg$$

⇒ chemiluminscene is also observed when alkali metal vapours react with halogens and with organic halidy and low pressure.

⇒ Grignard reagent emit chemiluminscence when they oxidise by air in ethereal soln. the luminscene is greenish blue and contains single broad band. only Grignard reagent in which mg atom is attached to unsaturated carbon atom are chemiluminscent in soln but in solid state both aliphatic and aromatic compounds exhibit.

⇒ It is reverse of photochemical reaction. Glow of phosphorous it is due to oxidation of phosphorous to P_2O_5

⇒ Glow of firefly it is due to oxidation of protein Luciferin.

Kinetics of Collisional quenching or) quenching of Fluoroscene:-

when a photochemically exited atom hay a chana to undergoy collisions with another atom or molecule before it fluoroscenes the intensity of Fluorosant radiation may be diminished or stopped. This phenomenon is known of quenching of Fluoroscene. It may also occur when the molecule changy from the singlet exited state to the triplet exited state. the phenomenon is called internal quenching. quenching may also result from the presence of an externally added speiy which takes up energy from the exited state molecule. The phenomenon is called external quenching.

Factors about the quenching of Fluoroscene:-

1. quenching of fluoroscene depends upon the concentration of the fluoroscene atom and of the quenching substance

2. At low pressure very little quenching will occur. At high pressure apperecible quenching taky place

3. quenching of Fluoroscene taky place apprecible in a liquid media because collisions are frequent.

Stern - volmer Equation:-

It is for the explanation of quenching of fluoroscene.

The fluoroscene may be quenched when the exited specie undergoy collisions with a normal molecule before it hay chana to fluoroscene. The quenching of fluoroscene occurs because of the energy transfer from exited speiy to the molecule changy from the singlet exited state to the

also result from the presence of externally added specy which take up energy from the exited state molecule the phenomenon is known as external quenching if 'Q' is the quencher we can write as

$$M + h\nu \xrightarrow{I_a} M^* \quad \text{[Activation]}$$

$$M^* \xrightarrow{K_f} M + h\nu \quad \text{[Flouroscene]}$$

$$\therefore M^* \xrightarrow{K} M \quad \text{[Internal quenching]}$$

$$M^* + Q \xrightarrow{K_Q} M + Q + K.E \quad \text{[External quenching]}$$

where K.E is Kinetic Energy

Apply steady state treatment to m^*, we have

$$\frac{d}{dt}[m^*] = I_a - K_f[m^*] - K[m^*] - K_Q[m^*][Q]$$

$$I_a = K_f[m^*] + K[m^*] + K_Q[m^*][Q]$$

where I_a is intensity of light absorbed.

$$I_f = K_f[m^*]$$

If I_f is the intensity of flouroscene, the quantum yield for the flouroscene is given by.

$$\phi_f = \frac{I_f}{I_a}$$

$$\phi_f = \phi_Q = \frac{I_f}{I_a} = \frac{K_f[m^*]}{K_f[m^*] + K[m^*] + K_Q[m^*][Q]}$$

$$= \frac{K_f}{K_f + K + K_Q[Q]}$$

i.e $\frac{\text{No of molecule flouresed}}{\text{No of photons absorbed}} = \frac{K_f}{K_f + K + K_Q[Q]}$

In the absence of quenching i.e $[Q] = 0$

$$\phi_0 = \frac{K_f}{K_b + K}$$

Hence the ratio of the two quantum yields

$$\frac{\phi_0}{\phi_Q} = \frac{K_f + K + K_Q[Q]}{K_b + K} = 1 + \frac{K_Q[Q]}{K_b + K}$$

$$= 1 + K_Q \tau [Q]$$

$$= 1 + K_{SV}[Q]$$

where $K_{SV} = K_Q \tau$ & $\tau = \frac{1}{K_b + K}$

$$\therefore \frac{\phi_0}{\phi_Q} = 1 + K_{SV}[Q]$$

This eqⁿ is known as the stern – volmer eqⁿ and K_{SV} is called stern – volmer constant. τ is life time of (M^*) in the absence of external quenching. From stern volmer eqⁿ we see that ϕ_0 / ϕ_Q depends linearly on $[Q]$. The slope of the line gives $K_Q \tau$ from which τ can be determined.

Solar Energy conversion and storage :-

photogalvanic cell :-

In photosynthesis solar energy is stored in two products namely carbohydrates and oxygen. The energy is released when carbohydrates burn in air. Here solar energy is convert into chemical energy. It is due to photosynthetic membrane in green plants. It is naturally occuring proces.

In development of such model system for storage and [illegible] of solar energy by direct conversion of lights quanta

solar energy quantum conversion devicy are used. these are based on two objectives.

1) conversion of light energy into thermal energy by suitable energy storing i.e Endergonic photochemical reaction.

2) conversion of light energy into Electrical energy by suitable photo Electrochemical devicy

1) The energy storing photo reactions occur with positive free energy change ($+\Delta G$). So these are thermodynamically unstable.

$$R \underset{\text{thermally forbidden}}{\overset{\text{photochemi allowed}}{\rightleftharpoons}} P$$

If the reverse back reaction is prevented or forbidden by other considerations, the energy remain stored in the photo products.

2) photo Electrical devicy to convert light energy into electrical energy consists of battery which undergoy cyclical charging and discharging proceff. on illumination the cell is charged. light energy is convert into chemical energy by driving a suitable reaction aganist potential gradient

$$\underset{\text{oxd}_1}{A_1} + \underset{\text{red}_2}{D_2} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \underset{\text{Red}_1}{D_1} + \underset{\text{oxd}_2}{A_2}$$

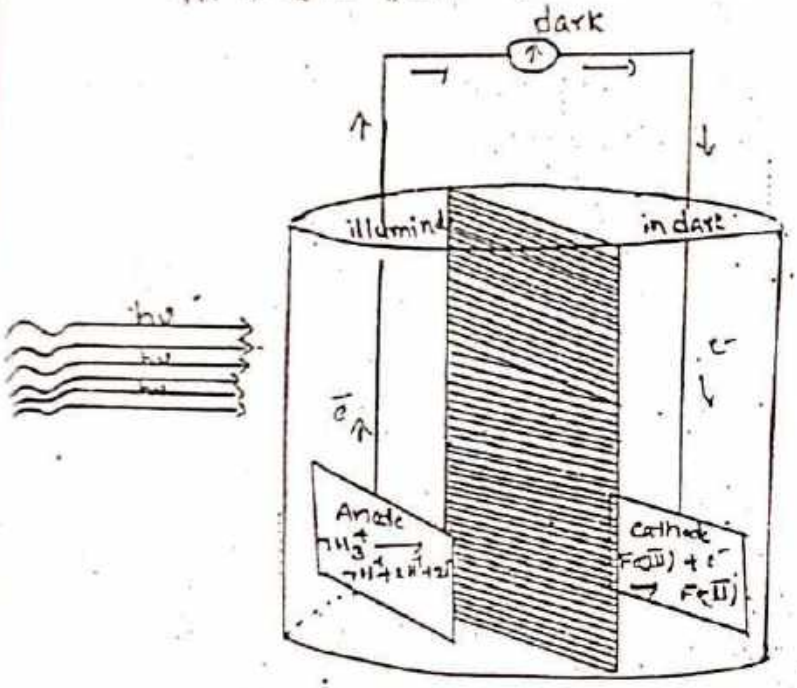
Where D and A represents the reduced forms and oxidised form of donor - acceptor system respectively. The reaction reverse spontaneously in the dark using the external circuit for Electron transfer. In the procen chemical energy is converted into Electrical energy and the cell is discharged. therefore an ideal system,

the system should function as rechargeable battery without any loss of efficiency, these are known as photogalvanic cells.

Eg :- Reversible photo bleaching of thionine by Fe^{+2} ion. Thionine exist as a cation at low pH and can be represented as TH^+

over all reaction is

$$TH^+ + 2Fe^{+2} + 2H^+ \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} TH_3^+ + 2Fe^{3+}$$



$$TH^+ + 2Fe^{+2} + 2H^+ \xrightarrow{h\nu} TH_3^+ + 2Fe(III)$$

The efficiency of photogalvanic device for solar energy conversion is not very good mainly because of

(i) Difficulty in preventing the spontaneous back recombination reaction

(ii) They can utilize the total solar spectrum