

## Chemical Kinetics

**Chemical kinetics** is that branch of chemistry which deals with the rates of reactions, the factors on which the rates of reactions depend and the mechanism by which the reactions take place.

### Rate of reaction

(1) **The rate of reaction** is defined as the change in the concentration of any one of the reactants or products per unit time i.e. it is the rate of change of concentration of a reactant or a product.

(i) For the reaction  $PCl_5 \rightarrow PCl_3 + PCl_2$ .

$$\text{Rate} = -\frac{\Delta[PCl_5]}{\Delta t} = +\frac{\Delta[PCl_3]}{\Delta t} = +\frac{\Delta[Cl_2]}{\Delta t}$$

The minus sign implies decrease in concentration whereas plus implies increase in concentration.

(ii) **Units of the rate of reaction** are  $\text{mol L}^{-1} \text{time}^{-1}$  or for gaseous reaction, these are  $\text{atm time}^{-1}$ .

(iii) Rate of reaction does not remain constant during the complete reaction because rate depends upon the concentration of reactants which decreases with time.

(iv) (Change in concentration/ time interval) gives the **average rate of reaction** if the interval is large.

(2) **Instantaneous rate of reaction** is the rate of reaction at any particular instant of time and is equal to small change in concentration ( $dx$ ) during a small interval of time ( $dt$ ) at that particular instant of time divided by the time interval i.e. equal to  $dx/dt$ .

(i) For a reaction of the type  $aA + bB \rightarrow xX + yY$

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{x} \frac{d[X]}{dt} = +\frac{1}{y} \frac{d[Y]}{dt}$$

(ii) For the reaction  $N_2 + 3H_2 \rightarrow 2NH_3$

$$\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = +\frac{1}{2} \frac{d[NH_3]}{dt}$$

$$\text{Rate of disappearance of } N_2 = -\frac{d[N_2]}{dt}$$

$$\text{Rate of disappearance of } H_2 = -\frac{d[H_2]}{dt}$$

$$\text{Rate of formation of } NH_3 = +\frac{d[NH_3]}{dt}$$

**Note** : □ In the expressions for rate, rates of change of concentration are divided by respective coefficients but rates of disappearance or formation do not involve coefficients.

**(3) Factors on which rate of reaction depends are :**

(i) *Concentration of the reactants* : Greater the concentration, faster is the reaction.

(ii) *Temperature effect* : The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient which is a ratio of two rate constants differing by a temperature of 10 K . Generally, the temperature selected are 298 K and 308 K . It is mathematically expressed as,

$$\text{Temperature coefficient} = \frac{\text{rate constant at } 308 \text{ K}}{\text{rate constant at } 298 \text{ K}}$$

According to collision theory the reaction rate depends on **collision frequency** and **effective collisions**.

For a molecule to have effective collision it should fulfill two conditions:

(a) Proper orientation, (b) Sufficient energy

It is observed that the reaction rate doubles for 10 K rise in temperature from 298 K to 308 K. This is presumably because the effective collisions double for 10 K rise in temperature from 298 K to 308 K. It must be noted that only reactions whose activation energy falls in the range of 50 – 55 kJ are found to double their rate for this range of temperature.

*Arrhenius derived* a mathematical expression to give a quantitative relationship between rate constant and temperature. The expression is

$$K = A.e^{-E_a/RT}$$

(Here, A = Frequency factor;  $E_a$  = activation energy; R = gas constant and T = temperature).

The doubling of reaction rate for 10 K rise in temperature from 298 K to 308 K can also be explained by calculating rate constants for the above temperature. Since  $E_a$  for majority of reactions falls in range 50 – 55 kJ mol<sup>-1</sup> therefore the rate of reaction doubles for all such reaction when the temperature is increased from 298 K to 308 K .

Arrhenius equation may also be written as  $\log K = \log A - E_a / 2.303 RT$ . A plot of  $\log K$  with  $\frac{1}{T}$  gives a straight line with slope  $= -\frac{E_a}{2.303 R}$

If  $K_2$  and  $K_1$  are rate constant at temperature  $T_2$  and  $T_1$  then.

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

Arrhenius equation can also be written in the form  $\frac{d \ln K}{dT} = \frac{E_a}{RT^2}$

For a reaction whose temperature coefficient is 2, if the reaction temperature is raised from  $25^{\circ}C$  to  $65^{\circ}C$  the rate increases by a factor  $2^4 = 16$  times.

(iii) *Effect of nature of reactants on rate of reaction* : The reaction rate depends on the physical state of reactants (physical nature). In general, smaller the particle size, more is the surface area it provides for the reaction and more is the rate of reaction.

Low activation energy reactions are fast whereas, high activation energy reactions are slow reactions.

(iv) *Effect of presence of a catalyst on rate of reaction* : The rate of a reaction enhances by the presence of a catalyst. A catalyst is specific in nature and accelerates the rate by providing alternative path of lower activation energy to the reactants.

(v) *Presence of light* : It provides the necessary activation energy and the reaction starts (photochemical reactions).

### Rate constant or specific reaction rate

It is the rate of reaction when the concentration of each reactant is 1 mol/L. For a given reaction it is constant at a particular temperature and is independent of the concentration of the reactants.

The units of the rate constant of a reaction depends on the order of the reaction. For an  $n^{\text{th}}$  order reaction

$$dx / dt = k(\text{conc.})^n$$

$$\therefore k = \frac{dx}{dt} \times \frac{1}{(\text{conc.})^n} = \frac{\text{conc.}}{\text{time}} \times \frac{1}{(\text{conc.})^n} = \frac{1}{\text{time}} \times \frac{1}{(\text{conc.})^{n-1}}$$

For zero order, first order and second order reaction ( $n=0, 1, 2$  respectively) units of rate constant,  $K$  are  $\text{mol L}^{-1} \text{time}^{-1}$ ,  $\text{time}^{-1}$  and  $\text{L mol}^{-1} \text{time}^{-1}$  respectively.

In case of gaseous reactions, concentration is expressed in terms of pressure having units of atmosphere.

### Factors influencing rate constant :

(1) **Temperature** : With increase in temperature, rate constant increases. Variation of rate constant is of the same degree as the variation of the rate of the reaction.

(2) **Catalyst** : Presence of catalyst (positive catalyst) lowers the energy of activation and therefore influences the rate as well as the rate constant of the reaction.

### Molecularity and order of reaction

Molecularity of reaction	Order of reaction
1. It is defined as the no. of molecules of reactant taking part in a chemical reaction. e.g. $NH_4NO_2 \rightarrow N_2 + 2H_2O$ $\therefore m = 1$	1. It is defined as the no. of molecules of reactants whose concentration determines the rate of reaction. $NH_4NO_2 \rightarrow N_2 + 2H_2O$ and rate $K[NH_4NO_2]$ $\therefore O.R. = 1$

## Chemical Kinetics

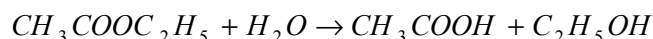
2. It can neither be zero nor fractional.	2. It may be zero, fractional or integer.
3. It is derived from mechanism of reaction	3. It is derived from rate expression.
4. It is theoretical value.	4. It is experimental value.
5. Reactions with molecularity $\geq 4$ are rare.	5. Reactions with <i>O.R.</i> $\geq 4$ are also rare.
6. Molecularity is independent of pressure and temperature	6. <i>O.R.</i> depends upon pressure and temperature

### • Salient features for determination of order of reaction :

(1) The rate expression is directly given, i.e.,  $2NO + O_2 \rightarrow 2NO_2$

$$\text{and Rate} = K[NO]^2[O_2]^1 \quad \therefore \text{O.R.} = 2 + 1 = 3$$

i.e., *O.R.* is also defined as sum of powers raised on concentration terms in order to write rate expression.



$$\text{and Rate} = K[CH_3COOC_2H_5]^1[H_2O]^0 \quad \therefore \text{O.R.} = 1 + 0 = 1$$

(2) The problem is provided up in form of language, i.e.,  $2A + B \rightarrow \text{Product}$

and given *A* shows first order kinetics and *B* shows zero order kinetics.

$$\therefore \text{O.R.} = 1 + 0 = 1 \text{ and rate} = K[A]^1[B]^0$$

(3) Either of reactant is mentioned as excess, i.e.

(i)  $2A + B \rightarrow \text{Products}$   
excess

$$\therefore \text{O.R.} = 2 + 0 = 2 \text{ and rate} = K[A]^2[B]^0$$

(ii)  $2A + B \rightarrow \text{Products}$   
excess

$$\therefore \text{O.R.} = 0 + 1 = 1 \text{ and rate} = K[A]^0[B]^1$$

(4) Experimental data is given :

(i) Case I : Rate is given using different conc. of A and B at same temperature.

Given that,	[A]	[B]	Rate
	$a_1$	$b_1$	$r_1$
	$a_2$	$b_2$	$r_2$
	$a_3$	$b_3$	$r_3$

$$\therefore r_1 = K[a_1]^m [b_1]^n; r_2 = K[a_2]^m [b_2]^n; r_3 = K[a_3]^m [b_3]^n$$

Where *m* and *n* are order for *A* and *B* respectively

Solve these to get *m* and *n*

$$\therefore \text{O.R.} = (m + n)$$

**Types of order of reactions****(1) Zero order reaction :**

Rate =  $K [ ]^0$       For       $A \rightarrow$       product

i.e.  $\frac{dx}{dt} = K$        $t = 0$        $a$        $0$

$t = t$        $(a - x)$        $x$

On integrating       $\frac{x}{t} = K$

**Characteristics :** • Rate remains constant through out the course of reaction.

• Unit of rate constant =  $\frac{\text{mol}}{\text{litre} \times \text{time}}$

• Half life period  $t_{1/2} \propto (a)$ , Where  $a$  is initial concentration.

**(2) 1<sup>st</sup> order reaction :**

Rate =  $K [ ]^1$       For       $A \rightarrow$       product

i.e.  $\frac{dx}{dt} = K [ ]^1$        $t = 0$        $a$        $0$

=  $K[a - x]^1$        $t = t$        $(a - x)$        $x$

On integrating, we get       $K \times t = 2.303 \log_{10} \frac{a}{(a - x)}$

**Characteristics :** • Rate continuously decreases with time.

• Unit of rate constant is  $\text{time}^{-1}$

• Half life period :  $t_{1/2} \propto (a)^0$ , i.e. half life for 1<sup>st</sup> order is independent of initial conc.

**(3) 2<sup>nd</sup> order reaction :**

**Case I:** If one reactant or two reactants with same initial concentration :

For       $A \rightarrow$       Product

$t = 0$        $a$        $0$

$t = t$        $(a - x)$        $x$

Rate =  $K [ ]^2$  or  $\frac{dx}{dt} = K(a - x)^2$

On integrating, we get,  $K \times t = \frac{1}{a} \frac{x}{(a - x)}$

**Case II :** If reactant are two and initial concentrations are different.

For       $A + B \rightarrow$       Products

at       $t = t$        $(a - x)$        $(b - x)$

Rate =  $K [ ]^1 [ ]^1$

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$$\frac{dx}{dt} = K[a-x][b-x]$$

on integrating, we get  $K \times t = \frac{2.303}{(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

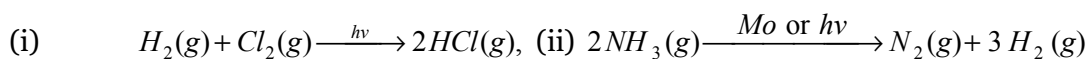
**Characteristics :** • Rate continuously decreases with time

• Unit of rate constant :  $\text{mol}^{-1} \text{litre}^{-1} \text{time}^{-1}$

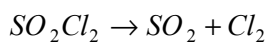
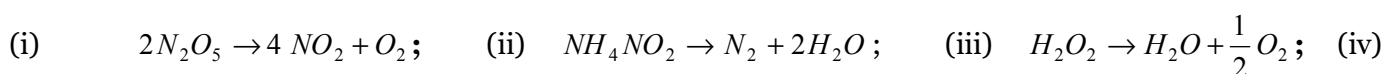
• Half life period :  $t_{1/2} \propto (a)^{-1}$  or  $t_{1/2} \propto \frac{1}{a}$

## Examples of reaction of different order

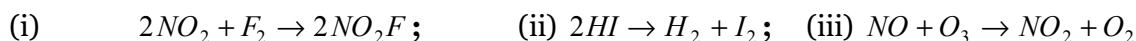
(1) Reactions of zero order



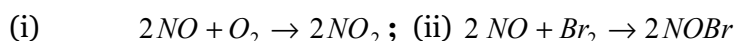
(2) Reactions of 1<sup>st</sup> order



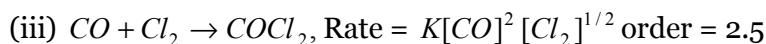
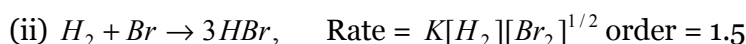
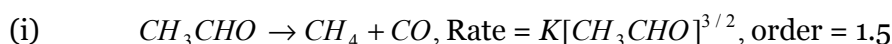
(3) Reactions of 2<sup>nd</sup> order



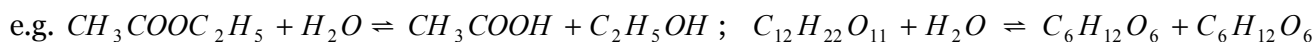
(4) Reactions of 3<sup>rd</sup> order



(5) Reactions of fractional order



(6) **Pseudo unimolecular reaction** : Reactions with O.R. = 1 but molecularity  $\geq 2$ , O.R. = 1, Molecularity = 2 for reaction given below



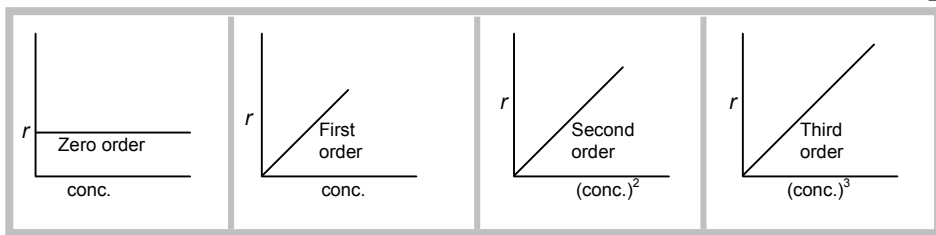
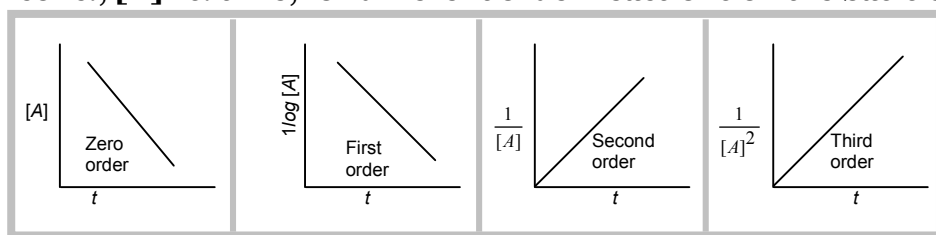
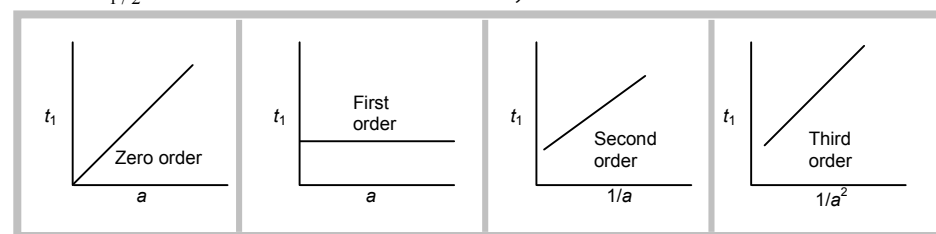
(7) **Pseudo bimolecular reaction** : Reactions with O.R. = 2 but molecularity  $\geq 3$

**Modified expressions for rate constants of some common reactions of first order**

Reaction	Expression for rate constant
(i) $N_2O_5 \rightarrow 2NO_2 + 1/2O_2$	$K = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$ ; Here $V_t$ = volume of $O_2$ after time $t$ and $V_\infty$ = volume of $O_2$ after infinite time.
(ii) $NH_4NO_2(aq) \rightarrow 2H_2O + N_2$	Same as above, here $V_t$ and $V_\infty$ are volumes of $N_2$ at time $t$ and at infinite time respectively.
(iii) $H_2O_2 \rightarrow H_2O + 1/2O_2$	$K = \frac{2.303}{t} \log \frac{V_0}{V_t}$ ; Here $V_0$ and $V_t$ are the volumes of $KMnO_4$ solution used for titration of same volume of reaction mixture at zero time (initially) and after time $t$
(iv) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	$K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$ ; Here $V_0$ , $V_t$ and $V_\infty$ are the volumes of $NaOH$ solution used for titration of same volume of reaction mixture after time 0, $t$ and infinite time respectively.
(v) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ <small><math>d</math>-sucrose                      <math>d</math>-glucose          <math>l</math>-fructose</small> (After the reaction is complete the equimolar mixture of glucose and fructose obtained is laevorotatory)	$K = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$ ; Here, $r_0$ , $r_t$ and $r_\infty$ are the polarimetric readings after time 0, $t$ and infinity respectively.

**Salient features of rate constant and half life period**

Order of reaction	Half life	Unit of rate constant
0	$t_{1/2} \propto (a)$	$mol \text{ litre}^{-1} \text{ time}^{-1}$
1	$t_{1/2} \propto (a)^0$	$time^{-1}$
2	$t_{1/2} \propto (a)^{-1}$	$mol^{-1} \text{ litre}^+ \text{ time}^{-1}$
3	$t_{1/2} \propto (a)^{-2}$	$mol^{-2} \text{ litre}^2 \text{ time}^{-1}$
$n$	$t_{1/2} \propto (a)^{1-n}$	$mol^{1-n} \text{ litre}^{n-1} \text{ time}^{-1}$

**Method of determination of order of reaction****(1) Graphical method :****(i) Plots of rate vs concentration for different order reactions [Rate = k (conc.)<sup>n</sup>]****(ii) Plots of conc., [A] vs. time, for different order reactions on the basis of integrated rate laws****(iii) Plots of  $t_{1/2}$  vs. initial concentration, a for different order reactions [ $t_{1/2} \propto a^{1-n}$ ]**

**(2) Initial rate method :** A number of experiments are carried out by varying concentration of a reactant w.r. to which, the order is to be determined keeping the concentrations of all other reactants constant. The initial rate of the reaction at each concentration is determined by concentration-time curves. The order of the reactant is then calculated from the rates at various concentrations. The experiments are repeated with other reactants in a similar way. Likewise, the order w.r. to all reactants are determined. The overall order is the sum of the orders of all the reactants.

**(3) Half life method :** Starting with two different concentrations  $a_1$  and  $a_2$  for the same reaction, the half lives,  $(t_{1/2})_1$  and  $(t_{1/2})_2$  are determined

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \quad \text{or} \quad n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1}; \quad n \text{ is the order of reaction.}$$

**(4) Van't hoff differential method :** For the different initial concentrations  $c_1$  and  $c_2$  equations can be written in the form  $-\frac{dc_1}{dt} = Kc_1^n$  and  $-\frac{dc_2}{dt} = Kc_2^n$

Taking logarithms of two equations and then subtracting, 
$$n = \frac{\log\left(\frac{dc_1}{dt}\right) - \log\left(\frac{dc_2}{dt}\right)}{\log c_1 - \log c_2}$$



**(5) Integrated rate equation method :**

(i) For a zero order reaction :  $K = \frac{[A]_0 - [A]}{t} = \frac{x}{t}$  and  $t_{1/2} = \frac{a}{2K}$

(ii) For a first order reaction :  $K = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{a}{a-x}$ ,  $t_{1/2} = 0.693 / K$

Amount of substance left after n half lives of a first order reaction =  $\frac{[A]_0}{n}$

(iii) For a second order reaction :  $K = \frac{1}{t} \left[ \frac{1}{[A]} - \frac{1}{[A]_0} \right] = \frac{1}{t} \left[ \frac{x}{a(a-x)} \right]$   $t_{1/2} = \frac{1}{Ka}$

(iv) For a third order reaction :  $K = \frac{1}{t} \left[ \frac{1}{[A]^2} - \frac{1}{[A]_0^2} \right] = \frac{1}{2t} \left[ \frac{x(2a-x)}{a^2(a-x)^2} \right]$   $t_{1/2} = \frac{3}{2Ka^2}$

Time taken to complete 75% of the reaction,  $t_{0.75} = 2 \times t_{0.50}$  where  $t_{0.50}$ , is the time taken to complete 50% of reaction i.e.,  $t_{1/2}$ .

(v) General expression for integrated rate equation of n<sup>th</sup> order reaction and its  $t_{1/2}$  :  $-\frac{d[A]}{dt} = K[A]^n$  [ $n \neq 1$ ]

On integrating  $K = \frac{1}{t(n-1)} \left[ \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$

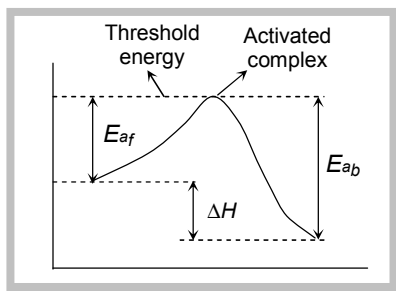
$$t = \frac{1}{K(n-1)} \left[ \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$

$$t_{1/2} = \frac{2^{n-1} - 1}{K(n-1)a^{n-1}} \quad [\text{For } n \neq 1]$$

These equations are not valid for first order reactions.

**Activated complex theory**

According to this theory when activation energy is supplied to a reaction it absorbs to form intermediate activated complex. An activated complex is a high energy, unstable intermediate which exists very briefly. Once formed it immediately decomposes to form products of lower energy state or more stability.



**Photochemical reactions**

(1) **Photochemical reactions** are those reactions which take place only in the presence of light but not in the dark.

(i) Red light has lowest energy. Hence photochemical reactions which can be initiated by red light can be initiated by all other radiations of visible light.

(ii) Temperature has very little effect on the rate of a photochemical reaction. Instead, the intensity of light has a marked effect.

(iii) Free energy change ( $\Delta G$ ) of a photochemical reaction may not be negative. This is because a part of the light energy absorbed by the reactants is converted into free energy of the products.

(iv) **Photosensitizer** is a substance which when added to a reaction mixture helps to start the photochemical reaction but itself does not undergo any chemical change *e.g.* chlorophyll in photosynthesis and *Hg* vapours in dissociation of  $H_2$ .

(v) **Vision** also involves a photochemical reaction in which the compound, retinal, present in the eye undergoes isomerisation by absorbing the light falling on it.

(2) **Quantum yield or Quantum efficiency of a photochemical reaction is :**

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

(i) **Photosynthesis of  $HCl$  has high quantum yield whereas photosynthesis of  $HBr$  has low quantum yield** : This is because after the primary process ( $Cl_2 \xrightarrow{h\nu} 2Cl$  or  $Br_2 \xrightarrow{h\nu} 2Br$ .) the first step of the secondary process of photosynthesis of  $HCl$  ( $Cl + H_2 \rightarrow HCl + H$ ) is exothermic whereas that of  $HBr$  ( $Br + H_2 \rightarrow HBr + H$ ) is endothermic.

(ii) Vision is a fast photochemical reaction in which the compound, retinal, present in the eye undergoes geometrical isomerisation by absorbing a photon of light.

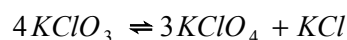
(3) **Luminiscence** : The emission of light during a process other than by the action of heat i.e. emission of cold light is called luminiscence. This can be of the following different types-

(i) **Chemiluminiscence** : The emission of cold light during a chemical reaction is called chemiluminiscence *e.g.* glow worm i.e. fire flies glow due to oxidation of protein, luciferin present in them.

(ii) **Fluorescence** : Some substances when exposed to light absorb it and immediately start re-emitting it. The glow continues so long as the light falls on the substance. The glow thus produced is called fluorescence and the substances producing the glow are called fluorescent substances *e.g.* fluorite ( $CaF_2$ ).

(iii) **Phosphorescence** : Some substances like  $ZnS$  continue to glow for some time even after the light is cut off. Such substances are called phosphorescent substances and the phenomenon is called phosphorescence.

(iv) **Bioluminiscence** : Certain living organisms emit light and show the phenomenon of chemiluminiscence. It is known as Bioluminiscence *e.g.*, light emission in fire flies.



(v) **Grothus-Draper law** : When light falls on a substance, a part of light is absorbed, a part is reflected and a part is transmitted. Only that part of light which is absorbed cause a particular reaction to occur.

(vi) **Stark's Einstein law of photochemical equivalence:** According to this law, every atom or molecule taking part in a photochemical reaction absorbs only one quantum of radiation.

(vii) Kinetics of fast reactions can be studied by (i) Relaxation method (ii) Flash photolysis technique etc.

### Some Important points

(1) Activation energy = Threshold energy – Energy of colliding molecules.

(2) Effective collisions are those in which colliding molecules must have

(i) Energy equal to or greater than the threshold energy, (ii) Proper orientation

(3) The value of temperature coefficient for most of the reactions lies between 2 to 3.

(4) The reaction  $NO + 1/2O_2 \rightarrow NO_2$  exhibits a small negative temperature coefficient and the rate of reaction decreases with increase in temperature.

(5) In the Arrhenius equation the quantity  $e^{-E_a/RT}$  is known as Boltzmann factor.

(6) Autocatalysis is a phenomenon in which the product formed is itself a catalyst and therefore enhances the rate:  $2MnO_4^- + 6H^+ + 5(COOH)_2 \rightleftharpoons 2Mn^{2+} + 10CO_2 + 8H_2O$   $Mn^{2+}$  ions formed catalyse the reaction.

(7) Promoters are substances which do not act as catalysts but enhance the efficiency of a catalyst for example,  $Mo$  acts as a promoter while  $Fe$  acts as a catalyst in Haber process for the manufacture of  $NH_3$ .

(8) Negative catalysts or Inhibitors are those substances which decrease the rate of a reaction.

(9) Catalyst can be poisoned by many substances.

(10) Enzyme catalysed reactions are faster than metal catalysed reactions, the former has lower activation energy.

(11) In the Arrhenius equation when  $T \rightarrow \infty$ , then,  $R = A.e^0 = A$  When  $E_a = 0, K = A$  and the rate of reaction becomes independent of temperature.

(12) The rate of reaction is never negative value. Minus sign in expression of the rate law indicates that the concentration of the reactant is decreasing the reaction.

(13) Generally rate of reaction with increase in temperature but remember for the reaction  $2NO + O_2 \rightarrow 2NO_2$ .

(14) The rate decreases slightly increases with increase in temperature.

When  $E_a = 0$ , the rate of reaction becomes independent of temperature ( $E_a =$  Energy of activation)

(15) Free energy ( $\Delta G$ ) for thermochemical reactions is always negative but remember,  $\Delta G$  for photochemical reactions may not always be negative. It may be +ve also, because a part of the light energy is converted into free energy of the products.

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