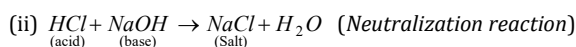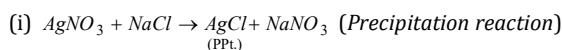B. Sc. II-Sem

Chemical Kinetics

The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst etc., on the reaction rates is called the chemical kinetics.

Types of chemical reactions

On the basis of reaction rates, the chemical reactions have been classified into the following three types,
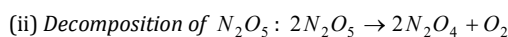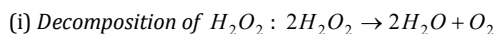
(1) **Very fast or instantaneous reactions:** These reactions occur at a very fast rate generally these reactions involve ionic species and known as ionic reactions. It is almost impossible to determine the rates of these reactions.

Examples

(i) $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$ (*Precipitation reaction*)
(PPt.)

(ii) $HCl + NaOH \rightarrow NaCl + H_2O$ (*Neutralization reaction*)
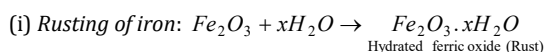(acid) (base) (Salt)

(2) **Moderate reaction:** These reactions proceed with a measurable rates at normal temperature and it is *these reactions are studied in chemical kinetics.* Mostly these reactions are molecular in nature.

Examples

(i) *Decomposition of* H_2O_2 : $2H_2O_2 \rightarrow 2H_2O + O_2$

(ii) *Decomposition of* N_2O_5 : $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

(3) **Very slow reactions:** These reactions are extremely slow and take months together to show any measurable change.

Examples

(i) *Rusting of iron*: $Fe_2O_3 + xH_2O \rightarrow Fe_2O_3.xH_2O$
Hydrated ferric oxide (Rust)

(ii) $2H_2 + O_2 \xrightarrow{\text{Room temperatu re}} 2H_2O$

Rate of a reaction

The rate (*speed or velocity*) *of a reaction is the change in concentration in per unit time.*

$\frac{\Delta x}{\Delta t}$ or $\frac{dx}{dt} = \left(\frac{x_2 - x_1}{t_2 - t_1}\right)$

where Δx or dx is the concentration change, *i.e.*, $(x_2 - x_1)$ in the time interval Δt or dt, *i.e.*, $(t_2 - t_1)$.

Concentration is generally expressed in active mass, *i.e.*, mole L^{-1}

• The rate measured over a long time interval is called *average rate* and the rate measured for an infinitesimally small time interval is called *instantaneous rate* and

Instantaneous rate $= (\text{Average rate})_{\Delta t \to 0}$

• For the reaction $aA + bB \rightarrow cC + dD$

Rate of disappearance of a reactant is negative

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

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

Rate of formation of a product is positive

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

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

• In terms of stoichiometric coefficient rate may be expressed as

$\frac{dx}{dt} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$
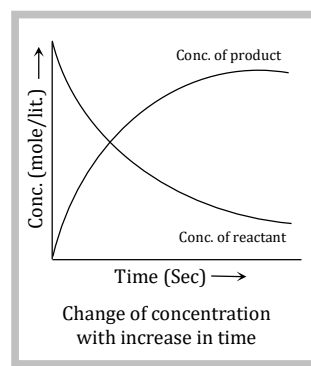
• The rate of reaction is always ***positive***.

• The rate of chemical reaction decreases as the reaction proceeds.

• Unit of rate of a reaction = $\frac{\text{Unit of conc.}}{\text{Unit of time}}$ =$mole\ L^{-1}\ time^{-1}$

In term of gaseous reaction the unit is *atm time^{-1}* and
Rate in *atm time^{-1}* = Rate in mole $L^{-1} time^{-1} \times RT$

Change of concentration with increase in time
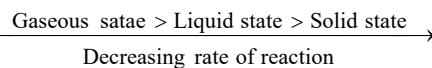
Factors affecting rate of a reaction

The rate of a chemical reaction depends on the following things

(1) **Nature of reactants**

(i) *Physical state of reactants*: This has considerable effect over rate of reaction.

Gaseous satae > Liquid state > Solid state
Decreasing rate of reaction

(ii) *Physical size of the reactants*: Among the solids, rate increases with decrease in particle size of the solid.

(iii) *Chemical nature of the reactants*

(a) Reactions involving polar and ionic substances including the proton transfer reactions are usually very fast. On the other hand, the reaction in which bonds is rearranged, or electrons transferred are slow.

(b) Oxidation-reduction reactions, which involve transfer of electrons, are also slow as compared to the ionic substance.

(c) Substitution reactions are relatively much slower.

(2) **Effect of temperature:** The rate of chemical reaction generally increases on increasing the temperature. The rate of a reaction becomes almost double or tripled for every 10^oC rise in temperature.

Temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differing by (generally $25°C$ and $35°C$) $10°C$.

$$\mu = \text{Temperature coefficient} = \frac{k \text{ at } (t+10^{\circ}C)}{k \text{ at } t^{\circ}C} = \frac{k_{35^{\circ}C}}{k_{25^{\circ}C}}$$

(3) **Concentration of reactants:** The rate of a chemical reaction is directly proportional to the concentration of the reactants means rate of reaction decreases with decrease in concentration.

(4) **Presence of catalyst:** The function of a catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate.

A catalyst changes the reaction path
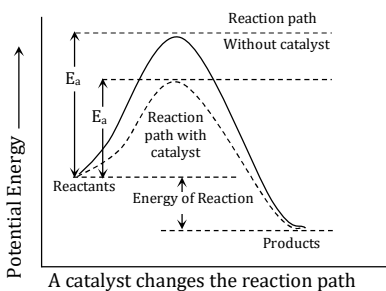
(5) **Effect of sunlight :** There are many chemical reactions whose rate are influenced by radiations particularly by ultraviolet and visible light. Such reactions are called photochemical reactions. For example, Photosynthesis, Photography, Blue printing, Photochemical synthesis of compounds etc.

The radiant energy initiates the chemical reaction by supplying the necessary activation energy required for the reaction.

Law of mass action and Rate constant

The rate at which a substance reacts is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances.

- For a reaction, $aA + bB \rightarrow$ product

$$\text{Rate} = \left(\frac{dx}{dt}\right) \propto [A]^a [B]^b \; ; \; \left(\frac{dx}{dt}\right) = k[A]^a [B]^b$$

Where k is called **rate constant** or **velocity constant**.

When $[A] = [B] = 1 \, mol/litre$, then $\frac{dx}{dt} = k$

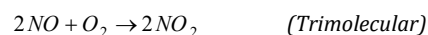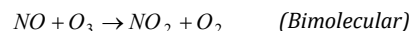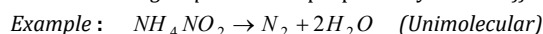Thus, rate constant k is also called **specific reaction rate**.

- The value of rate constant depends on, nature of reactant, temperature and catalyst. It is independent of concentration of the reactants.

- Unit of rate constant $= \left[\dfrac{\text{litre}}{\text{mol}}\right]^{n-1} \times \sec^{-1} = \left[\dfrac{\text{mol}}{\text{litre}}\right]^{1-n} \times \sec^{-1}$

Where n = order of reaction.

Rate law: Molecularity and Order of a reaction

Molecularity is the sum of the number of molecules of reactants involved in the balanced chemical equation. Molecularity of a complete reaction has no significance and overall kinetics of the reaction depends upon the rate determining step. *Slowest step is the rate-determining step.* This was proposed by *Van't Hoff.*

$$\textit{Example}: \quad NH_4NO_2 \rightarrow N_2 + 2H_2O \quad \textit{(Unimolecular)}$$
$$NO + O_3 \rightarrow NO_2 + O_2 \quad \textit{(Bimolecular)}$$
$$2NO + O_2 \rightarrow 2NO_2 \quad \textit{(Trimolecular)}$$

The total number of molecules or atoms whose concentration determine the rate of reaction is known as order of reaction.

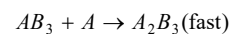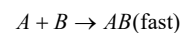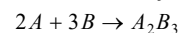*Order of reaction = Sum of exponents of the conc. terms in rate law*

For the reaction $xA + yB \rightarrow$ Products

The rate law is $\text{Rate} = [A]^x [B]^y$

Then the overall order of reaction. $n = x + y$

where x and y are the orders with respect to individual reactants.

- If reaction is in the form of reaction mechanism then the order is determined by the slowest step of mechanism.

$$2A + 3B \rightarrow A_2B_3$$
$$A + B \rightarrow AB(\text{fast})$$
$$AB + B_2 \rightarrow AB_3(\text{slow}) \qquad (\textit{Rate determining step})$$
$$AB_3 + A \rightarrow A_2B_3(\text{fast})$$

(Here, the overall order of reaction is equal to two.)

- Molecularity of a reaction is derived from the mechanism of the given reaction. Molecularity can not be greater than three because more than three molecules may not mutually collide with each other.

- Molecularity of a reaction can't be zero, *negative* or fractional. order of a reaction may be zero, negative, positive or in fraction and greater than three. Infinite and imaginary values are not possible.

- When one of the reactants is present in the large excess, the second order reaction conforms to the first order and is known as *pesudo unimolecular reaction*. (Table 11.1)

Table : 11.1 Order and molecularity of some reaction

S. No.	Chemical equation	Molecularity	Rate law	Order w.r.t.		
				First reactant	Second reactant	Overall
1.	$aA + bB \rightarrow$ product	$a + b$	$\left(\dfrac{dx}{dt}\right) = k[A]^a [B]^b$	a	b	$a + b$
2.	$aA + bB \rightarrow$ product	$a + b$	$\left(\dfrac{dx}{dt}\right) = k[A]^2 [B]^0$	2	zero, if B is in excess	2
3.	$2H_2O_2 \xrightarrow{Pt,\Delta} 2H_2O + O_2$	2 (Bimolecular)	$\left(\dfrac{dx}{dt}\right) = k[H_2O_2]$	1*	-----	1
4.	$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	2 (Bimolecular)	$\left(\dfrac{dx}{dt}\right) = k[CH_3COOC_2H_5]$	1*	Zero, if H_2O is in excess	1
5.	$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+}$	2 (Bimolecular)	$\left(\dfrac{dx}{dt}\right) = k[C_{12}H_{22}O_{11}]$	1*	Zero, if H_2O is in excess	1

		$C_6H_{12}O_6 + C_6H_{12}O_6$ Glucose Fructose				
6.	$(CH_3)_3 CCl + OH^- \rightarrow$ $(CH_3)_3 COH + Cl^-$	2 (Bimolecular)	$\left(\dfrac{dx}{dt}\right) = k[(CH_3)_3 CCl]$	1*	Zero, if OH^- does not take part in slow step	1
7.	$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$	2 (Bimolecular)	$\left(\dfrac{dx}{dt}\right) = k[CH_3Cl][OH^-]$	1	1	2
8.	$C_6H_5N_2Cl \xrightarrow{\Delta} C_6H_5Cl + N_2$	1 (Unimolecular)	$\left(\dfrac{dx}{dt}\right) = k[C_6H_5N_2Cl]$	1	----	1
9.	$CH_3CHO \xrightarrow{\Delta} CH_4 + CO$	1 (Unimolecular)	$\left(\dfrac{dx}{dt}\right) = k[CH_3CHO]^{3/2}$	1.5	----	1.5
10.	$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$	5	$\left(\dfrac{dx}{dt}\right) = k[H_2O_2][I^-]$	1	1 ($H^+$is medium)	2
11.	$2O_3 \rightarrow 3O_2$	2 (Bimolecular)	$\left(\dfrac{dx}{dt}\right) = k[O_3]^2[O_2]$	1	-1 with respect to O_2	1

*Pseudo-unimolecular reactions.

Table : 11.2 Rate constant and other parameters of different order reactions

Order	Rate constant	Unit of rate constant	Effect on rate by changing conc. to m times	(Half-life period) $T_{50}=$
0	$k_0 = \dfrac{x}{t}$	conc. time^{-1} (mol L^{-1} s^{-1})	No change	$\dfrac{a}{2k_0}$
1	$k_1 = \dfrac{2.303}{t} \log_{10}\left(\dfrac{a}{a-x}\right)$, $C = C_0 e^{-k_1 t}$ $N = N_0 e^{-k_1 t}$, $k_1 = \dfrac{2.303}{(t_2 - t_1)} \log_{10} \dfrac{(a - x_1)}{(a - x_2)}$	time^{-1} (s^{-1})	m times	$\dfrac{0.693}{k_1}$
2	$k_2 = \dfrac{1}{t}\left[\dfrac{1}{(a-x)} - \dfrac{1}{a}\right] = \dfrac{x}{ta(a-x)}$ (for the case when each reactant has equal concentration) $k_2 = \dfrac{2.303}{t(a-b)} \log_{10}\left[\dfrac{b(a-x)}{a(b-x)}\right]$ (for the case when both reactants have different concentration)	conc^{-1} time^{-1} (mol L^{-1}) s^{-1} L mol^{-1} s^{-1}	m^2 times	$\dfrac{1}{k_2 a}$
3	$k_3 = \dfrac{1}{2t}\left[\dfrac{1}{(a-x)^2} - \dfrac{1}{a^2}\right]$	conc^{-2} time^{-1} (mol L^{-1})$^{-2}$ s^{-1} L^2 mol^{-2} s^{-1}	m^3 times	$\dfrac{3}{2k_3 a^2}$
n	$k_n = \dfrac{1}{(n-1)t}\left[\dfrac{1}{(a-x)^{n-1}} - \dfrac{1}{(a)^{n-1}}\right]$; $n \geq 2$	conc$^{(1-n)}$ time^{-1} (mol L^{-1})$^{(1-n)}$ s^{-1} $L^{(n-1)}$ mol$^{(1-n)}$ s^{-1}	m^n times	$\dfrac{2^{n-1} - 1}{(n-1)k_n (a)^{n-1}}$

Methods for determination of order of a reaction

(1) **Integration method** (Hit and Trial method)

(i) The method can be used with various sets of a, x and t with integrated rate equations.

(ii) The value of k is determined and checked for all sets of a, x and t.

(iii) If the value of k is constant, the used equation gives the order of reaction.

(iv) If all the reactants are at the same molar concentration, the kinetic equations are :

$k = \dfrac{2.303}{t} \log_{10} \dfrac{a}{(a-x)}$ (*For first order reactions*)

$k = \dfrac{1}{t}\left[\dfrac{1}{a} - \dfrac{1}{a-x}\right]$ (*For second order reactions*)

$k = \dfrac{1}{2t}\left[\dfrac{1}{(a-x)^2} - \dfrac{1}{a^2}\right]$ (*For third order reactions*)

(2) **Half-life method:** This method is employed only when the rate law involved only one concentration term.

$t_{1/2} \propto a^{1-n}$; $t_{1/2} = ka^{1-n}$; $\log t_{1/2} = \log k + (1-n) \log a$

A plotted graph of $\log t_{1/2}$ *vs log a* gives a straight line with slope $(1-n)$, determining the slope we can find the order n. If half-life at different concentration is given then,
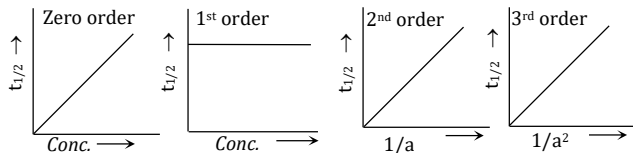
$(t_{1/2})_1 \propto \dfrac{1}{a_1^{n-1}}$; $(t_{1/2})_2 \propto \dfrac{1}{a_2^{n-1}}$; $\dfrac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\dfrac{a_2}{a_1}\right)^{n-1}$

$$\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)\left[\log_{10} a_2 - \log_{10} a_1\right]$$

$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10} a_2 - \log_{10} a_1)}$$

This relation can be used to determine order of reaction 'n'

Plots of half-lives Vs concentrations ($t_{1/2} \propto a^{1-n}$)

(3) **Graphical method:** A graphical method based on the respective rate laws, can also be used.

(i) If the plot of $\log(a-x)$ Vs t is a straight line, the reaction follows first order.

(ii) If the plot of $\dfrac{1}{(a-x)}$ Vs t is a straight line, the reaction follows second order.
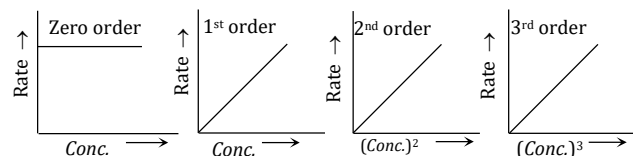
(iii) If the plot of $\dfrac{1}{(a-x)^2}$ Vs t is a straight line, the reaction follows third order.

(iv) In general, for a reaction of nth order, a graph of $\dfrac{1}{(a-x)^{n-1}}$ Vs t must be a straight line.

Plots from integrated rate equations
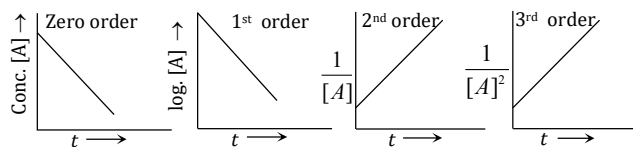
Plots of rate Vs concentrations [Rate = k(conc.)ⁿ]

(4) **Van't Haff differential method:** The rate of reaction varies as the nth power of the concentration Where 'n' is the order of the reaction. Thus for two different initial concentrations C_1 and C_2 equation, can be written in the form,

$$\frac{-dC_1}{dt} = kC_1^n \text{ and } \frac{-dC_2}{dt} = kC_2^n$$

Taking logarithms,

$$\log_{10}\left(\frac{-dC_1}{dt}\right) = \log_{10} k + n\log_{10} C_1 \qquad .....(i)$$

and $$\log_{10}\left(\frac{-dC_2}{dt}\right) = \log_{10} k + n\log_{10} C_2 \qquad .....(ii)$$

Subtracting equation (ii) from (i),

$$n = \frac{\log_{10}\left(\frac{-dC_1}{dt}\right) - \log_{10}\left(\frac{-dC_2}{dt}\right)}{\log_{10} C_1 - \log_{10} C_2} \qquad .....(iii)$$

$\dfrac{-dC_1}{dt}$ and $\dfrac{-dC_2}{dt}$ are determined from concentration Vs time graphs and the value of 'n' can be determined.

(5) **Ostwald's isolation method** (Initial rate method)

This method can be used irrespective of the number of reactants involved *e.g.,* consider the reaction, $n_1 A + n_2 B + n_3 C \rightarrow$ Products .

This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants (A, B, C).

Suppose it is observed as follows,

(i) Keeping the concentrations of B and C constant, if concentration of A is doubled, the rate of reaction becomes four times. This means that, Rate $\propto [A]^2$ *i.e.,* order with respect to A is 2

(ii) Keeping the concentrations of A and C constant, if concentration of B is doubled, the rate of reaction is also doubled. This means that, Rate $\propto [B]$ *i.e.,* order with respect to B is 1

(iii) Keeping the concentrations of A and B constant, if concentration of C is doubled, the rate of reaction remains unaffected. This means that rate is independent of the concentration of C *i.e.,* order with respect to C is zero. Hence the overall rate law expression will be, Rate $= k[A]^2 [B] [C]^0$

$\therefore$ Overall order of reaction $= 2 + 1 + 0 = 3$.

Theories of reaction rate

(1) **Collision theory**

(i) The basic requirement for a reaction to occur is that the reacting species must collide with one another. This is the basis of *collision theory* for reactions.

(ii) The number of collisions that takes place per second per unit volume of the reaction mixture is known as *collision frequency* (Z). The value of collision frequency is very high of the order of 10^{25} to 10^{28} in case of binary collisions.

(iii) Every collision does not bring a chemical change. The collisions that actually produce the product are *effective collisions*. The effective collisions, which bring chemical change, are few in comparison to the total number of collisions. The collisions that do not form a product are *ineffective elastic collisions, i.e.,* molecules just collide and disperse in different directions with different velocities.

Distribution of energies at a definite temperature
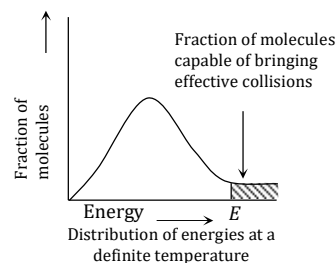
(iv) For a collision to be effective, the following two barriers are to be cleared,

(a) *Energy barrier:* "*The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as **threshold energy***".

• In the graph '*E*' corresponds to minimum or threshold energy for effective collision.

• There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy to cross the energy barrier.

(b) *Orientation barrier:* The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed. For example, $NO_2(g) + NO_2(g) \rightarrow N_2O_4(g)$. During this reaction, the products are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions.

Collisions not properly oriented
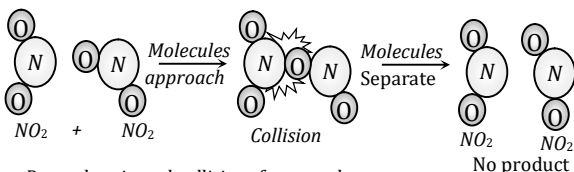
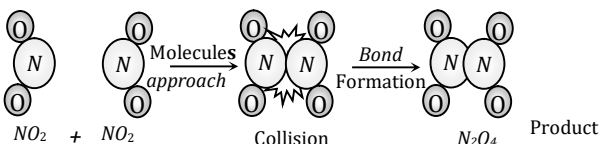*Properly oriented collisions form products*

Fig. 11.1

(v) Thus, the main points of **collision theory** are as follows,

(a) For a reaction to occur, there must be collisions between the reacting species.

(b) Only a certain fraction of the total number of collisions is effective in forming the products.

(c) For effective collisions, the molecules should possess sufficient energy as well as orientation.

(vi) The fraction of effective collisions, under ordinary conditions may vary from nearly zero to about one for ordinary reactions. Thus, the rate of reaction is proportional to :

(a) The number of collisions per unit volume per second (Collision frequency, Z) between the reacting species

(b) The fraction of effective collisions (Properly oriented and possessing sufficient energy), f *i.e.,* $\text{Rate} = \dfrac{-dx}{dt} = f \times Z$

Where f is fraction of effective collision and Z is the collision frequency.

(vii) The physical meaning of the activation energy is that it is the minimum relative kinetic energy which the reactant molecules must possess for changing into the products molecules during their collision. This means that the fraction of successful collision is equal to $e^{-E_a/RT}$ called **Boltzmann factor.**

(viii) It may be noted that besides the requirement of sufficient energy, the molecules must be properly oriented in space also for a collision to be successful. Thus, if Z_{AB} is the

collision frequency, P is the **orientation factor** (Steric factor) then, $k = PZ_{AB}.e^{-E_a/RT}$. If we compare this equation with Arrhenius equation. $k = A e^{-E_a/RT}$

We know that pre-exponential form '*A*' in Arrhenius equation is, $A = PZ_{AB}$.

Concept of activation energy

The excess energy (Over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called **activation energy** (E_a)**,**

$$E_a = E_{(\text{Threshold energy})} - E_{(\text{Reactants})}$$

Activation energy = Threshold energy – Average kinetic energy of the reacting molecules.

(a) *Zero activation energy* = Fraction of effective collision (f) will be very large = Very fast reaction (Instantaneous reaction).

(b) *Low activation energies* = Fraction of effective collision (f) will be large = Fast reactions.

(c) *High activation energies* = Fraction of effective collision (f) will be small = Slow reaction.

The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products.

According to the concept of activation energy, the reactants do not change directly into the products. The reactant first absorb energy equal to activation energy and form activated complex. At this state, the molecules must have energy at least equal to the threshold energy. This means that the reaction involves some energy barrier which must be overcome before products are formed. The energy barrier is known as **activation energy barrier**.
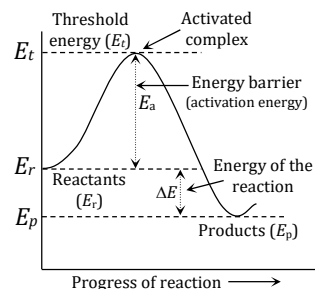
(2) **Transition state theory**

(i) According to transition state theory the activated complex is supposed to be in equilibrium with the reactant molecules.

(ii) Once the transition state is formed it can either return to the initial reactants or proceeds to form the products.

(iii) Assuming that once formed the transition state proceeds to products we can say that rate is proportional to concentration of transition state.

Mathematically, Rate $\propto$ Transition state

Rate= Constant × Transition state

(iv) The activation energy for the forward reaction, (E_a^f) and the activation energy for the reverse reaction (E_a^r) are

related to the enthalpy (ΔH) of the reaction by the equation $\Delta H = E_a^f - E_a^r$.

(a) *For endothermic reactions*, $\Delta H > 0$, so that $E_a^r < E_a^f$

(b) *For exothermic reaction*, $\Delta H < 0$, so that $E_a^r > E_a^f$.

Arrhenius equation

Arrhenius proposed a quantitative relationship between rate constant and temperature as,

$$k = A\,e^{-E_a/RT} \qquad\qquad .....\text{(i)}$$

The equation is called ***Arrhenius equation***.

In which constant A is known as ***frequency factor***. This factor is related to number of binary molecular collision per second per litre.

E_a is the activation energy.

T is the absolute temperature and

R is the gas constant

Both A and E_a are collectively known as ***Arrhenius parameters***.

Taking logarithm equation (i) may be written as,

$$\log k = \log A - \frac{E_a}{2.303\,RT} \qquad\qquad .....\text{(ii)}$$

The value of activation energy (E_a) increases, the value of k decreases and therefore, the reaction rate decreases.

When log k plotted against $1/T$, we get a straight line. The intercept of this line is equal to log A and slope equal to $\dfrac{-E_a}{2.303\,R}$.

Therefore $E_a = -2.303\,R \times$ slope.
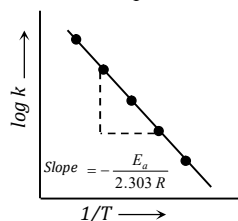
Rate constants for the reaction at two different temperatures T_1 and T_2,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad\qquad .....\text{(iii)}$$

where k_1 and k_2 are rate constant at temperatures T_1 and T_2 respectively $(T_2 > T_1)$.

Mechanism of the reaction

(1) **Reaction involving first order consecutive reactions**

(i) In such reactions, the reactions form a stable intermediate compound before they are finally converted into the products.

(ii) For example, reactants (R) are first converted to intermediate (I) which is then converted to product (P) as

$$R \xrightarrow{\ k_1\ } I \xrightarrow{\ k_2\ } P$$
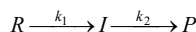
Therefore, the reaction takes place in two steps, both of which are first order i.e.,

Step I : $R \xrightarrow{\ k_1\ } I$; Step II : $I \xrightarrow{\ k_2\ } P$
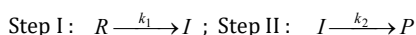
This means that I is produced by step I and consumed by step II. In these reactions, each stage will have its own rate and rate constant

the reactant concentration will always decrease and product concentration will always increase as shown in fig.
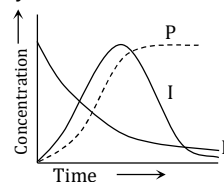
Concentration profile of reactants (R), intermediate (I) and products (P) as a function of time

(2) **Reaction involving slow step:** When a reaction occurs by a sequence of steps and one of the step is slow, then the rate determining step is the slow step. For example, in the reaction
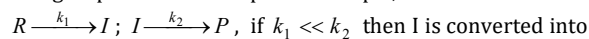
$R \xrightarrow{\ k_1\ } I$; $I \xrightarrow{\ k_2\ } P$, if $k_1 \ll k_2$ then I is converted into products as soon as it is formed, we can say that

$$\frac{-d[R]}{dt} = \frac{d[P]}{dt} = k_1[R]$$

(3) **Parallel reactions:** In such type of reactions the reactants are more reactive, which may have different orders of the reactions taking place simultaneously. For example, in a system containing NO_2 and SO_2, NO_2 is consumed in the following two reactions, $2NO_2 \xrightarrow{\ k_1\ } N_2O_4$; $NO_2 + SO_2 \xrightarrow{\ k_2\ } NO + SO_3$
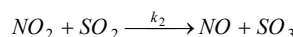
The rate of disappearance of NO_2 will be sum of the rates of the two reactions *i.e.*, $-\dfrac{d[NO_2]}{dt} = 2k_1[NO_2]^2 + k_2[NO_2][SO_2]$