# CHEMICAL KINETICS ①

Chemical Kinetics concerns with the measurement of rates of reactions under given conditions of temperature, pressure and concentrations. Such studies have been found very useful in working out conditions for getting maximum yields of several industrial products.

<u>Rate of Chemical reactions</u> ⊢ The rate of a reaction gives an information about the speed at which reaction occurs.

Consider a reaction:

$$A \longrightarrow P$$
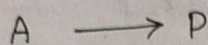
The rate of the reaction at any given time will depend upon the concentration of the reactant 'A' at that time.

$$Rate = r = -\frac{d[A]}{dt} = \frac{d[P]}{dt} = k[A]$$

The (-)ve sign refers that the concentration of reactant 'A' keeps on falling with time, on the other hand product concentration increases. k is the constant called rate constant or velocity constant of the reaction.

For a general reaction

$$aA + bB + cC \longrightarrow Product.$$
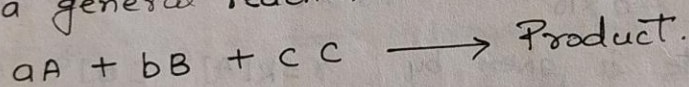
$$Rate = k[A]^a [B]^b [C]^c$$

and the differential rate eqn is:

$$\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = -\frac{1}{C}\frac{d[C]}{dt} = k[A]^a [B]^b [C]^c.$$

The rate constant 'k' have a definite value for a particular reaction. It is independent of the concentration but depends on the temperature. The larger the value of 'k' the faster will be the reaction.

Example - 1 :- Write down the differential rate eqⁿ for the following reactions:

(a) $A + 2B + 3C \longrightarrow$ Product

(b) $A + 3B \longrightarrow 2C + D + 2E.$
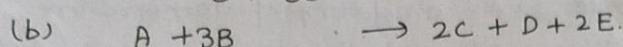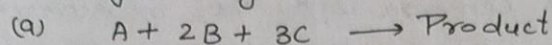
Example - 2 :- The rate of the homogeneous gaseous reaction $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$ is doubled when the chlorine concentration is doubled but increases by a factor of eight when the concen of both the reactants are doubled. determine the overall reaction order and the order with r.t NO and Cl_2.

$\Rightarrow$ rate $= k[NO]^a [Cl_2]^b.$

Example - 3 :- For a reaction $2A + 2B \longrightarrow C + 3D$

(+)	A mole dm^{3-}	B mole dm^{3-}	Rate (r) mole dm^{3-} sec^{-1}
(1)	6.0×10^{-3}	1.0×10^{-3}	0.012
(2)	6.0×10^{-3}	2.0×10^{-3}	0.024
(3)	2.0×10^{-3}	1.5×10^{-3}	0.002
(4)	4.0×10^{-3}	1.5×10^{-3}	0.008

if the rate is given by $r = k[A]^a [B]^b.$ calculate

(i) order of reaction.   (ii) order of reaction w.rt [A] and B.

(iii) Rate law eqⁿ   (iv) calculate the rate constant.

$\Rightarrow$ rate const $R = \dfrac{r}{[A]^a [B]^b}.$

**Example - 4** :- Determine the units of rate constant k for zero, first, second, $\frac{3}{2}$ - order reactions.

$\Rightarrow \quad r = {}^\circ k[A] = -\dfrac{d[A]}{dt}$

[for first order.

$k = -[A] \dfrac{d[A]}{dt}$

mole/lit

$= \dfrac{1}{mole \, dm^{-3}} \dfrac{mole \, dm^{3-}}{sec^{*}}$

$= sec^{-1}.$

for $3/2$ order $n = 3/2$

$r = k[A]^{3/2} = -\dfrac{dA}{dt}$

$k = \dfrac{1}{(mole dm^{-3})^{3/2}} \times \dfrac{mole dm^{-3}}{sec^{*}}$

$= mole^{-1/2} dm^{3/2} sec^{-1}$

<u>Order of a Reaction</u> :- The order of a reaction is defined as the number of the molecules whose concentrations determine the rate of the chemical reaction at a given temp. It can also be defined as the sum of the powers to which the concentration terms are raised in the rate law expression.

For a reaction

$$aA + bB + cC \longrightarrow Products.$$
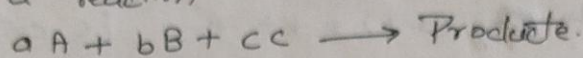
$$Rate = k [A]^P [B]^q [C]^r$$

Order of the reaction = $p + q + r$.

The order of reaction may not always be a whole number. It can be a fractional quantity also [e.g pyrolysis of acetaldehyde is of $3/2$ order].
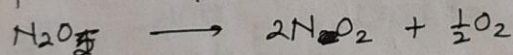
<u>First order reaction</u> :-

Reaction whose rate is determined by the change of only one concentration term are known as first order reactions e.g.

(a) Decomposition of Ammonium Nitrate.

$$NH_4 NO_2 \longrightarrow N_2 + 2H_2O$$
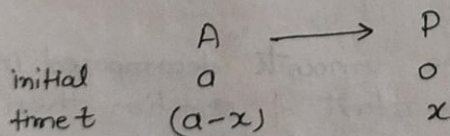
$$r = k [NH_4 NO_2]$$

(b) Decomposition of Nitrogen penta oxide.

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

$$r = k [N_2O_5]$$

(c) All the radioactive disintegrations follows the first order kinetics.

<u>Integrated rate expression</u> :- Consider a general reaction

$$A \longrightarrow P$$

	A	P
initial	a	0
time t	(a-x)	x

where a & (a-x) are the concentrations of reactant 'A' at zero time & at time 't' respectively.

④

$$\text{Rate} = r = \frac{dx}{dt} = k\,(a-x).$$

$$\frac{dx}{(a-x)} = k\,dt$$

on integrating

$$\int \frac{dx}{(a-x)} = \int k\,dt$$

$-\ln \log (a-x) = kt + c$ [c constant of intgration.

at $t = 0$ $x = 0$.

so $-\ln \log a = c$

$-\log (a-x) = kt - \log a$
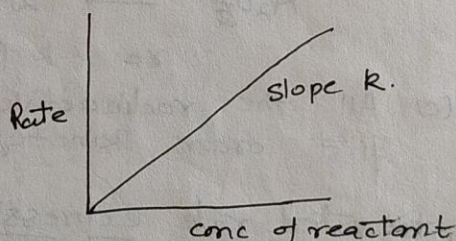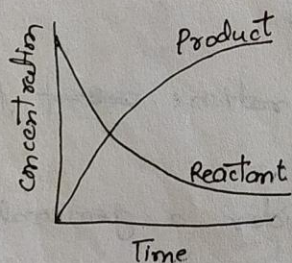
$kt = \log a - \log (a-x)$

$kt = \ln\log \frac{a}{(a-x)}$

$$R = \pm \frac{1}{t} \log_e \frac{a}{(a-x)}$$

<u>changing the common logarithm</u>
$$\boxed{k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}}$$

The above eqn shows that the concentration of reactant in a first order reaction decreases exponentially with time.

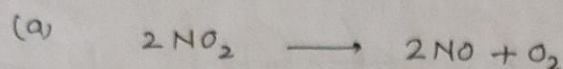If x_1 and x_2 are the amounts decomposed in time t_1 & t_2 respectively from the start of reaction then.

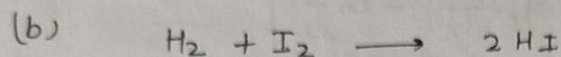$$\boxed{k = \frac{2.303}{t_2 - t_1} \log \frac{(a-x_1)}{(a-x_2)}}$$

Second order reactions :-

Reactions whose rate is determined by the change of two concentration terms (same of different) are known as second order reaction. e.g.
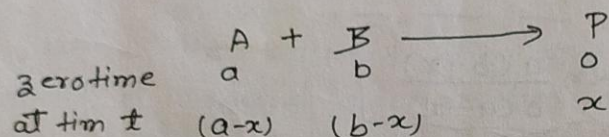
(a) $2NO_2 \longrightarrow 2NO + O_2$

$\quad\quad r = R[NO_2]^2$

(b) $H_2 + I_2 \longrightarrow 2HI$

$\quad\quad r = k[H_2][I_2]$

Integrated rate expression :- Consider a second-order reaction

$$A + B \longrightarrow P$$

zero time a b O

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

'a' and 'b' are the concentration of reactant A & B at zero time. At t time the concentration of 'A' & 'B' are $(a-x)$ & $(b-x)$ respectively.

The differential rate expression for the second order reaction is :

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2[A][B].\quad\quad - - - (1)$$

$$r = \frac{dx}{dt} = k_2(a-x)(b-x)\quad\quad \text{(at time } t\text{)}.$$

$$\neq \frac{dx}{(a-x)(b-x)} = k_2\,dt$$

$$\frac{dx}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right] = k_2\,dt.\quad\quad --(2)$$

Integrating the above eqn.

$$\frac{1}{(a-b)}\left[\int \frac{dx}{(b-x)} - \int \frac{dx}{(a-x)}\right] = \int k_2\,dt$$

$$\frac{1}{(a-b)}\left[-\ln(b-x) - \{-\ln(a-x)\}\right] = k_2 t + C$$

$$\frac{1}{(a-b)} \ln \frac{(a-x)}{(b-x)} = k_2 t + c \quad \{c \text{ is the constant}\} \quad -- (3)$$

at $t=0$ $\quad x=0$ then from above eq^n

$$c = \frac{1}{(a-b)} \log \left(\frac{a}{b}\right)$$

Then from eq^n (3)

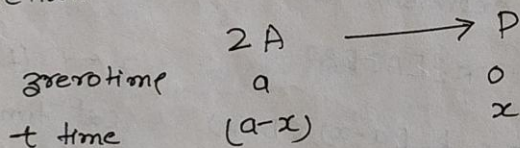$$\frac{1}{(a-b)} \ln \left(\frac{a-x}{b-x}\right) = k_2 t + \frac{1}{(a-b)} \ln \left(\frac{a}{b}\right)$$

$$k_2 t = \frac{1}{(a-b)} \left[\log \left(\frac{a-x}{b-x}\right) - \ln \frac{a}{b} \right]$$

$$\left| k_2 t = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} \right| \quad --- (4)$$

eq^n (4) is valid if $a > b$. If $b > a$ then eq^n (4) is transformed to.

$$\left| k_2 t = \frac{1}{(b-a)} \ln \frac{a(b-x)}{b(a-x)} \right|$$

When both the reactants are same & In such case two molecules of the same reactant are involved in the chemical reaction.

$$2A \longrightarrow P$$

zero time $\qquad a \qquad\qquad 0$

t time $\qquad (a-x) \qquad x$

The rate of the above reaction can be expressed as.

$$r = -\frac{1}{2} \frac{dA}{dt} = \frac{dP}{dt} = \frac{dx}{dt} = k_2 (a-x)^2$$

$$k_2 (a-x)^2 = \frac{dx}{dt}$$

$$\frac{dx}{(a-x)^2} = k_2 dt \qquad --- ①$$

On Integration we get

$$\int \frac{dx}{(a-x)^2} = \int k_2 dt.$$

$$\left[-\frac{1}{(a-x)}\right](-1) = k_2 t + c$$

$$\frac{1}{(a-x)} = k_2 t + c \qquad\qquad -(2)$$

at $t=0 \qquad x=0$

so we get $\qquad c = \frac{1}{a}$

then from eqn (2)

$$\frac{1}{(a-x)} = k_2 t + \frac{1}{a}$$

$$k_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

$$\boxed{k_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]}$$

This is the required integrated expression for the rate constant of a second-order reaction in which two molecules of the same reactant take part in the reaction.

Half-Life time of a reaction :- It is defined as the time required for the reaction to be half completed and is denoted by the symbol '$t_{1/2}$'.

$t_{1/2}$ for a first order reaction :- The integrated rate expression for the first order reaction is.

$$k = \frac{1}{t} \log \frac{(a)}{(a-x)} \qquad\text{at}\quad x = \frac{a}{2}, \ t = t_{1/2}.$$

then we get

$$k = \frac{1}{t_{1/2}} \log \frac{a}{a/2}$$

$$k = \frac{2.303}{t_{1/2}} \log 2$$

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

i.e the $t_{1/2}$ of first order reaction is independent of the concentration of the reactant.

(8) <u>$t_{1/2}$ for a second order reaction</u> - Rate expression for the second order reaction is

$$k_2 = \frac{1}{t}\left(\frac{x}{a(a-x)}\right) \qquad at \quad x = \frac{a}{2} \quad , t = t_{1/2}$$

$$k_2 = \frac{1}{t_{1/2}} \frac{a/2}{a \cdot a/2}$$

$$\boxed{t_{1/2} = \frac{1}{k_2 a}}$$

$t_{1/2}$ of a second order reaction is inversely proportional to the initial concentration of the reactant.

<u>$t_{1/2}$ for n^{th} order reaction</u> - The general eqn is

$$t_{1/2} \propto \frac{1}{a_0^{n-1}}$$

where a_0 is the initial concentration of the reactant & n is the order of reaction.

<u>Example</u> - A first order reaction take 40.5 min for the 25% decomposition of the reactant calculate the rate constant.

$\Rightarrow$ $t = 40.5$ min $\qquad a = a$ then $x = a - .25a = .75a$.

$$k = \frac{1}{40.5} \log \frac{a}{.75a} \qquad \Rightarrow k = 7.11 \times 10^{-3} min^{-1}$$

<u>Example</u> - Show that for a first order reaction, the time required for 99.9% completion of the reaction is 10 times that required for 50% completion

$$\Rightarrow \frac{t(99.9\%)}{t(50\%)} = \frac{\frac{1}{k_1} \log \frac{100}{100-99.9}}{\frac{1}{k_1} \log \frac{100}{100-50}} = 10 \quad \begin{bmatrix} rat\ constant\ for \\ the\ reaction\ will \\ be\ same \end{bmatrix}.$$

<u>Example</u> :- The half life time of the homogeneous gaseous reaction
$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$, which obeys first order kinetics is 8.0 min. How long will it take for the conc of SO_2Cl_2 to be reduced to 1% of the initial value.

$$\Rightarrow k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{8} = 0.087\ min^{-1}.$$

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \Rightarrow t = \frac{2.303}{0.083} \log \frac{100}{1} = 52.93\ min.$$

Example : The $t_{1/2}$ of a reaction is halved as the initial concentration of the reactant is doubled. What is the order of reaction.

$\Rightarrow$ $\quad t_{1/2} \propto \dfrac{1}{(a_0)^{n-1}}$ $\quad$ in present case $\quad \dfrac{1}{2} t_{1/2} = \dfrac{1}{(2a_0)^{n-1}}$

$$\dfrac{t_{1/2}}{\frac{1}{2}t_{1/2}} = \dfrac{\frac{1}{(a_0)^{n-1}}}{\frac{1}{(2a_0)^{n-1}}}$$

$\Rightarrow \quad 2 = 2^{n-1}$

$\Rightarrow \quad 1 = n-1 \qquad \Rightarrow n = 2$

Second order

Zero order reaction:-

The rate of the reaction is independent of conc of reactants.

e.g. (a) Thermal decomposition of HI on gold surface

$\qquad 2HI \longrightarrow H_2 + I_2$

(b) decomposition of NH_3 on Pt surface

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

consider a reaction $\qquad R \longrightarrow$ Products

$\qquad rate = -\dfrac{d[R]}{dt} = k[R]^0$

$\qquad - d[R] = k\,dt$

$\qquad dx = k\,dt$

$\qquad x = kt + c \qquad$ at $\quad t=0 \quad x=0$

$\qquad \qquad \qquad \qquad \qquad so \quad c=0$

$\boxed{x = kt} \qquad$ This shows
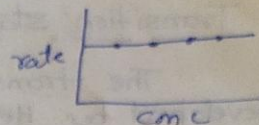
$t_{1/2}$ for zero order reaction -

$\qquad for \quad t = t_{1/2} \qquad x = \dfrac{x}{2}$

$\qquad \dfrac{x}{2} = k\,t_{1/2}$

$\qquad \boxed{t_{1/2} = \dfrac{x}{2k}}$

i.e $t_{1/2}$ is directly proportional to the initial conc of the reactant.

$\Rightarrow$ Calculate the activation energy of a reaction whose rate constant is tripled by a $10°C$ rise in temp in the vicinity of $27°C$,

$$2.303 \log \dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left[\dfrac{305 - 295}{305 \times 295}\right] \qquad = 82.18 \text{ kJ mole}^{-1}$$

$\Rightarrow$ The rate constant of a second order reaction is $5.70 \times 10^{-5} dm^3 mol^{-1} s^{-1}$ at $25°C$ & $1.65 \times 10^{-4} dm^3 mol^{-1} s^{-1}$ at $40°C$. calculate the activation energy.

Molecularity of a Reaction:-

Molecularity of a reaction is defined as the number of molecules involved in the step leading to the chemical reaction. If only one molecule is involved, the reaction is said to be unimolecular. If two bimolecular & so on...
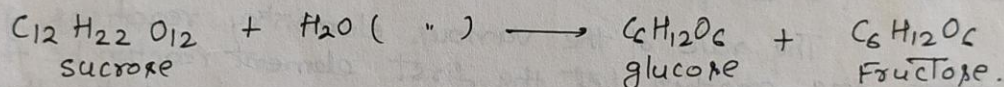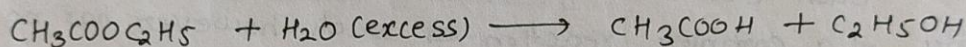
$$2HI \, (g) \longrightarrow H_2 + I_2$$

bimolecular. — (1)

$$2NO_2 + O_2 \longrightarrow 2NO_2$$
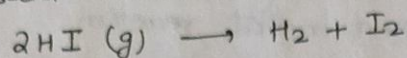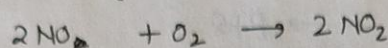
Trimolecular. — (2)

In general the molecularity of the reaction is equal to the order of reaction as eqn (1) is of second order and eqn (3) follows the third order kinetics.

In several reactions, the order is different from molecularity. This happens when one of the reactants is present in large excess. The exps are hydrolysis of ester and inversion of cane sugar.

$$CH_3COOC_2H_5 + H_2O \, (excess) \longrightarrow CH_3COOH + C_2H_5OH$$

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{12}} + H_2O \, (\, " \,) \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The molecularity of the above two reaction is 2 but their order is one. It is clear from the experiments that the rate of reaction varies directly to the conc of ester in first case. and that of sucrose in the second case. Since the water is present in large excess, it is assumed that it conc does not changes during the course of reaction.

(14)

i.e.
$$\frac{d \, [CH_3COOH]}{dt} = k \, [CH_3COOC_2H_5]$$

&

$$\frac{d \, [glucose]}{dt} = k \, [sucrose].$$

Therefore, such reactions which are not truly first order reactions but shows first order kinetics under certain conditions are termed as pseudo-first order reactions or pseudo-unimolecular reactions.

Effect of Temperature on Reaction Rate :-

It has been found that the rate of reaction largely depends on temp. The ratio of the rate constants of a reaction at two temperatures differing by 10°c is known as temperature coeffi- cient of the reaction.

$$\text{Temp coefficient} = \frac{\text{Rate constant at 35°c}}{\text{Rate constant at 25°c}} = \frac{k_{35}}{k_{25}}$$

It is observed that the rate constant generally doubles by 10°c rise in temp.

According to collision theory, for chemical reaction to occur, there must be collision beth the reactant molecules. How ever, most of the collission taking place beth the molecules are ineffective as they do not have much energy to under go chemical reaction. Only those collisions result in chemical reaction in which the colliding molecules are associated with a certain min amount of energy called threshold energy.

It has been found that the small increase in temp, increases the number of effective molecules (ie molecules having energy equal or greater than threshold energy) to large extent. and the collision beth such molecules results in chemical reaction. The small increase in temp increases the rate of reaction to large extent

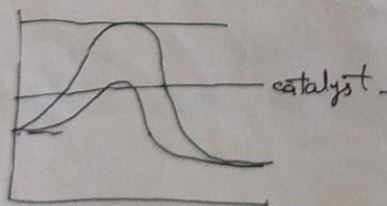Activation energy = Threshold energy — energy actually possessed by molecules.
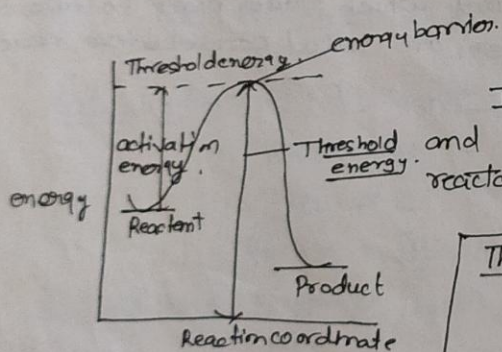
In Fig there is a energy barrier beth reactant and product. This barrier has to be crossed before reactants can convert into product.

The Arrhenius eqn :-

$$k = A\, e^{-Ea/RT}$$

$$2.303 \log \frac{k_2}{k_1} = \frac{Ea}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Activation energy calculated with the help of Arrhenius equation.

Theory of Reaction rates :-

I. Collision theory of reaction rates :

According to this theory, a chemical reaction takes place only by collision beth the reacting molecules. The two main conditions for a collision beth the reacting molecules are.

(i) **The reacting molecules must collide with proper orientation.**

The correct orientation is that which ensure direct contact beth the atoms involved in the breaking and forming of bonds.
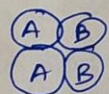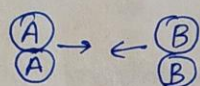
effective collision
(Head on collision)
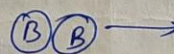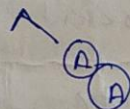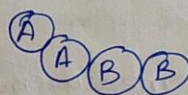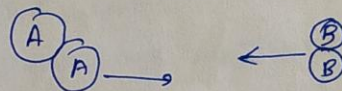
ineffective collision
side wise collision.

(ii) The molecule must collide with sufficient kinetic energy.

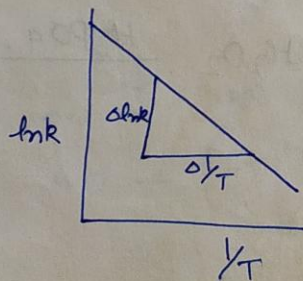## Calculation of Activation energy :

According to Arrhenius eqn-

$$K = A \, e^{-Eq/RT}$$

$$\ln k = -\frac{Eq}{R}\left(\frac{1}{T}\right) + \ln A.$$

By plotting a graph beth $\ln k$ versus $\frac{1}{T}$.

$$Slope = -\frac{Eq}{R} = \frac{\Delta \ln k}{\Delta \frac{1}{T}}$$

from the above eqn we can calculate the value of Eq.

$$Slope = \frac{\Delta \ln k}{\Delta \frac{1}{T}}$$

[2] **Transition state Theory :-**

The transition state or activated complex theory was developed by Henry Erying. This theory is also called the absolute rate theory because with its help it is possible to get the absolute values of the rate constant.

According of T.S.T during collision, the reactant molecules form a transition state or activated complex which decomposes to give the products.

$$A + B-C \longleftrightarrow AB\overset{\#}{C} \longleftrightarrow A-B + C.$$
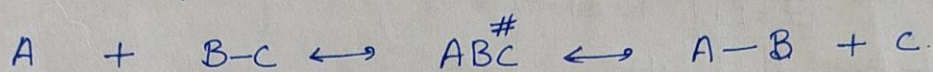
The main features of T-S.T are.

(i) In a collision, the fast approaching reactant molecules (A & BC) slow down due to gradual repulsion between their electron clouds. In the process, the kinetic energy of the two ~~electrons~~ molecules is converted into potential energy.

(2) A partial bond is formed between the atoms A & B with corresponding weakening of B-c bond. This leads to formation of an activated complex. The activated complex is unstable and decomposes to give the products.

$$A \quad B-C \longleftrightarrow A---B----C \longleftrightarrow A-B + C$$
$$\text{A.C}$$
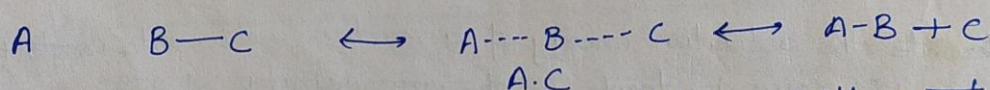
(3) The activated complex is in equilibrium with reactants.

eg example - S_N2 reactions
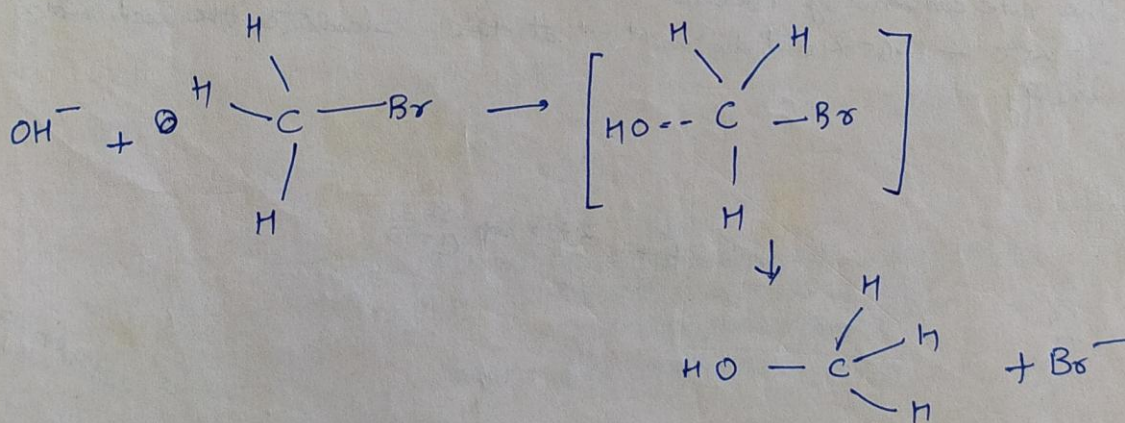
Rate constant is also called specific reaction rate.

3.4 Factors Affecting the Rate of a Reaction

Some of the important factors are as follows :

(i) **Effect of concentration** : Greater the concentration of reactants, greater will be the inter-molecular collisions and hence, greater will be the rate of reaction.

(ii) **Nature of reacting species** : The rates of chemical reactions are influenced by nature of reactants and products. In general, those reactions are generally fast at room temperature which do not involve breaking of old and formation of new bonds while those involve considerable bond rearrangements are slow at room temperature.

(iii) **Effect of catalyst** : The rates of many reactions may be increased by the presence of certain substances in the reacting system. These substances are called catalyst. *Catalyst provides a new path to the reaction by lowering its activation energy.*

(iv) **Effect of temperature** : The rate of reaction generally increases with the increase in temperature. The effect of temperature is represented in terms of **temperature coefficient** of a chemical reaction. It is defined as 'the ratio of rate constant of a reaction at two temperatures separated by 10°C (usually 25°C and 35°C)

$$\text{Temperature coefficient} = \frac{k_{35°C}}{k_{25°C}} \approx 2 \text{ or } 3$$

(v) **Effect of surface area of reactants** : In heterogeneous reactions the smaller particles react more rapidly than the larger particles because surface area increases with decreasing the particle size.

(vi) **Exposure to radiation** : The rate of certain reactions are enhanced due to absorption of photons (energy of each photon $= h\nu$) of different energies. Those reactions where photons are used are called photo chemical reactions.