Chemical Kinetics

The branch of chemistry which deals with the study of speed or rate of chemical reactions, the factor affecting the rate of reaction and the mechanism by which the reaction proceed is known as chemical kinetics.

Rate of Reaction :-

The rate of reaction is the change in the concentration of any one of the reactants or product per unit time.

$$R \longrightarrow P$$

$$\text{Rate of reaction} = \frac{-\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

Significance of negative and positive sign :-

- The rate of reaction is always positive.
- The minus sign along with first term is used to show that the concentration of reactant is decreasing.
- The plus sign along with second term is used to show that the concentration of product is increasing.

Unit $\boxed{M\ time^{-1}}$ or $\boxed{atm\ time^{-1}}$
↳ mol L^{-1} sec^{-1}

Rate - Average and Instantaneous :-

Average rate of reaction is change in concentratn ~~of~~ any of the reactant or any of product per unit time over a specified interval of time.

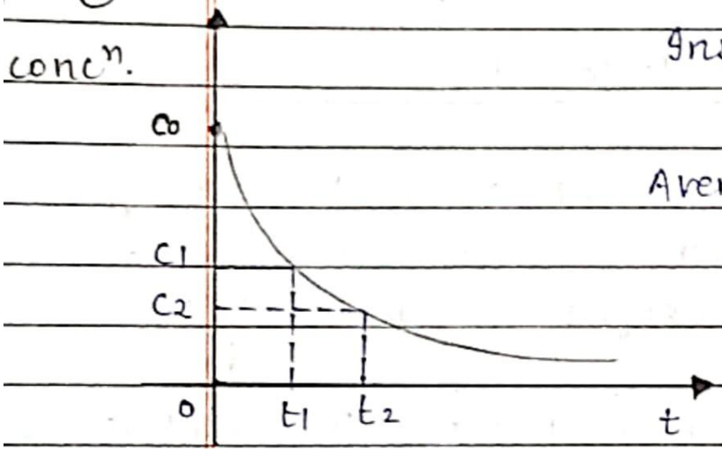
$$\text{rate}_{avg.} = \frac{-\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

Instantaneous rate of reaction i.e. rate of reaction at any instant of time is rate of change of conc. of any one of reactant or product at particular instant of time

$$rate_{inst.} = -\frac{d[R]}{dt} = +\frac{d[P]}{dt}, \text{ as } \Delta t \to 0.$$

Graphically :-

①

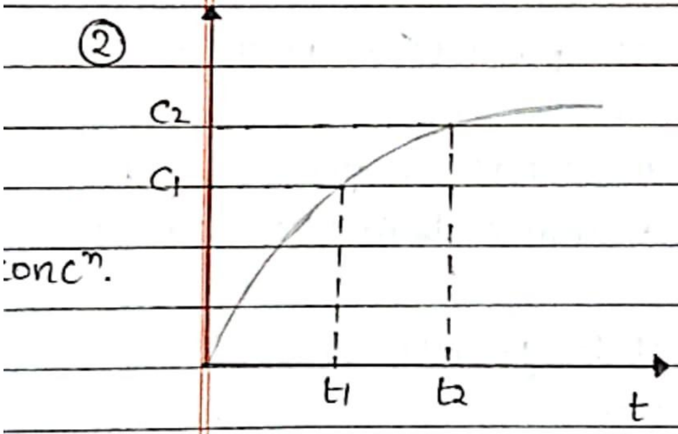


$$\text{Inst. rate} = -\frac{d[R]}{dt} = \text{slope of tangent.}$$

$$\text{Average rate} = -\frac{\Delta[R]}{\Delta t} = \frac{-(C_2 - C_1)}{t_2 - t_1}$$

$$C_1 > C_2$$

②



$$\text{Inst. rate} = \frac{d[P]}{dt} = \text{Slope of tangent.}$$

$$\text{Average rate} = \frac{\Delta[P]}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1}$$

$$C_2 > C_1$$

in general,

$$\alpha A + \beta B \longrightarrow \gamma C + \delta D$$

$$\text{Rate of reaction} = -\frac{d[A]}{\alpha\, dt} = -\frac{d[B]}{\beta\, dt} = \frac{d[C]}{\gamma\, dt} = \frac{d[D]}{\delta\, dt}$$

- equation must be balance.
- coefficient is multiplies for rate of reaction.

also, we can write as :

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

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

Rate of appearance of C $= +\frac{d[C]}{dt}$

Rate of appearance of D $= +\frac{d[D]}{dt}$

Factors Influencing Rate of reaction :-

1. Nature of reactant : different amount of energies are required for breaking of different bond & different amount of energies are released in formation of bond.
2. Concentration :- Greater the reactant's concentration, faster the reaction.
3. Temperature :- The rate of reaction increases on increasing of temperature.
4. Presence of catalyst :- A catalyst generally increase the speed of a reaction without being consumed in reaction.
5. Surface area of reactant :- greater the surface area, faster the reaction.
6. Poresence of radiation :- some reaction's rate increases with increase in intensity of light.

Rate law :-

It states that rate of chemical reaction is directly proportional to product of concentration of reactant to the some

$\alpha A + \beta B \longrightarrow \gamma C + \delta D$

power, which may or may not be equal to respective stoichiometric coefficient.

rate $\propto [A]^x [B]^y$

rate $= K [A]^x [B]^y$

$\therefore$ $\boxed{\text{rate} = K [A]^x [B]^y}$

where, K = rate constant or specific reaction rate

x = order with respect to A

y = order with respect to B.

$x + y$ = overall order of of reaction.

Rate Constant (K) :-

It may be defined as the rate of reaction when the molar concentration of each reactant is taken as unity. That is why rate constant is also called specific reaction rate.

Characterstics of rate constant :-

(i) • Rate constant is measure of rate of reaction.

(ii). Each reaction has definite value of K at a particular temperature.

(iii). value of rate constant for same reaction changes with temperature.

(iv). value of K does not depend upon concentration of reactant.

(v) The unit of rate constant depend upon order of rxn.

Unit of K : rate $= K[A]^n [B]^y$

$M\ sec^{-1} = K\ (M)^{n+y}$

$M\ sec^{-1} = K \cdot (M)^n$

$\therefore K = \dfrac{M\ sec^{-1}}{M^n} = \boxed{M^{1-n}\ sec^{-1} = K}$

order of reaction :-

The sum of exponent to which molar concentrations in rate law equation are raised to express the observed rate of reaction is called order of reaction.

$$\text{rate} = K[A]^x [B]^y$$

then , overall order of reaction = $x + y$.

Difference between rate of reaction and reaction rate constant :-

	Rate of reaction	Reaction rate constant
1.	It is change in concent. of a reactant or product per unit time	1. It is a constant of proportionality in the rate law equation and equal to rate of reaction when M of each reactant is unity.
2.	Rate of reaction at any instant of time depends upon the molar conc. of reactants at that time	2. It does not depend upon the concentration of reactants.
3.	unit is always, $M s^{-1}$	3. unit depends on the order of reaction.

MOLECULARITY OF A REACTION :-

The number of reacting species (atoms , ions or molecules) taking part in an elementary reaction , which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

eg. $$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$

$$\text{rate} = \frac{-d[H_2O_2]}{dt} = K\,[H_2O_2][I^-]$$

The reaction is first order w.r.to both H_2O_2 and I^-.

1) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (Slow)
2) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)

Step (1) (slow) is rate determining step.
Both steps are bimolecular elementary reaction.
IO^- is Hypoiodite ion and is intermediate.
Molecularity = 2
order = 2nd order reaction.

ORDER of reaction	Molecularity of reaction.
• Sum of power of concentration of reactant in rate equation.	• Sum of number of species participating in an elementary reacting.
• Based on experimental value.	• Theoretical concept.
• It can be positive, negative, zero and fractional.	• It can only be whole number like 1, 2, 3 etc.
• applicable for both elementary and complex reaction,	• applicable for elementary reaction only.

• order of reaction is given by the slowest step.	• molecularity of slowest step is same as the order of overall reaction.
• It have effect of temperature and pressure.	• No effect of order pressure and temperature.

Integrated Rate Equation :-

1) Zero order reaction :

$$R \rightarrow P$$

$$\text{rate} = \frac{-d[R]}{dt} = k[R]^0$$

rate of reaction is independent of conc. of reacti

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

$$d[R] = -k\,dt \quad — ①$$

integrating eq-① both side-

$$\int dR = \int -k\,dt$$

$$[R] = -kt + C \quad — ②$$

initially, $t = 0$, R_0 (initial concn.)

$$[R_0] = C \quad — ③$$

Putting the value of eq ③ in ② -

$$[R] = -kt + [R_0]$$

$$Kt = [R_0] - [R]$$

$$\boxed{K = \frac{[R_0] - [R]}{t}}$$

where R is concentration of reactant at any time.

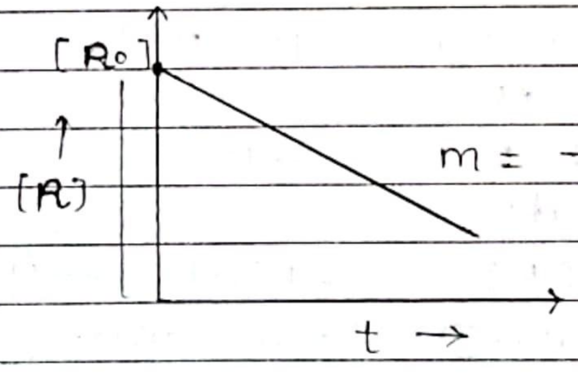
→ In zero order reaction, rate of reaction is independent of concentration of the reactant.

from above;

$$[R] = [R_0] - kt$$

$$y = mx + c$$

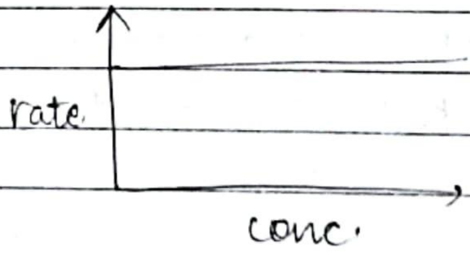
Graph:



$m = -k$ (slope)

$$\text{Rate} = k[R]^0$$
$$\text{Rate} = k$$
$$\text{Rate} \propto k$$

∵ rate is independent of concentration of reactant.



Examples :- (zero order reaction)

1). Those reaction in which a reactant is in excess.

Substrate $\xrightarrow{\text{enzyme}}$ Product
(excess)

2). $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$
(photochemical reaction)

3). $N_2O \xrightarrow{\Delta} N_2 + \frac{1}{2} O_2$

4) $NH_3 \xrightarrow{Mo} N_2 + 3H_2$

5). $2HI \xrightarrow{Au} H_2 + I_2$

6) $CH_3COCH_3 + I_2 \xrightarrow{H^+} HI + CH_2ICOCH_3$

2). <u>First Order Reaction</u> :

Those reaction in which rate of reaction is dependent on concentr. of any of the reactant (only one).

$$A \longrightarrow P$$

$t = 0$ (a)
$t = t$ $(a-x)$

$$\text{rate} = -\frac{dx}{dt} = K[A]^1$$

$$-\frac{dx}{dt} = K(a-x) \quad — ①$$

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

integrating equation on both side we get,

$$\ln(a-x) = -kt + c \quad — ②$$

initially, $t=0$, $x=0$

$$\ln(a) = c \quad — ③$$

$$\ln(a-x) = -kt + \ln a \quad — ④$$

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

$$kt = \ln\frac{[a]}{[a-x]}$$

also, $\ln = 2.303 \log_{10}$

$$kt = 2.303 \log_{10}\frac{[a]}{[a-x]}$$

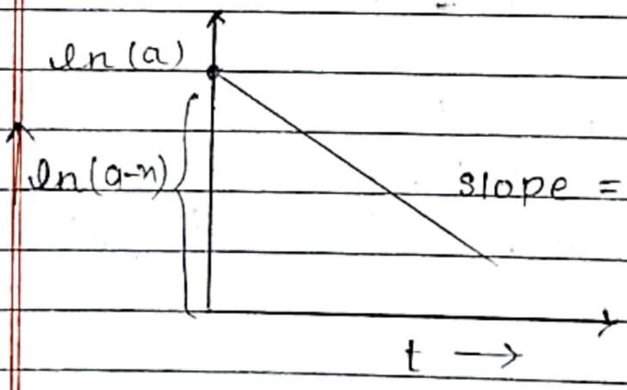
$$\boxed{k = \frac{2.303}{t}\log_{10}\frac{[a]}{[a-x]}}$$

where $[a]$ and $[a-x]$ is initial and final concentration respectively.

on comparing, the equation ④

$$y = mx + c.$$

Graph



Examples :-

i). $C_2H_4 + \underset{(excess)}{H_2} \xrightarrow{Pt / Pd / Ni} C_2H_6$

ii). $N_2O_5 \xrightarrow{\Delta} 2NO_2 + \frac{1}{2}O_2$

iii). ${}^{226}_{86}Ra \longrightarrow {}^{222}_{84}Rn + {}^{4}_{2}He$ (all radioactive decay).

iv). $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

v). $H_2O_2 \xrightarrow{-I} H_2O + \frac{1}{2}O_2$

vi). $C_{12}H_{22}O_{11} + \underset{(excess)}{H_2O} \xrightarrow{H^+} 2 \times C_6H_{12}O_6$ -

(hydralysis of sugar)

vii). $\underset{(ester)}{CH_3COOC_2H_5} + \underset{(excess)}{H_2O} \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

viii). $SO_2Cl_2 \xrightarrow{\Delta} SO_2 + Cl_2$

Thionyl chloride

FIRST ORDER REACTION IN TERMS OF PRESSURE

$A(g) \longrightarrow B(g) + C(g)$

t=0	P_i	0	0
t= t	$(P_i - n)$	x	x

at time t :-

$P_t = P_i - n + n + n$

$P_t = P_i - n$

(total pressure)

$P_t = P_i - x \Rightarrow x = P_t - P_i$

at time t ; P_A (Pressure of gas A at t)

$P_A = P_i - x \Rightarrow P_i - P_t + P_i = 2P_i - P_t$

initial pressure

$$\boxed{K = \frac{2.303}{t} \log_{10} \frac{[P_i]}{[2P_i - P_t]}}$$

Final pressure

Pseudo - Unimolecular or Pseudo first order reaction :-

Sometimes, in a reaction or in an intermediate step or rate determining step more than one reacting species is observed but the order of reaction remains one.

eg. $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
(ester) (excess)

rate $= K' [CH_3COOC_2H_5][H_2O]$

$K' [H_2O] = K$

$\because$ rate $= K [CH_3COOE_2H_5]'$

here molecularity = 2 but order = 1

eg. $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$
(cane sugar) (excess) (glucose) (fructose)

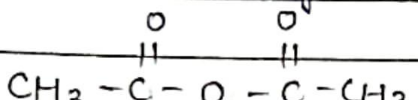
$rate = K' [C_{12}H_{22}O_{11}][H_2O]$

$K'[H_2O] = K$

$rate = K [C_{12}H_{22}O_{11}]^1$

molecularity = 2 , but order = 1.

eg.



$CH_3-\overset{O}{\overset{||}{C}}-O-\overset{O}{\overset{||}{C}}-CH_3 + 2C_2H_5OH \rightarrow 2CH_3COOC_2H_5 + H_2O$

(excess)

$rate = K' [(CH_3CO)_2O][C_2H_5OH][C_2H_5OH]$

$K = K' [C_2H_5OH][C_2H_5OH]$

$rate = K [(CH_3CO)_2O]$

molecularity = 3 but order = 1.

so, there are all example of pseudo first order reaction.

Temperature dependence of rate of reaction :-

Consider an example,

$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$

at 0°C → 10 days
25°C → 5 hours
50°C → 12 min

} the rate of chemical reaction is temperature dependent and generally it increases with increase in temp

* with increase in temperature by 10 °C - the rate of reaction doubles.

Arrhenius Equation-

Arrhenius explained the effect of temperature on rate of reaction.

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

where A is Arrhenius constant or free exponential factor / Frequency factor. ((because it gives the frequency of binary collision of reacting molecule per second per liter).

E_a is the energy of activation,

R is gas constant and

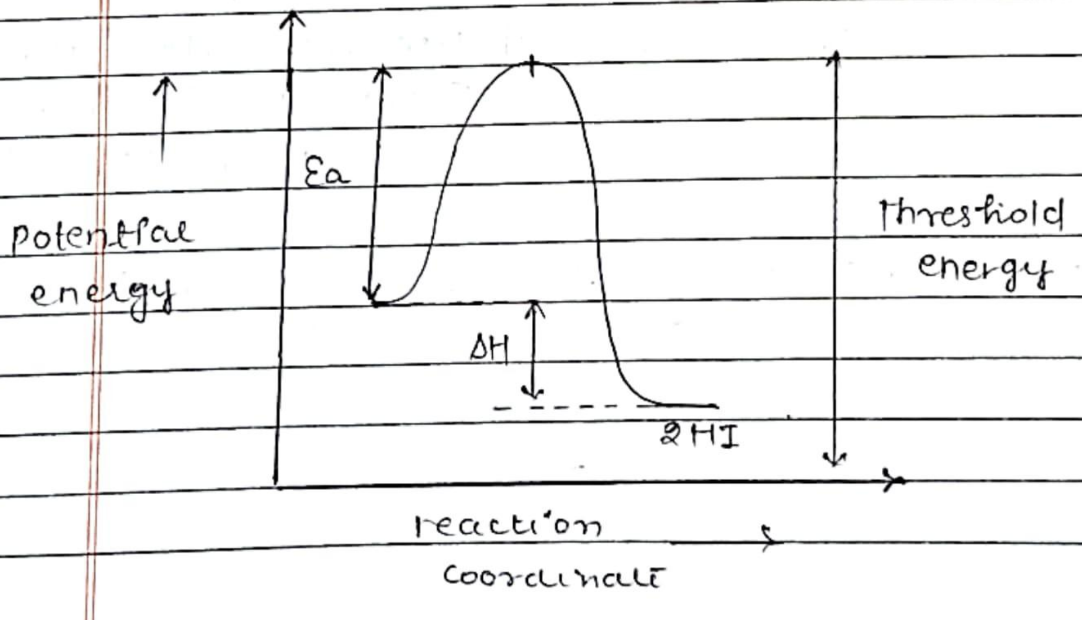
T is absolute temperature.

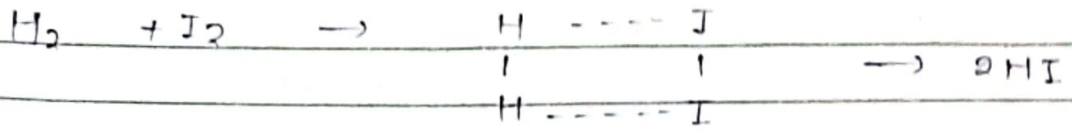
'A' and 'E_a' are collectively called Arrhenius parameters.

The factor $e^{-Ea/RT}$, gives fraction of molecule N_E / N_T having energy equal to or greater than activation energy.

N_T is total number of molecule and

N_E is molecule that have kinetic energy.

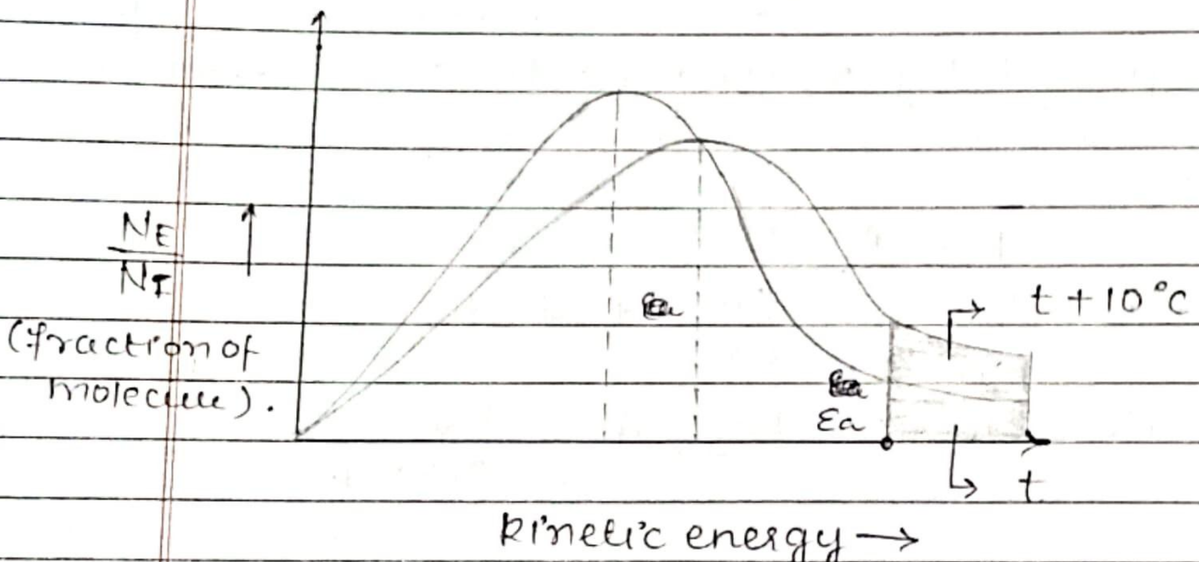




$$H_2 + I_2 \rightarrow \begin{matrix} H & \cdots & I \\ | & & | \\ H & \cdots & I \end{matrix} \rightarrow 2HI$$

(intermediate)
which is
highly unstable
high energy.

Threshald energy = Activation Energy + Energy possesed by reaction.



Initially at temperature t the gas have a lower most probable value of kinetic energy and lesser number of gas posses activation energy to carry the reaction and form product.

When t + 10°c, the most probable kinetic energy gases increases comparatively and large no. of gases occupy Ea.

∵ larger no. of product are formed.

∴ Rate of reaction increases on increasing the temperature by 10°c.

The peak of curve corresponds to the most probable kinetic energy.

$$\boxed{\log_{10} \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]}$$

Collision Theory :-

Reactant are considered as hard sphere, when the hard sphere collide with eachother with suitable kinetic energy they form an intermediate followed by product.

* The number of particles that collide per second in a given ~~molecule~~ volume is called as collision frequency (Z).

* In gaseous phase, for binary collision /system the Z is in range of $10^{25} - 10^{28}$.

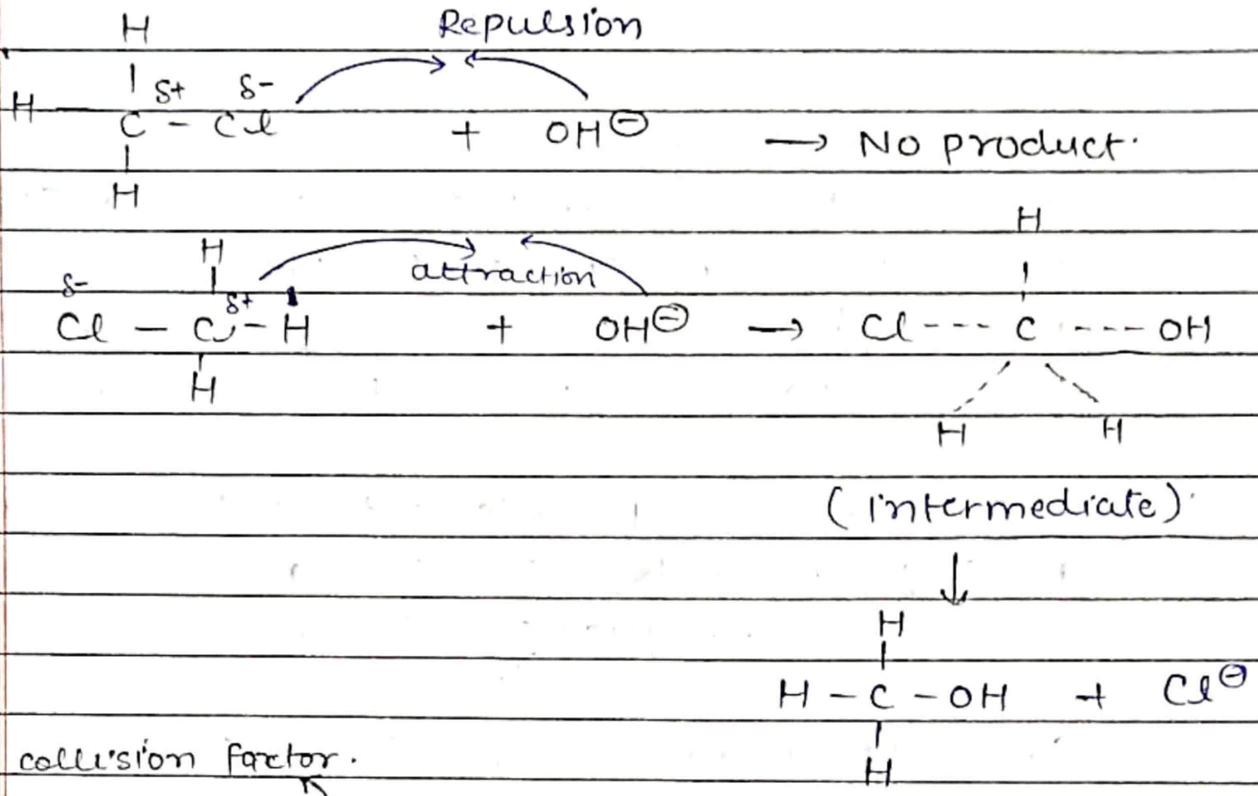
* If after collision they are able to form product then collision is effective.
∴ reaction will take a very short time and vice-versa

Factors affecting the effective collision:-

① Energy barrier: for an effective collision the reactants must have threshold energy.

Energy (no effective collision) < Threshold energy < Energy (effective collision)

② Orientation barrier.



$$\text{Rate} = \overset{\text{collision factor}}{Z_{AB}}\, e^{-E_a/RT}$$

$$\text{Rate} = \underset{\text{probability factor}}{P}\, Z_{AB}\, e^{-E_a/RT}$$

Effect on catalyst on rate of reaction :-

Catalyst :

Those substance that decreases or increases the rate of reaction without participating chemically in a reaction.

→ Catalyst never interfere with ΔG of a reaction (it will not start or stop the reaction).

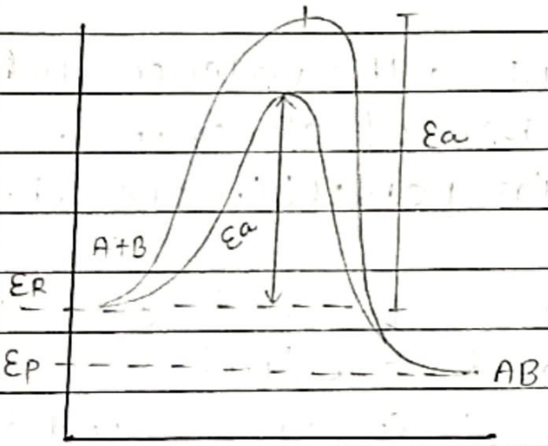
$\Delta G = 0$: no reaction
$\Delta G = +ve$: non - spontaneous reaction
$\Delta G = -ve$: spontaneous reaction.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

eg. $2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2\uparrow$

Step① $H_2O_2 + I^- \longrightarrow H_2O + OI^\ominus$
Step② $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^\ominus$

$2H_2O_2 \longrightarrow 2H_2O + O_2$.



Positive catalyst: are those that decrease the Ea of reactant ∵ rate of reaction increases because lower activation energy can be achieved earlier and faster.

Negative catalyst: those catalyst that increases Ea of reaction ∵ rate of reaction decrease because higher Ea can be achieved slower and R.O.R decreases.