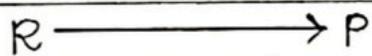


Chemical Kinetics

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.



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

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 M time^{-1} or atm time^{-1}
 $\hookrightarrow \text{mol L}^{-1} \text{sec}^{-1}$

Rate - Average and Instantaneous :-

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

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

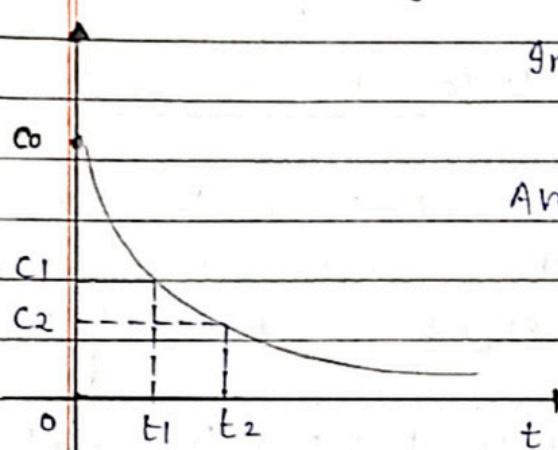
Instantaneous rate of reaction i.e. rate of reaction at any instant of time is rate of change of conc. of any one of reactant or product at particular instant of time

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

Graphically :-

(1)

concⁿ.



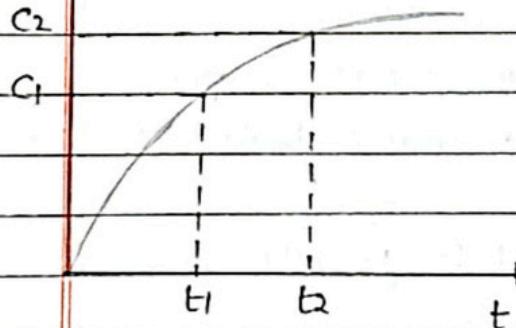
$$\text{Inst. rate} = - \frac{d[R]}{dt} = \text{slope of tangent}$$

$$\text{Average rate} = - \frac{\Delta [R]}{\Delta t} = - \frac{(c_2 - c_1)}{t_2 - t_1}$$

$c_1 > c_2$

(2)

concⁿ.

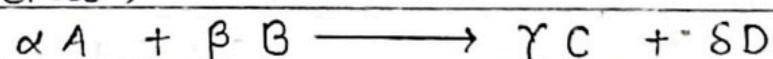


$$\text{Inst. rate} = \frac{d[P]}{dt} = \text{slope of tangent}$$

$$\text{Average rate} = \frac{\Delta [P]}{\Delta t} = \frac{c_2 - c_1}{t_2 - t_1}$$

$c_2 > c_1$

in general,



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

- equation must be balanced.

- coefficient is multiplied for rate of reaction.

also, we can write as :

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

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

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

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

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. Presence 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 same power.



Date: _____
Page: _____

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

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

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

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

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 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.

Characteristics 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 depends upon order of reaction.

Unit of K : $\text{rate} = K [A]^n [B]^y$

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

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

$$\therefore K = \frac{M \text{ sec}^{-1}}{M^n} = \underbrace{M^{1-n} \text{ sec}^{-1}}_{\text{Curly brace}} = K$$

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.

$$\text{rate} = k [A]^n [B]^y$$

Then, overall order of reaction = $n+y$.

Difference between rate of reaction and reaction rate constant :-

Rate of reaction	Reaction rate constant
1. It is change in concn. 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 :-

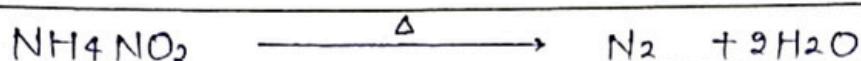
The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

On the basis of molecularity chemical reaction is of following type :-

1). Unimolecular Reaction :

when one reacting species is involved .

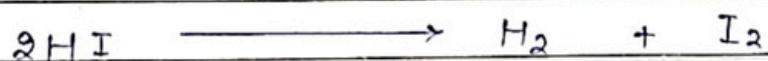
eg. decomposition of ammonium nitrate



2). Bimolecular Reaction :

when reaction involve simultaneous collision between two species .

eg. dissociation of Hydrogen Iodide .



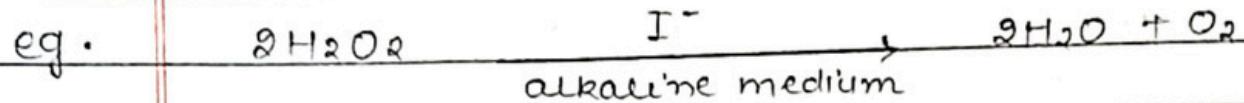
3). Trimolecular or termolecular reaction :

Reaction involve simultaneous collision between three reacting species .



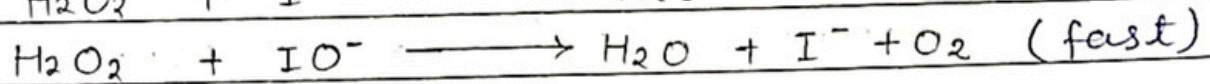
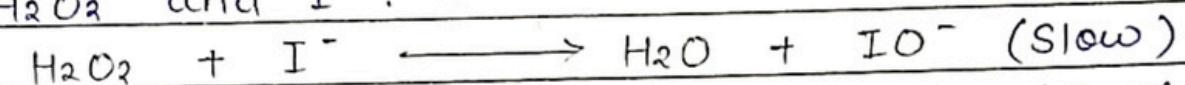
Note : The probability of reacting more than three molecule is very small and hence molecularity more than three is very rare.

* The overall rate of reaction is controlled by the slowest step in a reaction called the rate determining step .



$$\text{rate} = -\frac{d[\text{H}_2\text{O}_2]}{dt} = k [\text{H}_2\text{O}_2][\text{I}^-]$$

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



Step (1) (slow) is rate determining step.

Both steps are bimolecular elementary reaction.

IO^- is hypohalous ion and is intermediate.

Molecularity = 2

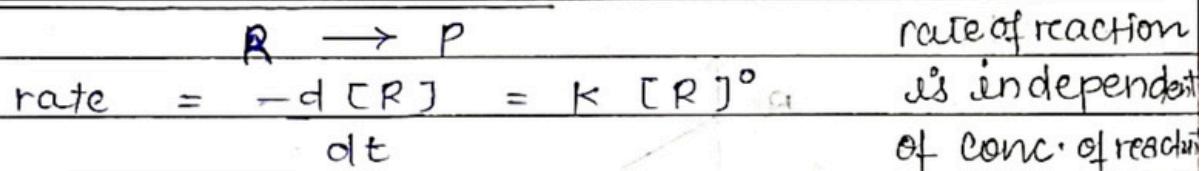
Order = 2nd order reaction.

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 reaction.
• 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 :



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

$$d[R] = -k dt \quad \text{--- (1)}$$

integrating eq-1 both sides-

$$\int d[R] = \int -k dt$$

$$[R] = -kt + C \quad \text{--- (2)}$$

initially, $t=0$, R_0 (initial conc?)

$$[R_0] = C \quad \text{--- (3)}$$

Putting the value of eq (3) in (2) -

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

$$k_t = [R_0] - [R]$$

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

where R is concentration of reactant at any time.

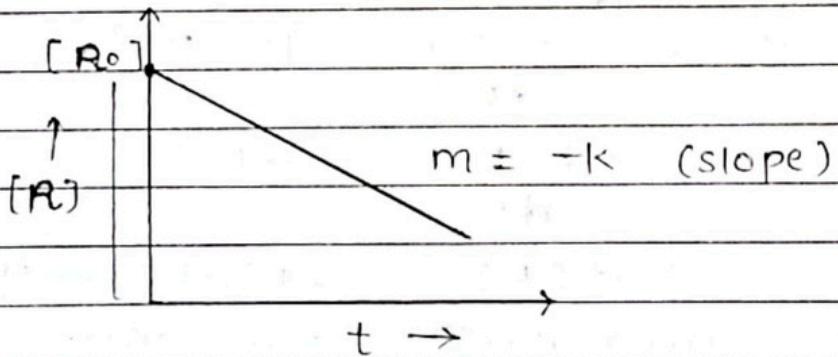
→ In zero order reaction, rate of reaction is independent of concentration of the reactant.

from above;

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

$y = mx + c$

Graph:

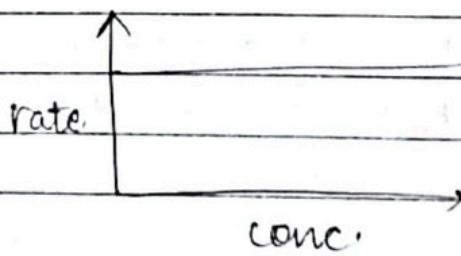


$$\text{Rate} = k[R]^0$$

$$\text{Rate} = k$$

$$\text{Rate} \propto k$$

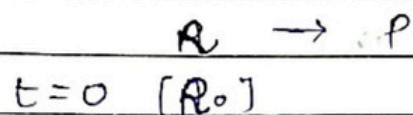
∴ rate is independent of concentration of reactant.



Half life of a reaction :-

It is the time period when the chemical rxn is half completed or finished.

for zero order reaction;



$$t = t_{\frac{1}{2}} \frac{[R_0]}{2}$$

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

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

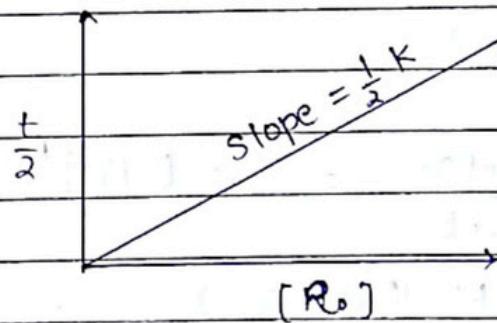
$$t_{\frac{1}{2}} = \frac{[R_0] - [R_0]/2}{k}$$

$t_{\frac{1}{2}} = \frac{[R_0]}{2k}$

where, $[R_0]$ is initial concentration.

on comparing,

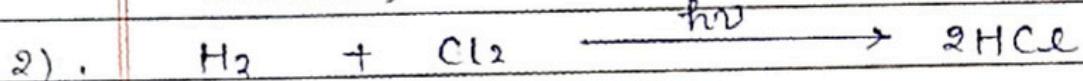
$$t_{\frac{1}{2}} \propto [R_0]$$



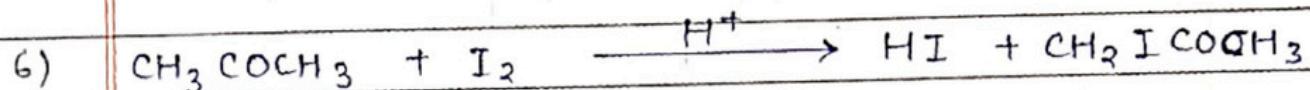
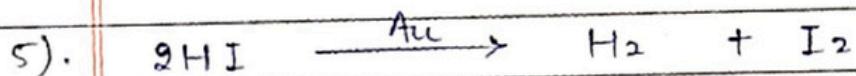
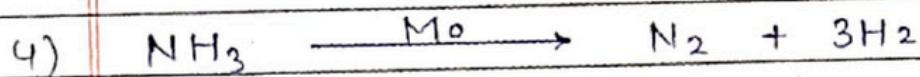
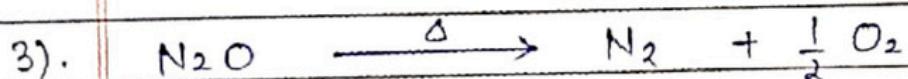
Examples :- (zero order reaction)

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

Substrate enzyme \rightarrow Product
(excess)

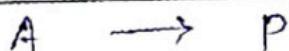


(photochemical reaction)



2). First Order Reaction :

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



$t=0 \quad (a)$

$t=t \quad (a-n)$

$$\text{rate} = -\frac{dn}{dt} = k[A]^n$$

$$-\frac{dn}{dt} = k(a-n) \quad \dots \textcircled{1}$$

$$\int \frac{dn}{(a-n)} = \int -k dt$$

Integrating equation on both sides we get,

$$\ln(a-n) = -kt + c \quad \text{--- (2)}$$

Initially, $t=0$, $n=0$

$$\ln(a) = c \quad \text{--- (3)}$$

$$\ln(a-n) = -kt + \ln a \quad \text{--- (4)}$$

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

$$kt = \ln \frac{a}{a-n}$$

$$[a-n]$$

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

$$kt = 2.303 \log_{10} \frac{a}{a-n}$$

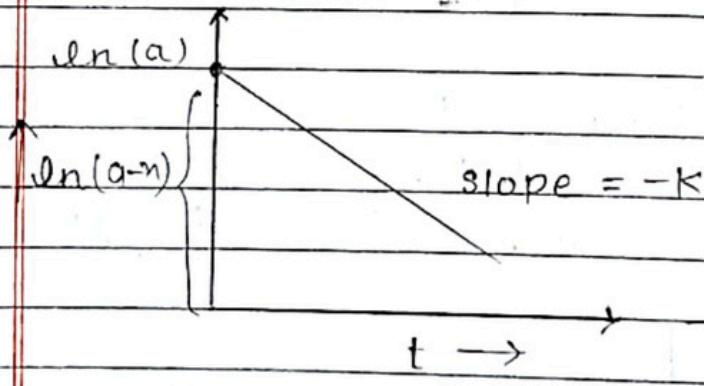
$$K = \frac{2.303 \log_{10} [a]}{t} \quad \boxed{\frac{[a-n]}{[a-n]}}$$

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

on comparing, the equation (4)

$$y = mn + c$$

graph



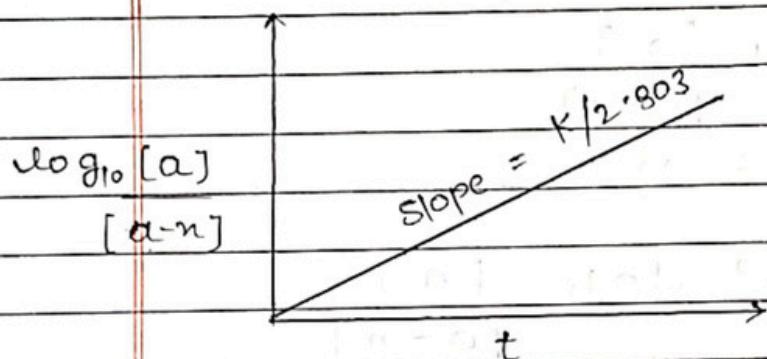
$$\log_{10} \frac{[a]}{[a-n]} = kt + \log_{10} [a]$$

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

$$\log_{10} \frac{[a]}{[a-n]} = \frac{k \times t}{2.303}$$

$\underbrace{\hspace{1cm}}$ $\underbrace{\hspace{1cm}}$

y



Half Life of first order reaction -



$$t=0 \quad a$$

$$t = \frac{t_1}{2} \quad a - \frac{a}{2} \quad (n = a/2)$$

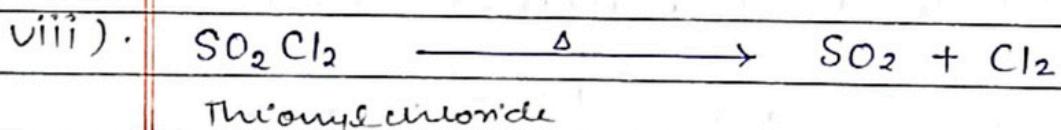
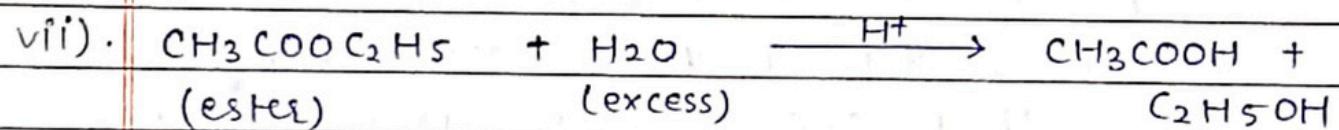
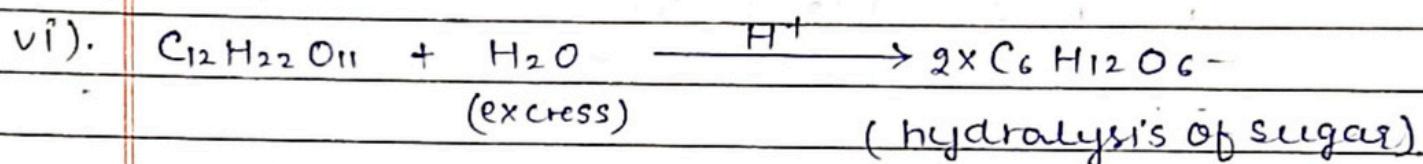
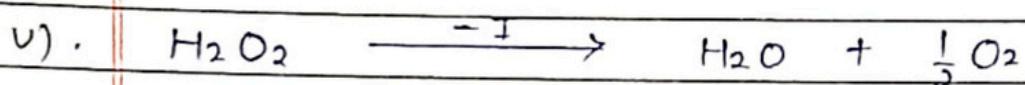
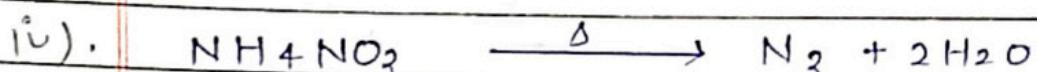
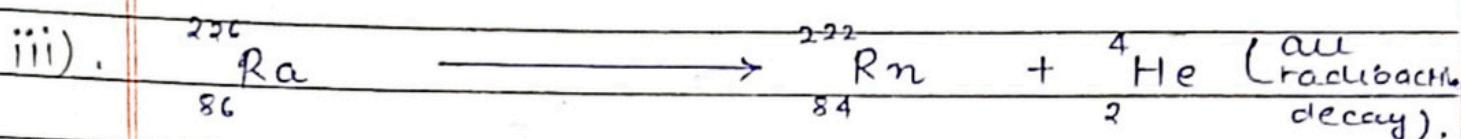
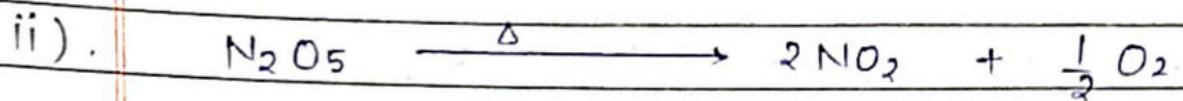
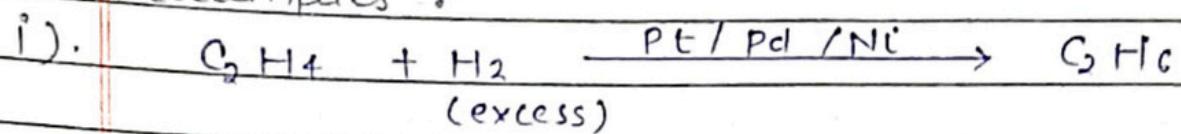
$$t = \frac{2.303}{k} \log_{10} \frac{a}{a-n}$$

$$\frac{t_1}{2} = \frac{2.303}{k} \log_{10} \frac{a}{a/2}$$

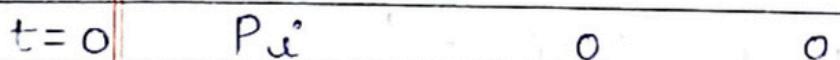
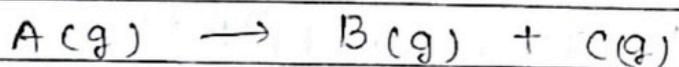
$$\frac{t_1}{2} = \frac{2.303}{k} \log_{10} 2 \quad (\log 2 = 0.301)$$

$\frac{t_1}{2} = 0.693$
k

Examples :-



FIRST ORDER REACTION IN TERMS OF PRESSURE



at time t :-

$$P_t = P_i - n + n + n$$

$$P_t = P_i - n$$

(total pressure)

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

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

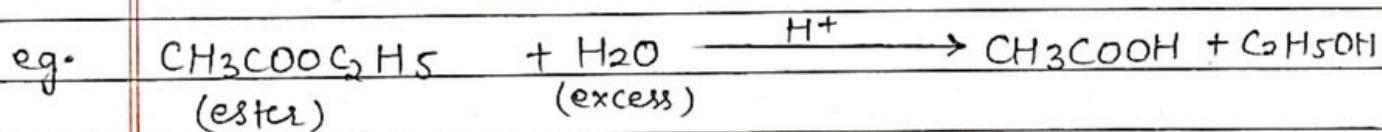
$$P_A = P_i - x \Rightarrow P_i - P_t + P_i = 2P_i - P_t$$

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

↑ initial pressure
↓ 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.

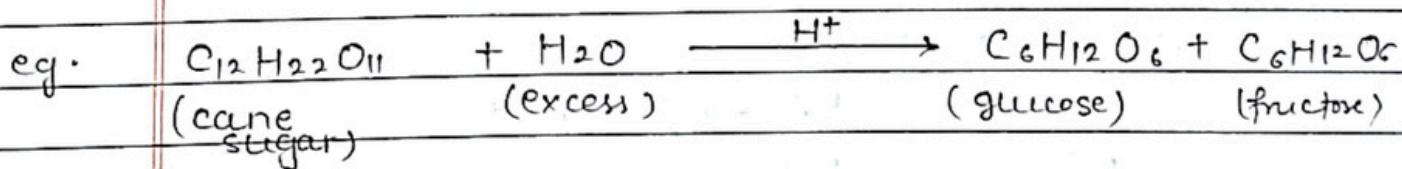


$$\text{rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

$$k' [\text{H}_2\text{O}] = k$$

$$\therefore \text{rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]^1$$

here molecularity = 2 but order = 1

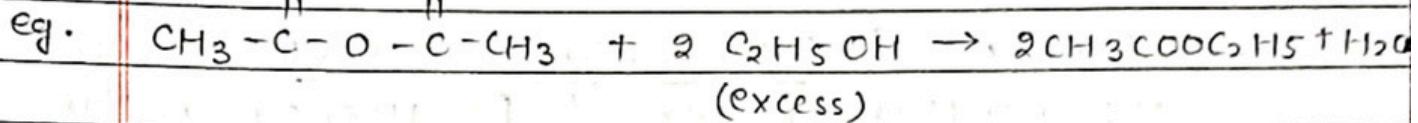
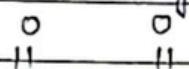


$$\text{rate} = k' [C_{12}H_{22}O_{11}] [H_2O]$$

$$k'[H_2O] = k$$

$$\text{rate} = k [C_{12}H_{22}O_{11}]^1$$

molecularity = 2 , but order = 1 .



$$\text{rate} = k' [(CH_3CO)_2O] [C_2H_5OH] [C_2H_5OH]$$

$$k = k' [C_2H_5OH] [C_2H_5OH]$$

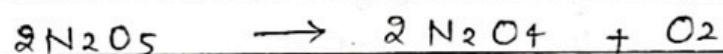
$$\text{rate} = k [CH_3CO)_2O]$$

molecularity = 3 but order = 1 . pseudo

so, there are all example of first order reaction.

Temperature dependence of rate of reaction :-

Consider an example,



at $0^\circ\text{C} \rightarrow 10$ days

$25^\circ\text{C} \rightarrow 5$ hours

$50^\circ\text{C} \rightarrow 12$ 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.

$$k = A e^{-E_a/RT}$$

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

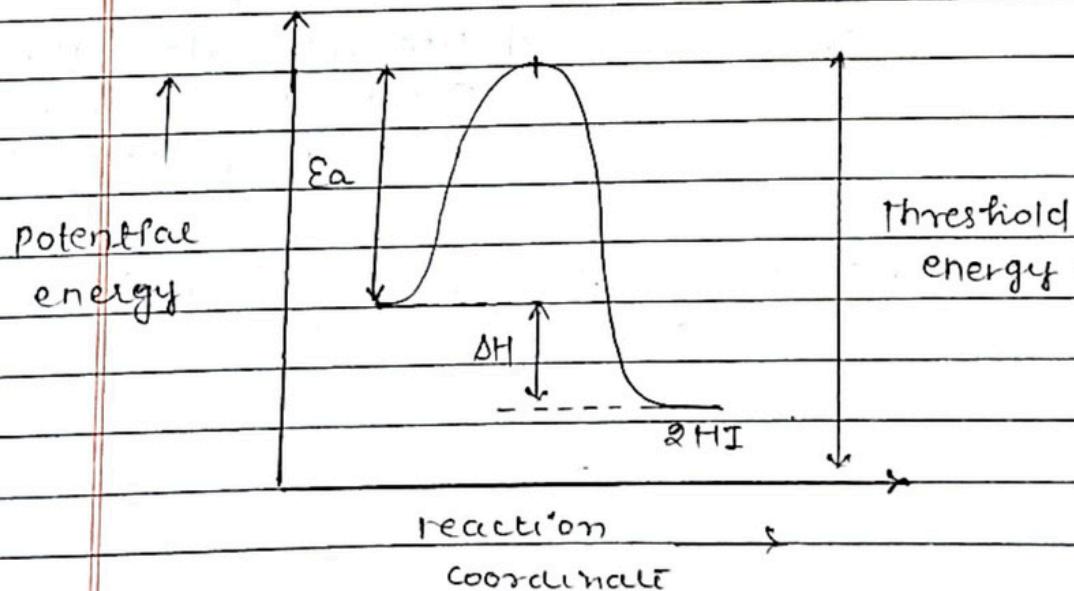
T is absolute temperature .

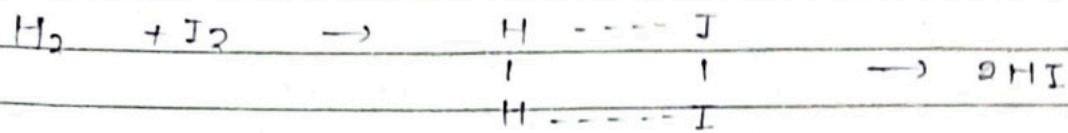
'A' and ' E_a ' are collectively called Arrhenius parameters.

The factor $e^{-E_a/RT}$, 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

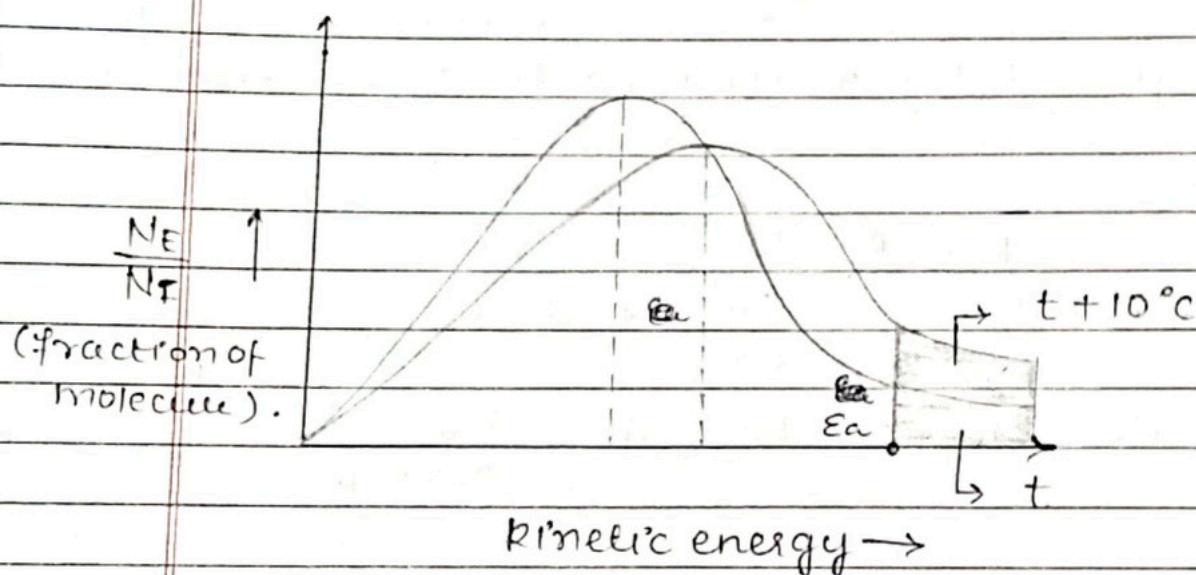
N_E is molecule that have kinetic energy.





(intermediate)
which is
highly unstable
high energy.

Threshold energy = Activation Energy + Energy possessed by reaction.



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

When $t + 10^\circ\text{C}$, the most probable kinetic energy gases increases comparatively and large no. of gases occupy E_a .

\therefore larger no. of product are formed.

\therefore Rate of reaction increases on increasing the temperature by 10°C .

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

Activation Energy :-

Activation energy is the energy given or required by reactant to reach the threshold point so that the intermediate can be formed and product formation takes place.

Threshold Energy :-

It's the minimum energy required by reactants to cause effective collision.

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

$$\ln K = -\frac{E_a}{RT} + \ln A$$

$$\log_{10} K = \log_{10} A - \frac{E_a}{2.303 RT}$$

$$\log_{10} K_1 = \log_{10} A - \frac{E_a}{2.303 RT_1} \quad \text{--- (1)}$$

$$\log_{10} K_2 = \log_{10} A - \frac{E_a}{2.303 RT_2} \quad \text{--- (2)}$$

Subtract (1) from (2) -

$$\log_{10} K_2 - \log_{10} K_1 = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

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

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Collision Theory :-

Reactants are considered as hard spheres, when the hard spheres collide with each other with suitable kinetic energy they form an intermediate followed by product.

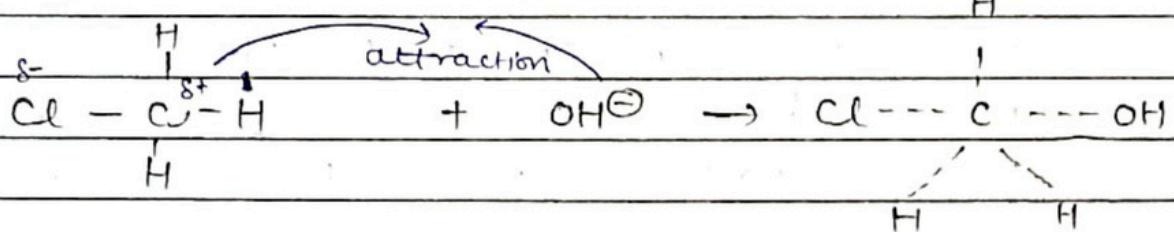
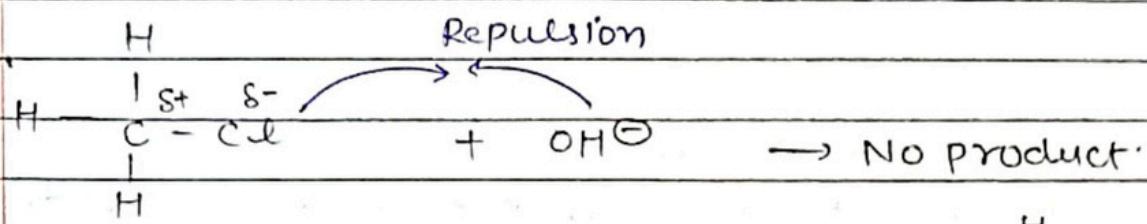
- * The number of particles that collide per second in a given molecule volume is called as collision frequency (Z).
- * In gaseous phase, for binary collision system the Z is in range of $10^{25} - 10^{28}$.
- * If after collision they are able to form product then collision is effective.
∴ reaction will take a very short time and vice-versa

Factors affecting the effective collision:-

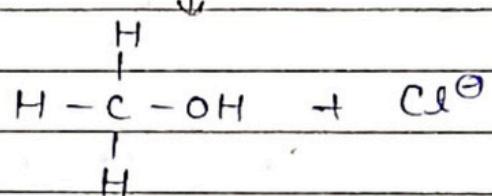
- ① Energy barrier: for an effective collision the reactants must have threshold energy.

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

② Orientation barrier



(intermediate)



collision factor.

$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$

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

↳ probability factor

Effect on catalyst on rate of reaction :-

Catalyst :

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

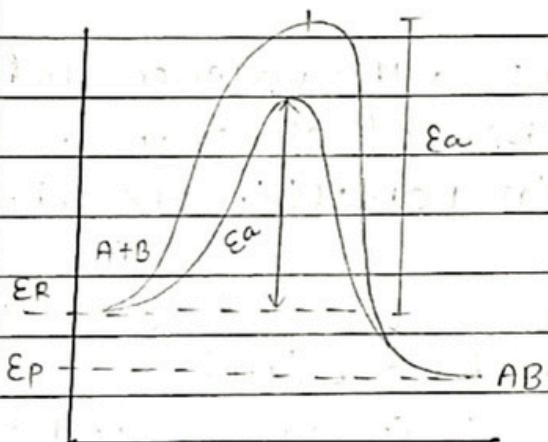
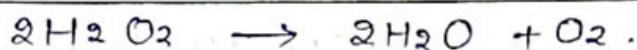
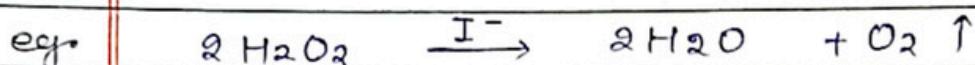
→ Catalyst never interfere with ΔG_f of a reaction (it will not start or stop the reaction).

$\Delta G_f = 0$: no reaction

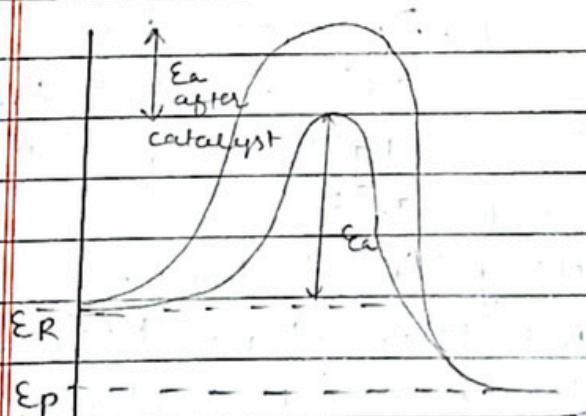
$\Delta G_f = +ve$: non-spontaneous reaction

$\Delta G_f = -ve$: spontaneous reaction.

$$\Delta G_f = \Delta H - T \Delta S$$



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



Negative catalyst: those catalyst that increases E_a of reaction \therefore rate of reaction decrease because higher E_a can be achieved slower and R.o.R decreases.