

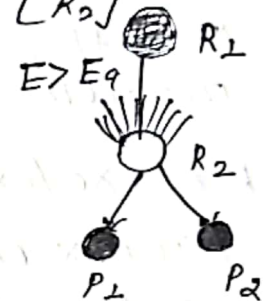
1.7 State and explain collision theory of chemical reaction with the rate expression of bimolecular gaseous reaction.

→ This theory is satisfactory for gaseous reaction. The essential requirements for reaction according to collision theory are:-

- 1.) Collisions between the reactants molecules.
- 2.) Activation of molecules
- 3.) proper orientation between two reaction R_1 and R_2

$$\text{Rate of collision} = \text{constant} \times [R_1] [R_2]$$

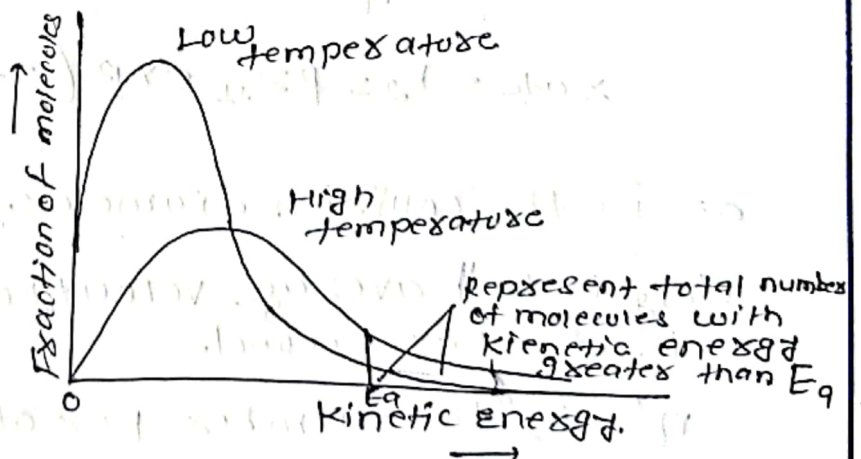
It is assumed in collision theory that a collision is successful only if the molecules collide with at least the activation energy of the reaction.



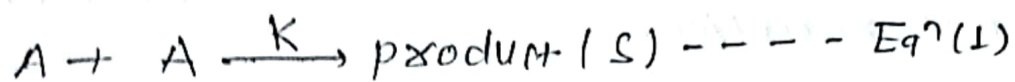
R_1 and R_2 are constant

P_1 and P_2 are products

The activation energy is the minimum energy required for reaction. The fraction of collision with at least the energy E_a is given by the Maxwell distribution of speed.



Let us find the expression for a bimolecular gaseous reaction.



According to collision theory.

$$-\frac{d[A]}{dt} = Z_{11} Q p \text{ --- Eq (2)}$$

Where,

Z_{11} is the number of collisions between the reacting molecules per second per dm^3

Q is the fraction of the total number of molecules which are activated, and

p is referred to as the probability or steric factor and is related to the geometry of the molecules.

From the kinetic theory of gases

$$Z_{11} = \frac{1}{2} \sqrt{2} \pi \sigma^2 (\eta')^2 v_{\text{avg}} \text{ --- (3)}$$

$$Q = \frac{\eta^*}{\eta'} = e^{-E_a/RT} \text{ --- (4)}$$

$$\text{rate} = k_2 = p Z_{11} \exp\left(-\frac{E_a}{RT}\right) \text{ --- (5)}$$

σ is the collision diameter.

v_{avg} is the average velocity of the molecules in dm per second.

η^* is the number per of molecules per dm^3 having $E > E_a$,

E_a is the activation energy



n' is the total number of molecules per cm^3 .

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad \text{----- Eq(5)}$$

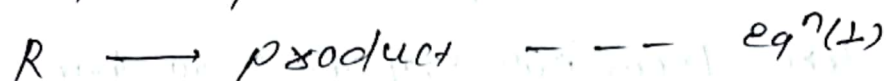
Therefore from eq 3, 4 and 5 we have

$$Z_{11} = \frac{1}{2} \sqrt{2} \pi \sigma^2 (n')^2 \sqrt{\frac{8RT}{\pi M}}$$

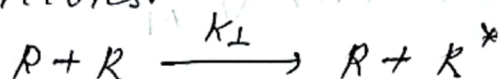
$$Z_{11} = 2 \sigma^2 (n')^2 \sqrt{\frac{\pi RT}{M}} \quad \text{----- Eq(6)}$$

2) Explain Lindemann theory of unimolecular reaction with the rate expression.

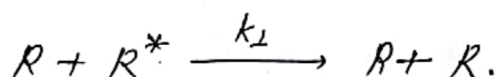
→ In unimolecular reaction, only one reactant molecule takes part in the reaction like



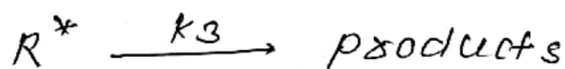
According to this theory, the reactant molecules (R) are first activated by collision with other reactant molecules.



The activated reactant molecules do not decompose immediately. For second bimolecular collisions,



If the time lag, activated reactant molecules are not deactivated, they will undergo a decomposition reaction leading to the formation of products



Rate of formation of $R^* =$ Rate of decomposition of R^*

$$k_1 [R]^2 = k_2 [R][R^*] + k_3 [R^*]$$

$$\Rightarrow [R^*] = \frac{k_1 [R]^2}{k_2 [R] + k_3}$$

case (I) $k_2 [R] \gg k_3$

$$\text{rate of reaction} = \frac{k_1 k_3}{k_2} [R]$$

first order rate eqn.

case II $k_2 [R] \ll k_3$,

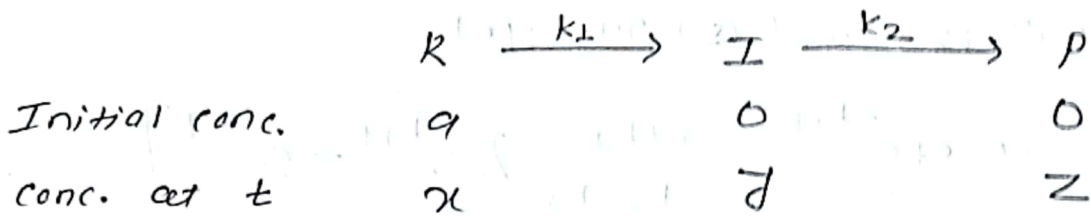
$$\text{rate of reaction} = k_1 [R]^2$$

second order rate eqn.



3) Derive the rate expression for consecutive reaction.

→ consider a simple consecutive 1st order rxn



The Rate of consumption of reactant

$$R = -\frac{dx}{dt} = k_1 x$$

Separating the variable of eqⁿ (1) and integrating between the limit

at $t=0$, $x=a$ & at $t=t$, $x=x$ we get

$$\int_a^x \frac{dx}{x} = -k_1 \int_0^t dt$$

$$\ln\left(\frac{x}{a}\right) = -k_1 t$$

$$x = a e^{-k_1 t} \quad \text{--- eqⁿ (2)}$$

Reactant R decrease exponentially with time

The rate of formation of intermediate

$$I = \frac{dy}{dt} = k_1 x - k_2 y \quad \text{--- eqⁿ (3)}$$

Substituting the value of x from eqⁿ (2) & (3) we get

$$\frac{dy}{dt} = k_1 a e^{-k_1 t} - k_2 y \quad \text{--- (4)}$$

eqⁿ (4) is a linear 1st order differential eqⁿ whose solution is

$$y = \frac{k_1 a}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}] \quad \text{--- (5)}$$

As per the condition of conservation of mass we have

$$a = x + y + z$$

The concentration of x and y from eqn (2) & (5) we get z

The concentration of product $p (= z)$ may be

$$z = a - x - y$$

from eqn (2) and (5) we get,

$$z = a - a e^{-k_1 t} - \frac{a k_1}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

$$= a \left[1 - e^{-k_1 t} - \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \right]$$

$$z = \frac{a}{k_2 - k_1} [(k_2 - k_1) e^{-k_1 t} - (k_1 - k_1) e^{-k_2 t}] \quad \text{--- (6)}$$

case I When $k_1 \gg k_2$ Then,

$$e^{-k_1 t} \ll e^{-k_2 t}$$

Hence $e^{-k_1 t}$ can be neglected in eqn (6)

$$z \approx \frac{a}{k_2 - k_1} [(k_2 - k_1) + k_1 e^{-k_2 t}]$$

$$\text{or, } k_2 \gg k_1$$

$$z = \frac{a}{-k_1} (-k_1 + k_1 e^{-k_2 t})$$

$$z = a (1 - e^{-k_2 t}) \quad \text{--- (7)}$$

The formation of product p therefore involving only k_2 which therefore is the rate determining step.

case (II) $k_1 \ll k_2$ then $e^{-k_1 t} \gg e^{-k_2 t}$.

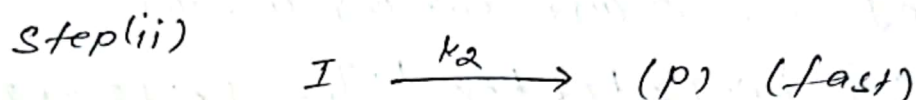
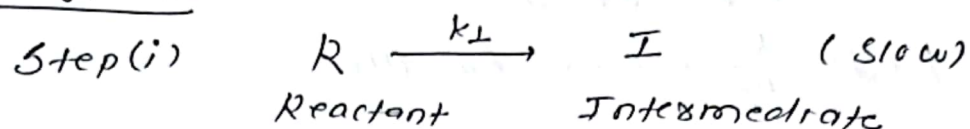
Then eqn (6) reduced to

$$z \approx a (1 - e^{-k_1 t}) \quad \text{--- Eqn (8)}$$

The concentration of x, y, z are plotted as functions of time in the consequence figure.

(4) Explain Type-I and Type-III complex reaction with example

Type I



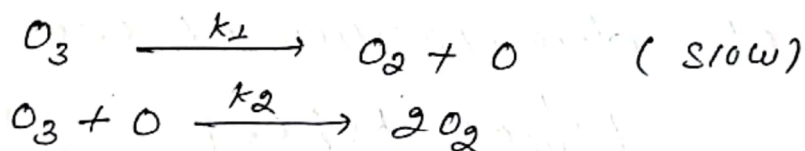
First step is slow, rate determining which is followed by rapid subsequent in which product is formed.

For example.

Decomposition of ozone



Decomposition of ozone may have the following proposed mechanism.



From the proposed mechanism, the rates of decomposition of O_3 can be given as

$$r_1 = -\frac{d}{dt} [O_3] = k_1 [O_3] \quad \text{--- eqn (1)}$$

$$r_2 = -\frac{d}{dt} [O_3] = k_2 [O_3] [O] \quad \text{--- eqn (2)}$$

Thus, the total rate of decomposition of ozone is given by $O_3 = r = r_1 + r_2$

$$-\frac{d}{dt} [O_3] = k_1 [O_3] + k_2 [O_3] [O]$$

$$= [O_3] \{k_1 + k_2 [O]\} \quad \text{--- eqn (3)}$$

Rate of formation of atomic oxygen = rate of consumption of atomic oxygen.

$$\Rightarrow k_1 [O_3] = k_2 [O_3] [O]$$

$$[O] = \frac{k_1}{k_2} \text{ --- eqn (4)}$$

Substituting $[O]$ from eqn (4) in eqn (3) we get,

$$-\frac{d}{dt} [O_3] = [O_3] \left\{ k_1 + k_2 \times \frac{k_1}{k_2} \right\} = [O_3] \{ 2k_1 \}$$

$$\Rightarrow -\frac{1}{2} \frac{d}{dt} [O_3] = k_1 [O_3] \text{ --- eqn (5)}$$

Now in the overall reaction

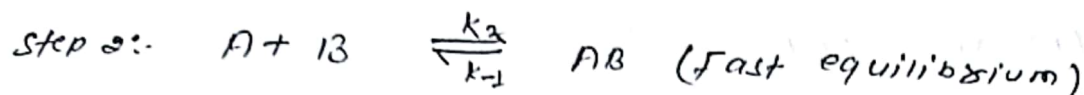
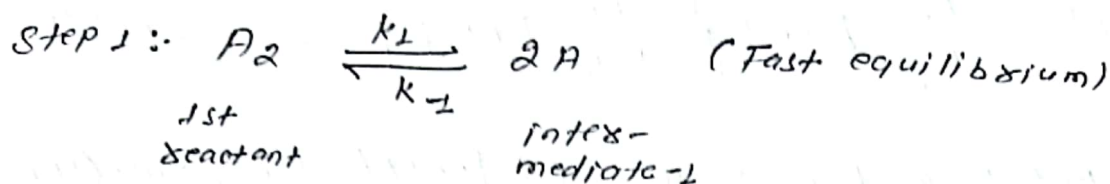


$$-\frac{1}{2} \frac{d}{dt} [O_3] = k_1 [O_3] \text{ --- eqn (6)}$$

From eqn (5) and (6) we can conclude the rate of decomposition of ozone.

$$-\frac{1}{2} \frac{d}{dt} [O_3] = k_1 [O_3]$$

$$\therefore \text{the rate is: } -\frac{1}{2} \frac{d}{dt} [O_3] = k_1 [O_3]$$

Type III

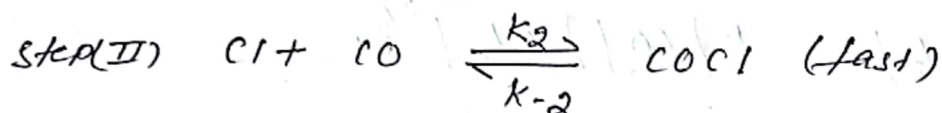
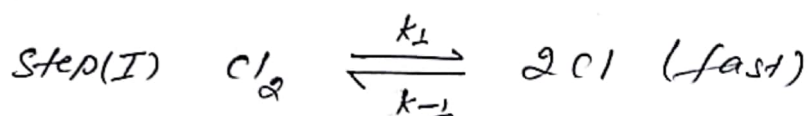
Such reaction involve more than two elementary steps with atleast one slow step.

For Example:-

The reaction for the formation of phosgene

$$CO + Cl_2 \longrightarrow COCl_2$$

For this reaction the following mechanism has been proposed.



the rate of formation of phosgene is

$$\frac{d}{dt} [COCl_2] = k_3 [COCl] [Cl_2] - eqn (1)$$

From step(II)

$$\frac{k_2}{k_{-2}} = \frac{[COCl]}{[Cl][CO]} \therefore [COCl] = \frac{k_2}{k_{-2}} [Cl][CO] - eqn (2)$$

From step(i)

$$\frac{k_1}{k_{-1}} = \frac{[Cl]^2}{[Cl_2]} \therefore [Cl] = \left\{ \frac{k_1}{k_{-1}} [Cl_2] \right\}^{1/2} - eqn (3)$$

Substituting the value of $[Cl]$ from eqn (3) in eqn (2) we get,

$$[COCl] = \frac{k_2}{k-2} [CO] \left\{ \frac{k_1}{k-1} [Cl_2] \right\}^{1/2} \text{--- eqn (4)}$$

Substituting this value of $[COCl]$ from eqn (4) in eqn (1) we get,

$$\frac{d[COCl_2]}{dt} = k_3 [Cl_2] \frac{k_2}{k-2} [CO] \left\{ \frac{k_1}{k-1} [Cl_2] \right\}^{1/2}$$

$$= \frac{k_1}{k-2} \left(\frac{k_1}{k-1} \right)^{1/2} \left(\frac{k_2}{k-2} \right) k_3 [CO] [Cl_2] [Cl_2]^{1/2}$$

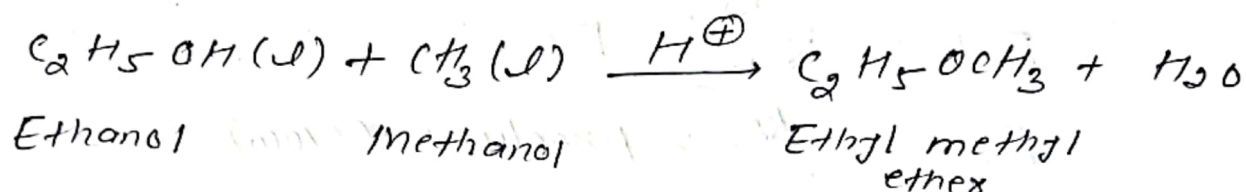
$$= k [CO] [Cl_2]^{3/2}$$

$$\therefore \frac{d}{dt} [COCl_2] = k [CO] [Cl_2]^{3/2}$$

(5) What do you mean by homogeneous and heterogeneous catalysts? Explain the Langmuir-Hinshelwood mechanism for heterogeneous catalysts.

→ Homogeneous catalysts:-

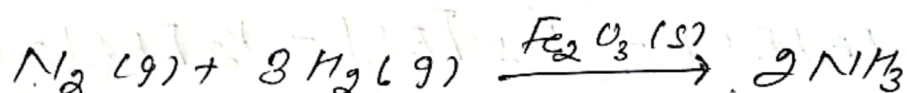
In homogeneous catalysts, the catalyst and the reactants are in same phase.



Heterogeneous Catalysts.

In heterogeneous catalysts, the catalyst and the reactants are in different phase.

Haber's process



The Langmuir-Hinshelwood Mechanism

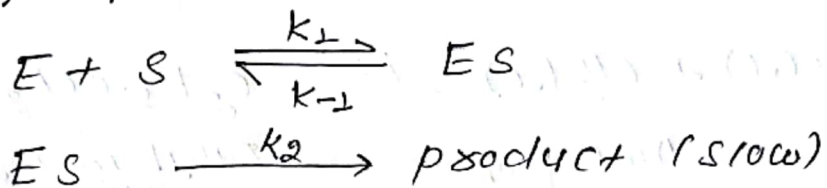
According to this Langmuir-Hinshelwood, a gaseous reaction taking place on the surface of a solid catalyst i.e., a surface reaction is believed to occur in the following steps:

- (i) Diffusion of reactant to surface,
- (ii) Adsorption of reactants at the surface
- (iii) chemical reaction at the surface
- (iv) Desorption of products from the surface
- (v) Diffusion of product away from the surface.

6. Briefly explain enzyme and derive Michaelis-Menten equation for enzyme catalysis.

→ Enzymes are biocatalyst and they catalyze biochemical reaction occurs in a biological system.

Let us consider a hypothetical enzyme catalyzed reaction.



from the reaction ES intermediate

$$\text{Rate} = k_2 [ES]$$

Applying steady state approximation to ES

$$k_1 [E][S] - k_{-1} [ES] - k_2 [ES] = 0$$

$$[ES] = \frac{k_1 [E][S]}{k_{-1} + k_2}$$

$$[ES] = \frac{[E][S]}{\left(\frac{k_{-1} + k_2}{k_1}\right)} = \frac{[E][S]}{K_m} \quad \text{--- (1)}$$

Where, $K_m = \frac{k_{-1} + k_2}{k_1}$ is known as Michaelis constant.

Let $E_0 \rightarrow$ total concentration of enzyme

$E \rightarrow$ conc. of free enzyme / ~~unreact~~ ^{unreact} enzyme



Amount of unreacted enzymes,

$$[E] = [E_0] - [ES]$$

$$\Rightarrow [ES] = [E_0] - [E] \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{i.e. } [E] + [ES] = [E_0]$$

$$\Rightarrow \frac{[E][S]}{k_m} = [E_0] - [E]$$

$$\Rightarrow \frac{[E][S]}{k_m} + [E] = [E_0]$$

$$\text{or, } [E] \left(1 + \frac{[S]}{k_m} \right) = [E_0]$$

$$[E] \left(\frac{k_m + [S]}{k_m} \right) = [E_0]$$

$$[E] = \frac{k_m [E_0]}{k_m + [S]} \quad \text{--- (ii)}$$

Now initially,

$$\begin{aligned} R &= k_2 [ES] \\ &= k_2 \frac{[E][S]}{k_m} \end{aligned}$$

$$R = \frac{k_2 \times k_m [E_0]}{(k_m + [S])} \times \frac{[S]}{k_m}$$

$$R = \frac{k_2 [E_0] [S]}{k_m + [S]}$$

Case I

If $k_m \gg [S]$

$$R = k_2 [E_0] [S] / k_m$$

$$\boxed{R = k_2 [E_0] [S]}$$

Case II

If $k_m \ll [S]$

$$R = \frac{k_2 [E_0] [S]}{[S]} = k_2 [E_0]$$

$$R = k_2 [E_0]$$

It is independent of substrate reactant