Module-3 Kinetics & Catalysis

Chemical Kinetics It deals with the study of rate of chemical reactions.

Rate of Rxn is defined as change in concn of reactants or products (or change in physical parameters which depends on concn such as conductance, absorbance, current etc) per unit time.

Kinetics also sheds light on rxn mechanism.

Factors affecting Rate of Reaction

(i) Nature of substance

(ii) physical state of substance

(iii) temp.

(iv) concn (soln)

(v) pressure (gaseous)

(vi) surface area of reactants

(vii) presence of catalyst

(viii) Intensity of radiation etc.

Rate of Reactions (ROR)

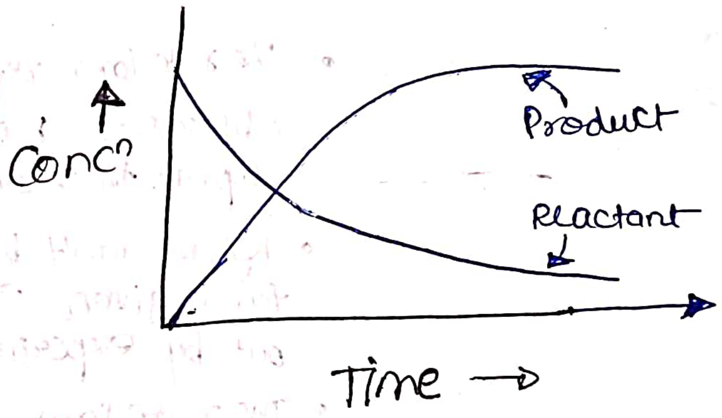
$$ROR = \frac{\text{change in the conc}^n \text{ of reactants or Pdt}}{\text{Time}}.$$

expressed in $mol\, L^{-1} s^{-1}$

Average rate of reaction

$$\text{Average rate } (r_{avg}) = \frac{\text{Change in conc}^n \text{ of reactants (or Pdt)}}{\text{Large interval of time}}$$

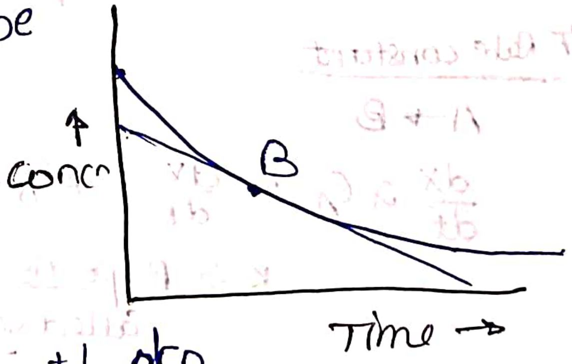
$$r_{avg} = \pm \frac{\Delta C}{\Delta t} = \pm \frac{(C_2 - C_1)}{(t_2 - t_1)}$$



Instantaneous Rate of reaction

↳ reaction rate during a very short interval of time (or ROR at particular time)

$$\text{Instantaneous rate} = \pm \lim_{\Delta t \to 0} \frac{\Delta C}{\Delta t} = \frac{dc}{dt} = \text{slope}$$



For rxn · $n_1 A + n_2 B \rightarrow m_1 C + m_2 D$

Instantaneous Rate of reaction

$$= \frac{-1}{n_1}\frac{d[A]}{dt} \pm \frac{-1}{n_2}\frac{d[B]}{dt} = \frac{+1}{m_1}\frac{d[C]}{dt} = \frac{+1}{m_2}\frac{d[D]}{dt}$$

Rate of rxn

$$= \frac{-1}{n_1}\frac{\Delta[A]}{\Delta t} = \frac{-1}{n_2}\frac{\Delta[B]}{\Delta t} = \frac{+1}{m_1}\frac{\Delta[C]}{\Delta t} = \frac{+1}{m_2}\frac{\Delta[D]}{\Delta t}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

$$ROR = \frac{\Delta[O_2]}{\Delta t} = \frac{-1}{2}\frac{\Delta[H_2O_2]}{\Delta t}$$

Rate law

$$mA + nB \rightarrow \text{Product}$$

$$\text{Rate, } R \propto [A]^m [B]^n$$

- It may not depend upon concn of each reactant or product of the reaction
- Rate of Rxn ∝ concn of reactants
- The rate law represents the experimentally observed rate of rxn which depends upon the slowest step of the reaction.
- Rate law can't be deduced from the eqn for a given reaction. It can be found out by experiments only.
- The rate law may not bear a simple relationship for the stoichiometric equation
- It may not depend upon the concn of species, which do not appear in the eqn for overall reaction.

Rate constant

$$A \rightarrow B$$

$$\frac{dx}{dt} \propto C_A \text{ or } \frac{dx}{dt} = kC_A.$$

k ⇒ Proportionality constant
Called velocity constant
or rate constant
or Specific reaction rate

At a fixed temperature,

if $C_A = 1$ then Rate $= \frac{dx}{dt} = k$.

unit of rate constant $= \left[\frac{1}{\text{Unit of Concn}}\right]^{n-1} \times \text{time}^{-1}$

$$= \left[\frac{1}{\text{mol/Ltr}}\right]^{n-1} \times \text{sec}^{-1}$$

$$= \left\{\left[\frac{\text{Ltr}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1}\right\}$$

$n \Rightarrow$ order of rxn

Order of rxn

↳ sum of powers to which concn terms are raised in order to determine rate of rxn.

$$mA + nB \rightarrow \text{pdt}$$

$$\text{Rate} = k[A]^p[B]^q$$

order of rxn, $\boxed{n = p+q}$

n can be negative, 0, fraction, integers

order w.r.t A, $= p$

order w.r.t B $= q$

	Zero order	First order	second order	nth Order
Rate-law (differential)	$-\frac{d[A]}{dt} = k$	$\frac{-d[A]}{dt} = k[A]$	$-\frac{d[A]}{dt} = k[A]^2$	$-\frac{d[A]}{dt} = k[A]^n$
Integrated Rate law	$[A]=[A]_0-kt$	$[A] = [A]_0 e^{-kt}$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0^{n-1}} + (n-1)kt$ (except 1st order)
units of Rate constant (K)	M/s	$1/s$	$\frac{1}{M \cdot s}$	$\frac{1}{M^{n-1} \cdot s}$
Linear plot to determine K.	$[A]$ vs t	$\ln[A]$ vs t	$\frac{1}{[A]}$ vs t	$\frac{1}{[A]^{n-1}}$ vs t (except 1st order)
Half life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln(2)}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$	$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k[A]_0^{n-1}}$ $\boxed{n \geq 2}$

Kinetics of some complex Reactions : chain, Parallel / competing side ; consecutive reactions

1. kinetics of chain reactions

Chain reactions usually involve free radicals.

example : gas phase reaction of hydrogen with bromine to give HBr. (T must be high enough that Br is a gas not liquid)

$$H_2 + Br_2 \longrightarrow 2HBr$$

Experimental rate law is obtained by Linde & Bodenstein.

$$\frac{d[HBr]}{dt} = \frac{k'[H_2][Br_2]^{1/2}}{1 + k''\frac{[HBr]}{[Br_2]}}$$

Postulated mechanism has 5 elementary reaction steps

① Initiation $Br_2 \xrightarrow{K_1} Br\cdot + Br\cdot$

② Propagation $Br\cdot + H_2 \xrightarrow{K_2} HBr + H\cdot$

③ Propagation $H\cdot + Br_2 \xrightarrow{K_3} HBr + Br\cdot$

④ Inhibition $H\cdot + HBr \xrightarrow{K_4} H_2 + Br\cdot$

⑤ Termination $Br\cdot + Br\cdot \xrightarrow{K_5} Br_2$

① Rate of Reaction of formation of HBr

$$\frac{d[HBr]}{dt} = K_2[\overset{\circ}{Br}][H_2] + K_3[\dot{H}][Br_2] - K_4[\dot{H}][HBr] \quad ①$$

$$\frac{d[\overset{\circ}{Br}]}{dt} = \text{Rate of formation} = \text{Rate of disappearance}$$

$$= \left[2K_1[Br_2] + K_3[\dot{H}][Br_2] + K_4[\dot{H}][HBr]\right]$$

$$= K_2[\overset{\circ}{Br}][H_2] + 2K_5[\overset{\circ}{Br}]^2$$

Similarly for $[H^\circ]$

$$\frac{d[\dot{H}]}{dt} = \text{Rate of formation of } [\dot{H}] = \text{Rate of disappearance of } [\dot{H}]$$

$$= K_2[\overset{\circ}{Br}][H_2] = K_3[\dot{H}][Br_2] + K_4[\dot{H}][HBr] \quad ③$$

Add eqn. ② & ③

$$\boxed{2K_1[Br_2]} + \cancel{K_3[\dot{H}][Br_2]} + \cancel{K_4[\dot{H}][HBr]}$$

$$= \cancel{K_2[\overset{\circ}{Br}][H_2]} + \boxed{2K_5[\overset{\circ}{Br}]^2} \quad ②$$

$$\cancel{K_2[\overset{\circ}{Br}][H_2]} = \cancel{K_3[\dot{H}][Br_2]} + \cancel{K_4[\dot{H}][HBr]}$$

$$\cancel{2}K_1[Br_2] = \cancel{2}K_5[\overset{\circ}{Br}]^2$$

$$K_1[Br_2] = K_5[\overset{\circ}{Br}]^2$$

$$[\dot{Br}]^2 = \frac{K_1 [Br_2]}{K_5}$$

Taking Square root both side

$$\boxed{[\dot{Br}] = \sqrt{\frac{k_1 [Br_2]}{K_5}}} \text{ — ④}$$

for determination of concⁿ of $[\dot{H}]$ use eqⁿ ③

$$K_2 [\dot{Br}] [H_2] = K_3 [\dot{H}] [Br_2] + K_4 [\dot{H}] [HBr]$$

$$K_2 [\dot{Br}] [H_2] = [\dot{H}] \{ K_3 [Br_2] + K_4 [HBr] \}$$

$$\boxed{[\dot{H}] = \frac{K_2 [\dot{Br}] [H_2]}{K_3 [Br_2] + K_4 [HBr]}} \text{ — ⑤}$$

Put eqⁿ ④ in eqⁿ ⑤

eqⁿ ⑤ becomes

$$\boxed{[\dot{H}] = \frac{K_2 \sqrt{\frac{K_1 [Br_2]}{K_5}} [H_2]}{K_3 [Br_2] + K_4 [HBr]}} \text{ — ⑥}$$

Put eqⁿ ④ & ⑥ in eqⁿ ①

$$\frac{d[HBr]}{dt} = k_2 \overset{\downarrow}{[Br^\bullet]}[H_2] + k_3 \overset{\downarrow}{[H^\bullet]}[Br_2] - k_4 \overset{\downarrow}{[H^\bullet]}[HBr]$$

$$\frac{d[HBr]}{dt} = k_2 \sqrt{\frac{k_1 [Br_2]}{k_5}}[H_2] + \frac{k_3 k_2 \sqrt{\frac{k_1[Br_2]}{k_5}}[H_2]\,[Br_2]}{k_3[Br_2]+k_4[HBr]} - \frac{k_4 k_2 \sqrt{\frac{k_1[Br_2]}{k_5}}[H_2][HBr]}{k_3[Br_2]+k_4(HBr)} \quad \text{—} ⑦$$

Take $k_2\sqrt{\frac{k_1}{k_5}[Br_2]}\,[H_2]$

$$\frac{d[HBr]}{dt} = k_2\sqrt{\frac{k_1}{k_5}[Br_2]}\,[H_2]\left\{1 + \frac{k_3[Br_2]}{k_3[Br_2]+k_4[HBr]} - \frac{k_4[HBr]}{k_3[Br_2]+k_4(HBr)}\right.$$

$$= k_2\sqrt{\frac{k_1}{k_5}[Br_2][H_2]}\left\{\frac{k_3[Br_2]+\cancel{k_4[HBr]}+k_3[Br_2]-\cancel{k_4(HBr)}}{k_3[Br_2]+k_4[HBr]}\right]$$

$$\frac{d[HBr]}{dt} = k_2\sqrt{\frac{k_1}{k_5}[Br_2]}\,[H_2]\left\{\frac{2k_3[Br_2]}{k_3(Br_2)+k_4(HBr)}\right]$$

$$\frac{d[HBr]}{dt} = k_2\sqrt{\frac{k_1[Br_2][H_2]}{k_5}}\left\{\frac{2k_3[Br_2]}{k_3[Br_2]+k_4[HBr]}\right.$$

Divide Numerator & denominator by $k_3[Br_2]$

$$\frac{d[HBr]}{dt} = k_2\sqrt{\frac{k_1[Br_2]}{k_5}}\,[H_2]\left\{\frac{\frac{2\cancel{k_3[Br_2]}}{\cancel{k_3[Br_2]}}}{\frac{\cancel{k_3[Br_2]}}{\cancel{k_3[Br_2]}}+\frac{k_4[HBr]}{k_3[Br_2]}}\right\}$$

$$\frac{d[HBr]}{dt} = k_2\sqrt{\frac{k_1[Br_2]}{k_5}}\,[H_2]\left\{\frac{2}{1+\frac{k_4[HBr]}{k_3[Br_2]}}\right\}$$

$$\frac{d[HBr]}{dt} = \frac{\boxed{2k_2\sqrt{\frac{k_1[Br_2]}{k_5}}}\;[H_2]}{1+\frac{k_4[HBr]}{k_3[Br_2]}}$$

Put $2k_2\sqrt{\frac{k_1}{k_5}} = k$

Put $\frac{k_4}{k_3} = k'$

$$d[HBr] = \frac{k[H_2][Br_2]^{1/2}}{1+k'\frac{[HBr]}{[Br_2]}}$$

Kinetics of

$$A \xrightarrow{k_1} \textcircled{B} \xrightarrow{k_2} C$$

Intermediate

$$\begin{aligned} A &\xrightarrow{k_1} \cancel{B} \\ \cancel{B} &\xrightarrow{k_2} C \\ \hline A &\longrightarrow C \end{aligned}$$

at $t=0$

$$\boxed{\begin{aligned} A_0 &\neq 0 \\ B_0 &= 0 \\ C_0 &= 0 \end{aligned}}$$ **

Also

$$[A_0] = [A]_t + [B]_t + [C]_t$$

Now, $\frac{A_t}{A_0} = e^{-k_1 t}$ ⇒ From 1st order

$$[A]_t = [A_0]\, e^{-k_1 t}$$

Now,

$$-\frac{d[A]}{dt} = k_1 [A]_t = k_1 [A]_0\, e^{-k_1 t} \quad \text{— ①}$$

$$\frac{d[B]}{dt} = k_1 [A]_t - k_2 [B]_t \quad \text{— ②}$$

$$-\frac{d[B]}{dt} = k_2 [B]_t$$

$[B]_t = ?$

Using ① & ②

$$\frac{dB}{dt} = k_1 [A]_t - k_2 [B]_t$$

$$\frac{dB}{dt} = k_1 [A]_0 e^{-k_1 t} - k_2 [B]_t$$

$$\left[\frac{dB}{dt} + k_2 [B]_t\right] = k_1 [A]_0 e^{-k_1 t}$$

multiply both side by $e^{k_2 t}$

$$\left[\frac{dB}{dt} + k_2 [B]_t\right] e^{k_2 t} = k_1 [A]_0 e^{-k_1 t} e^{k_2 t}$$

$$\left[\frac{dB}{dt} e^{k_2 t}\right] + k_2 \cancelto{0}{[B]_t e^{+k_2 t}} = k_1 [A]_0 e^{-(k_1 - k_2)t}$$

$$[B]_t = [B]_0 e^{-k_2 t}$$

$$[B]_0 = [B]_t e^{k_2 t}$$

$$0 = [B]_t e^{k_2 t}$$

$$\frac{dB}{dt} e^{k_2 t} = k_1 [A]_0 e^{-(k_1 - k_2)t}$$

$$dB\, e^{k_2 t} = k_1 [A]_0 e^{-(k_1 - k_2)t} dt$$

$$\int dB\, e^{k_2 t} = k_1 [A]_0 \int e^{-(k_1 - k_2)t} dt$$

$$[B]\, e^{k_2 t} = k_1 [A]_0 \times \frac{1}{-(k_1-k_2)} e^{-(k_1-k_2)t} + C$$

$$[B]\, e^{k_2 t} = k_1 [A_0] \left[-(k_1-k_2)\right]^{-1} e^{-(k_1-k_2)t} + C$$

Now to find

C = integration constant

$t = 0 \quad [B] = 0$

$$C = -k_1 [A]_0 \left[-(k_1-k_2)\right]^{-1} e^{0}$$

$$C = k_1 [A]_0 \left[(k_1-k_2)^{-1}\right]$$

$$C = \frac{k_1 [A]_0}{k_1-k_2}$$

Now;

$$[B]\, e^{k_2 t} = k_1 [A]_0 \left[\frac{e^{-(k_1-k_2)t}}{-(k_1-k_2)} + \frac{1}{k_1-k_2} \right]$$

$$[B]\, e^{k_2 t} = \frac{k_1 [A]_0}{(k_2-k_1)} \left[e^{-(k_1-k_2).t} - 1 \right]$$

$$[B] = \frac{k_1 [A]_0}{(k_2-k_1)} \left[\frac{e^{-(k_1-k_2)t}}{e^{k_2 t}} - \frac{1}{e^{k_2 t}} \right]$$

$$[B] = \frac{k_1 [A]_0}{(k_2-k_1)} \left[e^{-k_1 t + \cancel{k_2 t} - \cancel{k_2 t}} - e^{-k_2 t} \right]$$

$$\boxed{[B] = [A]_0 \frac{k_1}{(k_2-k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right]}$$

$$[A]_0 = [A]_0 e^{-k_1 t} + [A]_0 \frac{k_1}{(k_2-k_1)} \left[e^{-k_1 t} - e^{-k_2 t}\right] + [C$$

$$[C] = [A]_0 - [A]_0 e^{-k_1 t} - [A]_0 \frac{k_1}{k_2-k_1} \left[e^{-k_1 t} - e^{-k_2 t}\right]$$

$$[C] = [A]_0 \left\{ 1 - e^{-k_1 t} - \frac{k_1}{(k_2-k_1)} \left[e^{-k_1 t} - e^{-k_2 t}\right] \right\}$$

$$[C] = [A]_0 \left\{ 1 - \left\{ e^{-k_1 t} + \frac{k_1}{(k_2-k_1)} e^{-k_1 t} - \frac{k_1 e^{-k_2 t}}{(k_2-k_1)} \right\} \right\}$$

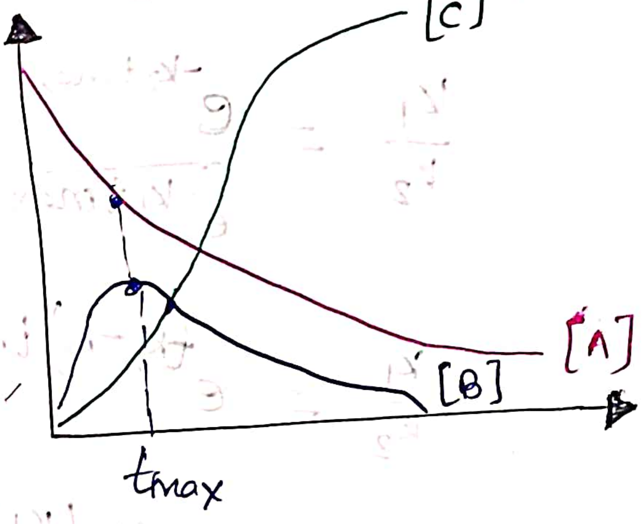
$$[C] = [A]_0 \left[1 - \left\{ \frac{(k_2-k_1) e^{-k_1 t} + k_1 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2-k_1)} \right\} \right]$$

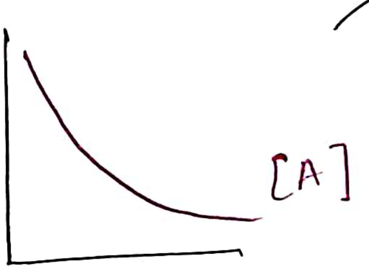
$$[C] = [A]_0 \left[1 - \left\{ \frac{k_2 e^{-k_1 t} - \cancel{k_1 e^{-k_1 t}} + \cancel{k_1 e^{-k_1 t}} - k_1 e^{-k_2 t}}{(k_2-k_1)} \right\} \right]$$

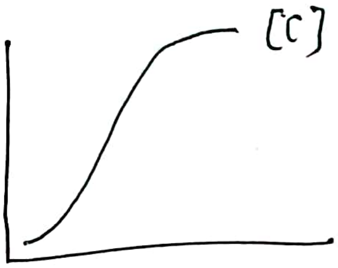
$$[C] = [A]_0 \left\{ 1 - \frac{(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})}{(k_2-k_1)} \right\}$$

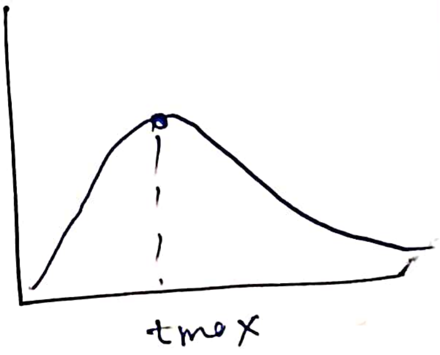
$$\boxed{\begin{aligned}
[A]_t &= [A]_0\, e^{-k_1 t} \\
[B]_t &= [A]_0 \left(\frac{k_1}{k_2-k_1}\right)\left[e^{-k_1 t} - e^{-k_2 t}\right] \\
[C]_t &= [A]_0 \left[1 - \frac{(k_2\, e^{-k_1 t} - k_1\, e^{-k_2 t})}{(k_2-k_1)}\right]
\end{aligned}}$$

$$\begin{aligned}
[A]_0 &= [A]_t + [B]_t + [C]_t \\
&= [A]_0 \left\{ e^{-k_1 t} + \frac{k_1}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \right. \\
&\qquad \left. + 1 - \frac{(k_2\, e^{-k_1 t} - k_1\, e^{-k_2 t})}{(k_2-k_1)} \right\}
\end{aligned}$$









Time at which maximum concentration of B :- $[B]_{max}$.

$$[B]_t = A_0 \frac{k_1}{k_2-k_1}\left[e^{-k_1t} - e^{-k_2t}\right]$$

But at maximum concn of B :

$$\frac{d[B]}{dt} = 0$$

$$\frac{d[B]}{dt} = \frac{d}{dt}\left[A_0 \frac{k_1}{k_2-k_1}\left(e^{-k_1t} - e^{-k_2t}\right)\right]$$

$$0 = A_0 \frac{k_1}{k_2-k_1}\left[-k_1e^{-k_1t} + k_2e^{-k_2t}\right]$$

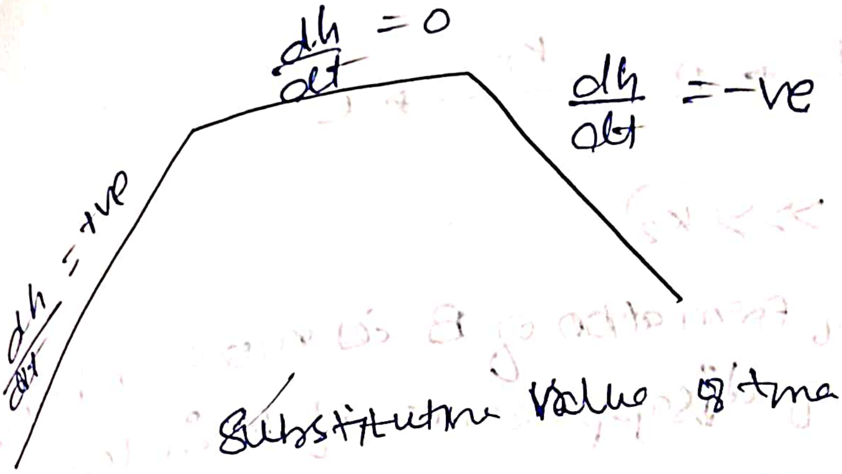
$$\therefore k_1 e^{-k_1 t_{max}} = k_2 e^{-k_2 t_{max}}$$

$$\frac{k_1}{k_2} = \frac{e^{-k_2 t_{max}}}{e^{-k_1 t_{max}}}$$

$$\frac{k_1}{k_2} = e^{(k_1-k_2)t_{max}}$$

$$(k_1-k_2)t_{max} = \ln\left(\frac{k_1}{k_2}\right)$$

$$\therefore \boxed{t_{max} = \frac{1}{(k_1-k_2)} \ln\left[\frac{k_1}{k_2}\right]}$$



Substituting value of tmax in $[B]_t$

$$[B]_{max} = [A]_0 \left(\frac{K_2}{K_1}\right)^{k_2(k_1-k_2)}$$

eg. 1st order consecutive rxn

- Radioactive decay
- Decomposition of dimethyl ether in gaseous phase & that of ethylene oxide

$$CH_3OCH_3 \xrightarrow{K_1} CH_4 + HCHO$$

$$HCHO \xrightarrow{K_2} H_2 + CO$$

$$(CH_2)_2O \xrightarrow{k_1} (CH_3CHO)^* \xrightarrow{K_2} CH_4 + CO.$$

steady State Approximation

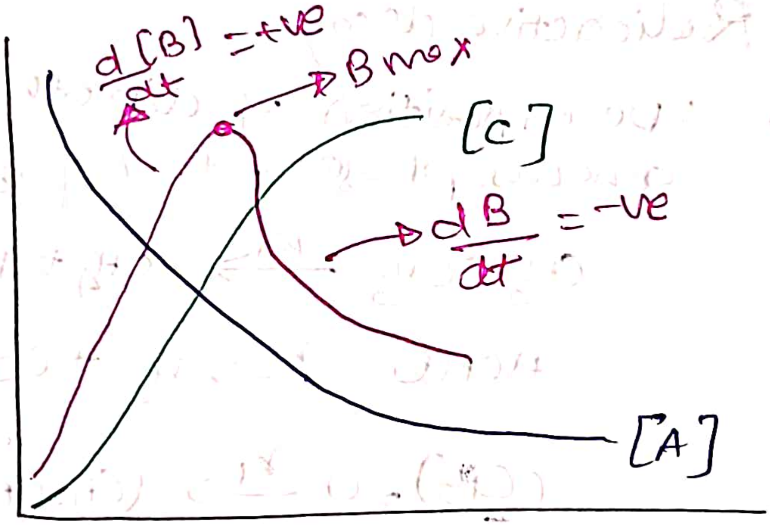
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

if $k_1 >>> k_2$

Rate of formation of B is more whereas rate of disappearance of B is less.

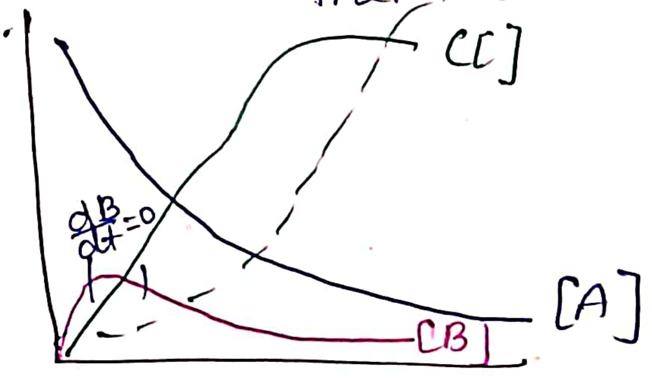
$$B_{\text{formation}} > B_{\text{disappearance}}$$

Since. $k_1 > k_2$ the conc^n of B reaches a maximum value then will decreas



But if $k_2 >> k_1$

the conc^n of B will be appreciabl
B disappears at a faster rat
then it is formed.



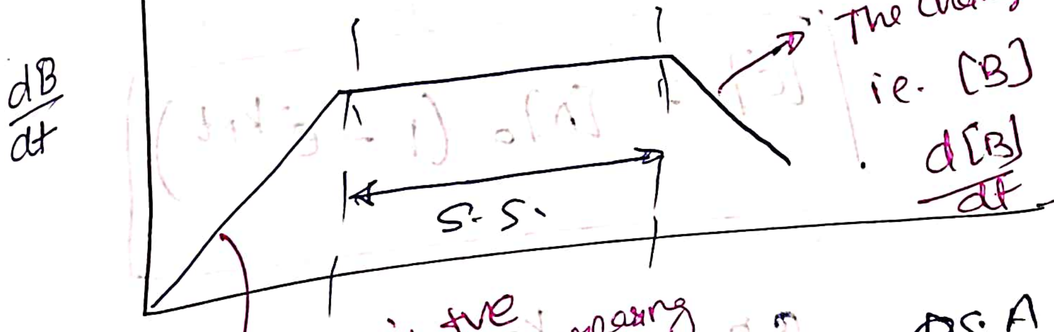
There, conc^n of [B] < [A] Here a condition arises [B] almost remains constant.

"The term steady state is used to describe a situation where some, not all of the state variables of a system are constant"

Note :
Steady state approximation does not assume conc^n of reaction to be zero rather it assume change in conc^n of reaction of Intermediate to be zero

The conc^n of [B] is constant not zero

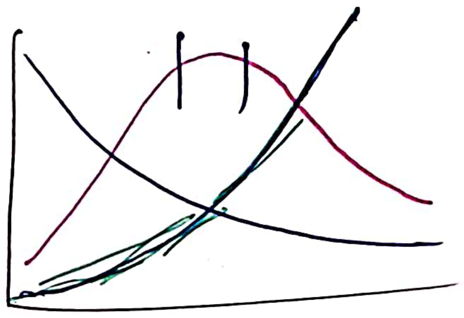
Hence $\frac{dB}{dt} = 0$



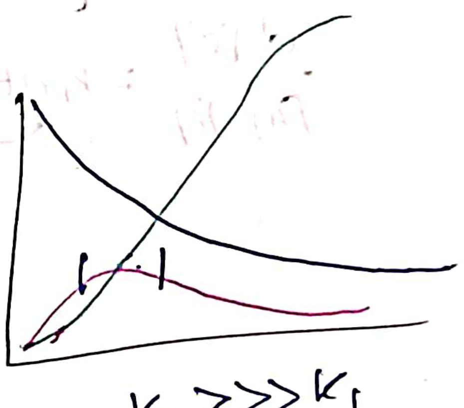
The change is -ve
i.e. [B] is decreasing
$\frac{d[B]}{dt} = -ve$

The change is +ve
i.e. [B] is increasing
$\frac{dB}{dt} = +ve$

S.S.A $\left[\frac{d[B]}{dt} = 0\right]$



$K_1 >>> K_2$



$K_2 >>> K_1$

$$A \overset{\text{fast.}}{\xrightarrow{k_1}} B \overset{\text{slow}}{\xrightarrow{k_2}} C$$

(1) Rate determining step. (slow)

$$k_2 >> k_1$$

$$e^{-k_2} << e^{-k_1}$$

$$[C] = [A]_0 \left\{ 1 - \frac{1}{k_2 - k_1} \left(\frac{k_2 e^{-k_1 t} - k_2 e^{-k_2 t}}{} \right) \right.$$

$$[C] = [A]_0 \left\{ 1 - \frac{1}{\cancel{k_2}} \left(\cancel{k_2} e^{-k_1 t} \right) \right.$$

$$\boxed{[C] = [A]_0 \left(1 - e^{-k_1 t}\right)}$$

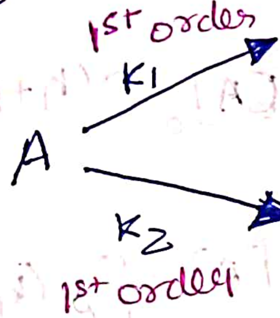
or $A \xrightarrow{k_2} C$

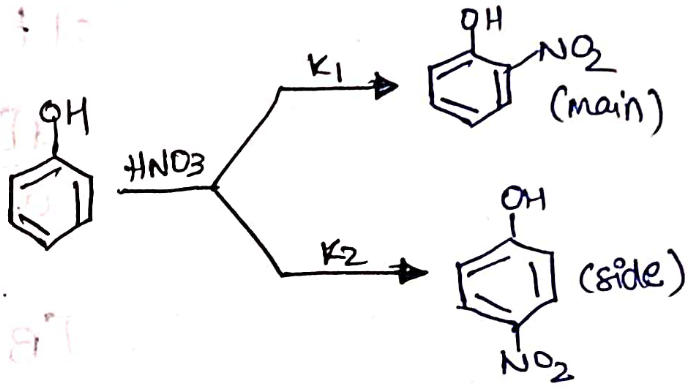
$$\frac{d[C]}{dt} = k_1[A] = k_1\left[[A]_0 - [C]\right] \Rightarrow [C] = [A]_0\left(1 - e^{-k_1 t}\right)$$

$$\frac{d[C]}{[A]_0 - [C]} = k_1\,dt$$

Kinetics of Parallel/Side/Competing Reactions:

Consider the reaction.





The differential rate expressions are.

$$\frac{d[B]}{dt} = +k_1[A] \longrightarrow ①$$

$$\frac{d[C]}{dt} = +k_2[A] \quad — ②$$

The overall reaction rate for the consumption of A can be written as:

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A]$$

$$\frac{d[A]}{dt} = -(k_1+k_2)[A]$$

$$\int_{A_0}^{A} \frac{d[A]}{[A]} = -\int (k_1+k_2)\,dt$$

Integrating both side

$$\ln\frac{[A]}{[A_0]} = -(k_1+k_2)t$$

$$\Rightarrow \boxed{[A] = [A]_0 e^{-(k_1+k_2)t}} \longrightarrow ③$$

use ③ in ①

$$\frac{d[B]}{dt} = k_1[A]$$

$$\frac{d[B]}{dt} = k_1 [A]_0\, e^{-(k_1+k_2)t}$$

$$[B] = \frac{-k_1}{k_1+k_2}[A]_0 \left[e^{-(k_1+k_2)t} \right) + c_1$$

at $t=0$ $[B]=0$,

Therefore,

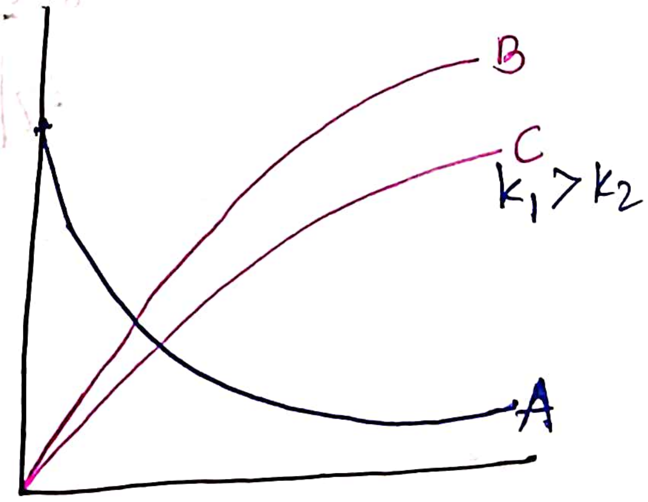
$$C_1 = \frac{k_1[A]_0}{k_1+k_2}$$

$$[B] = \frac{k_1 [A]_0}{k_1+k_2}\left[1-e^{-(k_1+k_2)t}\right]$$

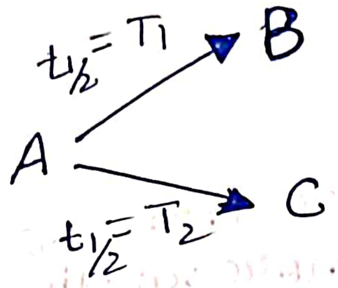
Similarly,

$$[C] = \frac{k_2 [A]_0}{k_1+k_2}\left(1-e^{-(k_1+k_2)t}\right)$$

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$



Effective Half-Life :



For 1st order rxn, $t_{1/2} = \frac{\ln 2}{k}$

$$T_1 = \frac{\ln 2}{K_1}$$

$$T_2 = \frac{\ln 2}{K_2}$$

Therefore, effective half-life

$$T_{eff} = \frac{\ln 2}{K_{eff}}$$

$$K_{eff} = \frac{\ln 2}{T_{eff}}$$

$$k_{eff} = K_1 + K_2$$

$$\frac{\ln 2}{T_{eff}} = \frac{\ln 2}{T_1} + \frac{\ln 2}{T_2}$$

$$\Rightarrow \boxed{\frac{1}{T_{eff}} = \frac{1}{T_1} + \frac{1}{T_2}}$$

Thermodynamics vs kinetic Control Product :-

$A \xrightarrow{K_1} B$ $\quad$ $A \xrightarrow{K_2} C$

Consider Reverse Rxn

$B \xrightarrow{K_{-1}} A$ $\quad$ $C \xrightarrow{K_{-2}} A$

$B \leftrightarrow C$

at eqm $\frac{K_1}{K_2} = \left\{ \frac{[B]/[A]}{[C]/[A]} \right\} = \frac{[B]}{[C]}$

Thermodynamic control
K = eqm Const

When any reverse rxns or Interconversion of B A can be neglected

$$\frac{[C]}{[B]} = \frac{K_1}{K_2}$$

Kinetic Control
K = Rate const.

When a reaction produces more than one products the product that is formed more rapidly is called **Kinetic Product.**
And the product which is most stable is called **Thermodynamic Product.**

⇒ Reactions that produce the kinetic product as major product, are said to be **Kinetically controlled** and the reactions that produce the thermodynamic product as major product, are said to be **Thermodynamically controlled reactions**

⇒ KCP [Kinetically Controlled Product]
Depends upon the rates at which they are formed

TCP [Thermodynamically controlled Product
The relative amount of products depends on their stability.

Methods to study Kinetics of Fast Reactions

What is fast Reaction ?

Ans → The chemical reaction which completes in less than 1 ps (one pico second) [10^{-12} s] times is known as the Fast Reactions.

It is popactically impossible to measure the speed of such reactions. The reason for a very fast rate of such reaction is that no chemicals bonds are to be broken among the reactants.

→ The fast reaction possesses a high rate of reaction & they possess smaller activation energy.

eg. ionic reaction, organic substitution reaction, neutralization reactions

striking a match, burning of petrol in the car engine

example – Mg ribbon is burnt in the flame of Bunsen burners it quickly gets combusted with a noticeable spark.

$$2Mg(s) + O_2(g) \xrightarrow{\Delta} 2MgO(s)$$

example, When HCl reacts with base NaOH it forms salt & water.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

eg. ppt of AgCl formation

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

These technique includes - Flow method, Relaxation method, Flash Photolysis.

Characteristics of Fast reactions :—

- The chemical reactions in which the rate constant lies between $10^1 - 10^{11}\ s^{-1}$ are called fast reactions. They have very short half-life 10^{-1} to 10^{-15} s
- They are so fast that they occur as soon as the reactants are brought together.
- ∴ ROR is high & possess smaller activation energy.
- It is practically not possible to measure the ROR of such reaction.
- The special experimental techniques used for measuring rate constant of fast reactions include : Relaxation Methods, Flash methods, ultrasonic and Resonance techniques.

Relaxation Method :—

Relaxation methods are classified into 3 groups have based on the extent of perturbation to attain a new equilibrium. They include :

- Small perturbation method
  - eg. Temp. Jump method & Pressure Jump method
- Large perturbation Method
  - eg. shock tube method & Flash photolysis
- Periodic perturbation method
  - eg. Ultrasonic method

- In relax is disturbed (perturbed) by a rapid change in one of the possible parameters like temperature or pressure or electric field Intensity.
- the relaxation is followed by using spectrometer or conductivity meter techniques.
- The time during which the reaction gets relaxed from equilibrium is called relaxation time
- The relaxation time can be determined by T-jump method or P-jump method.

Relaxation by Temperature Jump Method (T-Jump Method):

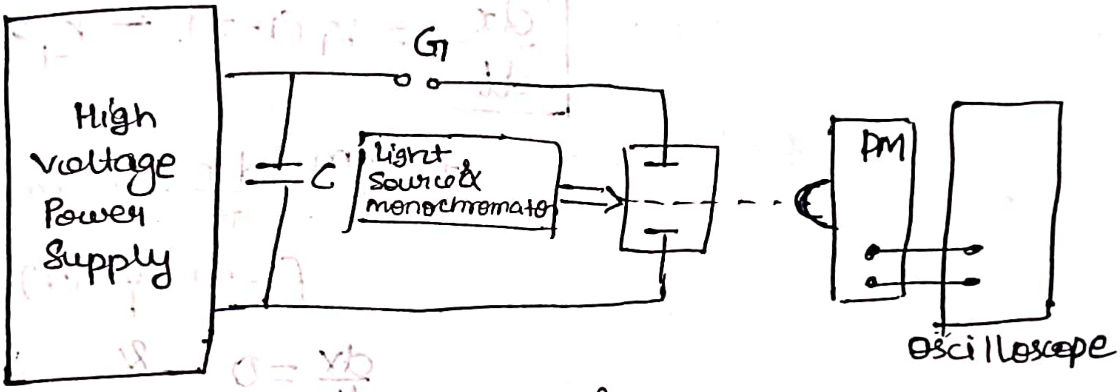


Fig. Apparatus for T-jump Method.

- In T-jump method a high voltage Power supply charges the capacitor.
- When a certain voltage is reached, the spark Gap (G) breaks down & thereby discharging the capacitor & sending a strong current through the cell containing reactive system at equilibrium.
- As the current passes, the temperature of the reactive system rises by about 10°C in few microseconds (μs). This temperature rise perturbs the system in such a way that concn of reactive species adjusts to a new equilibrium value.
- The speed with which the system approaches new equilibrium is monitored through spectrometer, in which the intensity of light leaving the cell is measured by using suitable photodetector (Photo multiplier tube - PMT)
- The output of PMT is displayed as the variation of concentration versus time on the oscilloscope screen.

Rate constant expression for Fast Reactions by T-jump Method :-

If disp from eqm is very small, rate of relaxation (restoration of equilibrium) always follows the 1st order kinetics.

$$A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$$

Let total concn of A be a & x be concn of B. at any time 't'.

$$\boxed{\frac{dx}{dt} = K_1(a-x) - K_{-1}x} \quad \text{— ①}$$

At eqm $\frac{dx}{dt} = 0$ and $x = x_0$

From eqn (1) we have

$$0 = K_1(a-x_0) - K_{-1}x_0 \quad \text{— (2)}$$

$$K_1(a-x_0) = K_{-1}x_0 \quad \text{— (3)}$$

The deviation from eqm (Δx)

$$\Delta x = x - x_0$$

$$x = \Delta x + x_0 \quad \text{— (4)}$$

$$\frac{d\Delta x}{dt} = K_1(a-x) - K_{-1}x$$

But $x = \Delta x + x_0$

$$\frac{d\Delta x}{dt} = k_1(a - \Delta x - x_0) - k_{-1}(\Delta x + x_0) \quad -(5)$$

$$\frac{d\Delta x}{dt} = k_1 a - k_1 \Delta x - k_1 x_e - k_{-1}\Delta x - k_{-1} x_e$$

$$\frac{d\Delta x}{dt} = k_1(a - x_e) - k_1\Delta x - k_{-1}\Delta x - k_{-1} x_e$$

$$\frac{d\Delta x}{dt} = \cancel{k_1(a - x_e)} - k_1\Delta x - k_{-1}\Delta x \cancel{- k_{-1} x_e}$$

$$k_1(a - x_0) = k_{-1} x_0$$

$$\frac{d\Delta x}{dt} = -\Delta x\,[k_1 + k_{-1}]$$

$$\frac{d\Delta x}{\Delta x} = -(k_1 + k_{-1})\,dt$$

where, $k_r = [k_1 + k_{-1}]$ is known as relaxation constant

The reciprocal of relaxation constant is known as relaxation time (τ^*)

$$\tau^* = \frac{1}{k_r} = \frac{1}{[k_1 + k_{-1}]}$$

$$\frac{d(\Delta x)}{\Delta x} = -k_r\,dt \quad — 8$$

Integrating both side

$$\int_{\Delta x = \Delta x_0}^{\Delta x = \Delta x} \frac{d(\Delta x)}{\Delta x} = -k_r \int_{t=0}^{t} dt$$

$$\ln\frac{\Delta x}{\Delta x_0} = -k_r t$$

$$\ln \frac{\Delta x}{\Delta x_0} = -k_r t$$

$$\frac{\Delta x}{\Delta x_0} = e^{-k_r t}$$

$$\boxed{\Delta x = \Delta x_0 e^{-k_r t}}$$

$$k_r = k_1 + k_{-1}$$

Q. The relaxation time for fast reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ is 10 μs & the eqm constant is 1×10^{-3} Calculate the rate constant for forward & reversible reaction

Sol^n $\tau^* = \frac{1}{k_1 + k_{-1}} = 10\,\mu s = 10 \times 10^{-6} s$

$\tau^* = 10^{-5} s$

Since $k_1 >>> k_{-1}$

$\therefore \tau^* = \frac{1}{k_1}$

$10^{-5} = \frac{1}{k_1}$

$k_1 = 10^{5} s^{-1}$

$$K = \frac{k_1}{k_{-1}}$$

$$K_1 = K \times K^{-1} = 10^{5} \times 10^{-3}$$

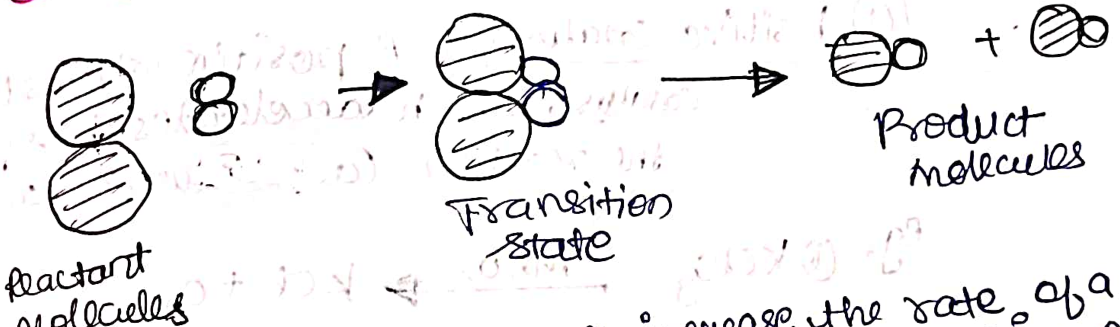
$k_1 = 10^{2} s^{-1}$

Catalysis

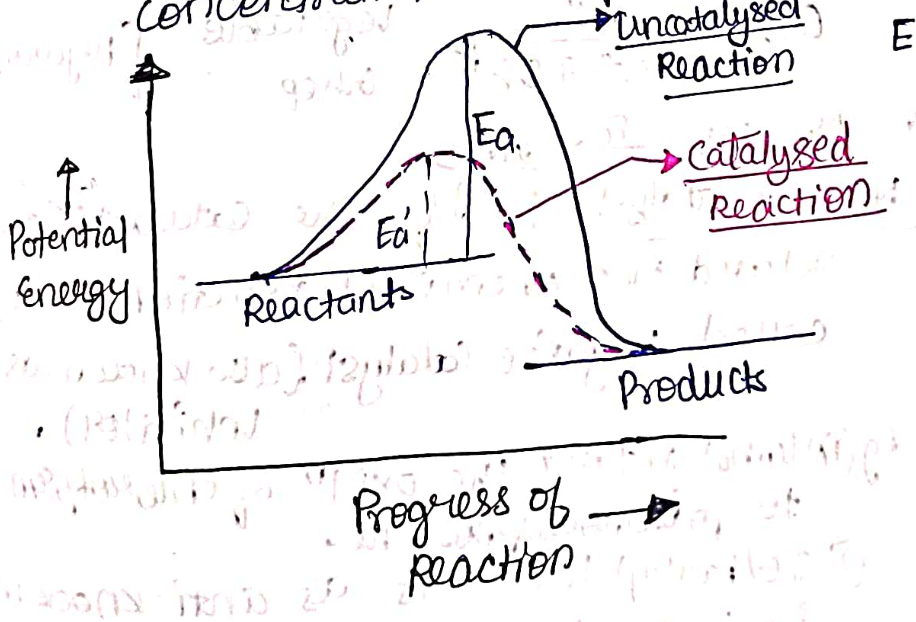
Catalyst

Catalyst is defined as a substance, small quantity of which alter (increase or decrease) the velocity of a chemical reaction by it's mere presence, without itself undergoing any change in mass & composition at the end of the reaction

The phenomenon of altering the velocity of achemical reaction by the presence of a catalyst is called Catalysis.



We can employ catalyst for increase the rate of a reaction: b'coz catalyst can provide alternative pathway with low activation energy, so more reactant molecules can cross the activation energy barrier at given concentration & temperature.



E_T : Threshold energy of the uncatalysed Rxn

E_T' : Threshold energy of the catalysed Rxn

E_R : Energy of the Reactant

E_P : Energy of the Product.

Advantages of using catalyst instead of using high temperature to promote a chemical reaction :-

→ a) Better to control of the reaction

b) Low energy cost due to lower temperature (more economical).

c) Fewer side reactions thereby providing higher yield of the desired product.

Types of Catalyst :-

(a) **Positive Catalyst** : A positive catalyst is a catalyst which accelerates the speed of the reaction (also known as accelerator)

eg. ① $KClO_3 \xrightarrow{MnO_2} KCl + O_2$

(ii) Contact Process

$$SO_2(g) + O_2(g) \xrightarrow[\text{or } V_2O_5]{\text{Platinum Black}} SO_3$$

(iii) $Oil \xrightarrow[(150°-300°C)]{Ni}$ Vegetable Ghee [Hydrogenation]

(iv) $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$.

(b) **Negative Catalyst** : If the catalytic substance retard the chemical reaction, it is called negative catalyst (also known as inhibitor).

eg (i) Alcohol retard the oxid^n of chloroform to poisonous phosgene.

(ii) Tetraethyl lead acts as anti-knock material in internal combustion engine

$CHCl_3 \xrightarrow{OH^-} CoCl_3$

$2H_2 + O_2 \xrightarrow{CO} 2H_2O$

aracteristics of catalyst :-

1. Catalyst remains unchanged in mass & composition at the end of the reaction though a change in physical state, color etc may occur.

2. A small amount of catalyst is sufficient to bring an appreciable change in the velocity of the reaction. (↑es in surface area of catalyst ↑ rate of rxn)

3. A catalyst can exert a selective action like a key can open a particular lock. Some catalysts are very specific in respect of reaction and change of catalyst may divert the path of same reaction to diff. Pdt.

eg. $CO + H_2 \xrightarrow[400°C]{ZnO + Cr_2O_3} CH_3OH$

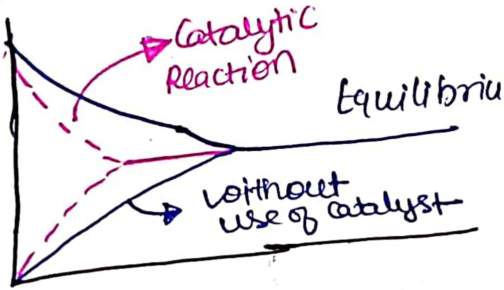
(water gas) $\xrightarrow[400°C]{Ni} CH_4 + H_2O$

eg. $HCOOH \xrightarrow{Al_2O_3 \text{ or } TiO_2} H_2O + CO$

$\xrightarrow{Cu \text{ or } ZnO} H_2 + CO_2$

enzymes also have specific catalytic activity.

4. A catalyst can only alter the speed of the reaction but does not affect the final state of eqm since it alters the rate of the forward as well as backward reaction to the same extent, thereby the composition of eqm remains same.



5. According to ostowald, the catalyst cannot initiate the reaction but can only decrease or increase its rate.

6. A catalyst is most active at a particular temperature, called optimum temperature.

7. The addition of a small amount of foreign substances which are not themselves catalytically active, sometimes increase the catalytic activity of the catalyst. Such substances which catalyze the catalyst are called promoters.

eg. $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$

Molybdenum
or mix of alumina, Al_2O_3 & K_2O
→ Promoter.

Properties of Promoters are

(i) selectively enhancement of the reactions
(ii) Increase catalyst lifetime.

8. The activity of catalyst is inhibited or complety destroyed by the presence of even minute traces of certain substances called catalystic poison or anti-catalyst.

eg. In manufacture of H_2SO_4 by contact process a trace of As_2O_3 destroys the catalytic activity & efficiency of spongy platinum.

Types of catalysis (homogeneous, heterogeneous & auto catalysis)

(A) Homogeneous Catalysis

Reactants & catalyst is present in the same phase (i.e. in gas phase or liq phase)

eg. $2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2$

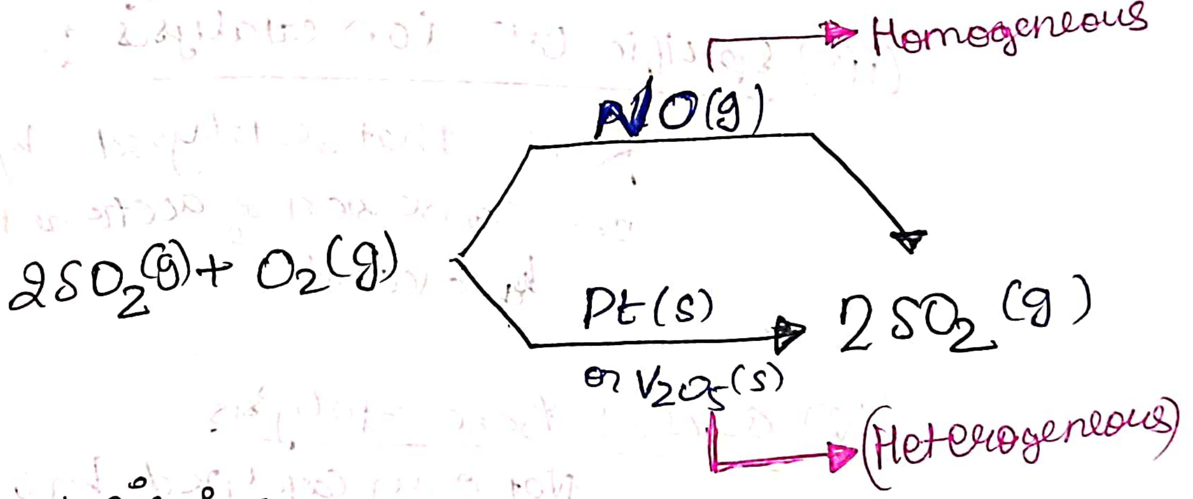
$H_2(g) + Cl_2(g) \xrightarrow{N_2O(g)} 2HCl(g$

$C_{12}H_{22}O_{11}(aq) + \underset{(l)}{H_2O} \xrightarrow{H_3O^+(aq)} \underset{Glucose}{C_6H_{12}O_6} + \underset{fructose}{C_6H_{12}O_6}$

(B) Heterogeneous Catalysis

Reactants & catalyst is present in the different phase, (Rxn proceeds at an interface b/w two discrete phases)

eg. $N_2(g) + 3H_2(g) \xrightarrow[Mo]{Fe_2O_3(s)} 2NH_3$



Auto-catalysis :-

When a product formed in the course of the reactions enhances the velocity of the reaction (or acts as a catalyst) the phenomenon is called catalysis.

In other word, if one of the product of a reaction is capable of catalyzing the same reaction in which it is produced this is called autocatalysis.

$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH.$

Acid-base catalysis :-

It is an example of homogeneous catalysis which is catalysed by Bronsted acid or base or both..

(i) Specific proton catalyzed rxn (H^+ ion catalysis):

A rxn which is catalyzed by H^+ or H_3O^+ ions
eg. solvolysis of esters, inversion of cane sugar
keto-enol tautomerism.

The term specific acid catalysis is used when the rxn rate is dependent on the eqm for protonation of the reactant & is governed by the concentration of H^+ ion, not other Bronsted acids.

(ii) General Acid catalysis :-

These are the rxns which are not only catalsed by H^+ ions but also acids including water.
eg. Iodination of acetone.

(iii) Specific OH^- ion catalysis :-

Rxn that is catalyzed by OH^- ion only
eg. conversion of acetone to diacetone ~~by~~ alcohol.

(IV) General Base catalysis

Not only catalyzed by OH^- but also by other bases. eg OAc^-

(V) Rxns that are catalysed by both H^+ & OH^- ions. Hydrolysis of ester.

Kinetics of Acid Catalyzed Reaction:—

Mechanism → organic, Biology

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ \xrightarrow{k_2} P + HA.$$

$$\frac{d[P]}{dt} = k_2[SH^+]$$ → Reaction Intermediate

applying (Steady state approximation) for SH^+

$$\frac{d[SH^+]}{dt} = 0 \Rightarrow \text{Rate of formation of } SH^+ = \text{Rate of consumption of } SH^+.$$

$$\Rightarrow k_1[S][AH^+] = k_{-1}[A^-][SH^+] + k_2[SH^+]$$

Solving for $[SH^+]$

$$[SH^+](k_{-1}[A^-] + k_2) = k_1[S][AH^+]$$

$$\boxed{[SH^+] = \frac{k_1[S][AH^+]}{k_{-1}[A]+k_2}}$$

Rate of formation of Product is given by,

$$\frac{d[P]}{dt} = k_2[SH^+]$$

$$\Rightarrow \frac{d[P]}{dt} = \frac{k_1k_2[S][AH^+]}{k_{-1}[A] + k_2}$$

$$\frac{dP}{dt} = \frac{K_1 K_2 [S][AH^+]}{K_{-1}[A] + K_2}$$

Case - I If $K_2 >> K_{-1}[A]$

So there will be a small amt of [SH

$$S + AH^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} SH^+ \xrightarrow{K_2} P$$

$$\frac{d[P]}{dt} = \frac{K_1 \cancel{K_2} [S][AH^+]}{\cancel{K_2}}$$

$$\boxed{\frac{d[P]}{dt} = K_1 [S][AH^+]}$$

** Rate $\propto [AH^+]$

General acid catalysis

Case - II If $K_2 << K_{-1}[A]$

SH^+ may be considered to be in eqm with reactant

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[A^-] = \frac{K_a [AH^+]}{[H^+]}$$

$$\frac{d[P]}{dt} = \frac{K_1 K_2 [S][AH^+]}{K_{-1}[A]}$$

$$\frac{d[P]}{dt} = \frac{K_1 K_2 [S]\cancel{[AH^+]}[H^+]}{K_{-1} K_a \cancel{[AH^+]}}$$

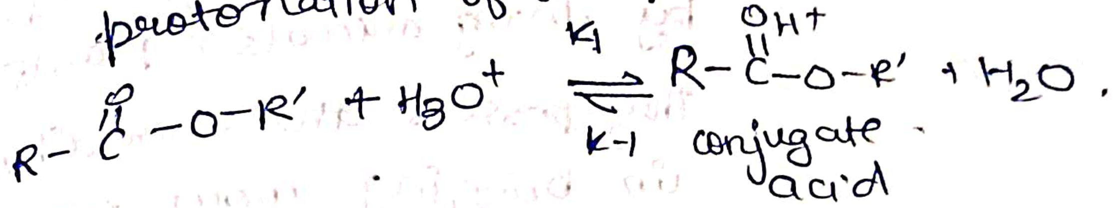
$$\boxed{\frac{d[P]}{dt} = K' [S][H^+]}$$

** Rate $\propto [H^+]$

Specific $[H^+]$ catalysis

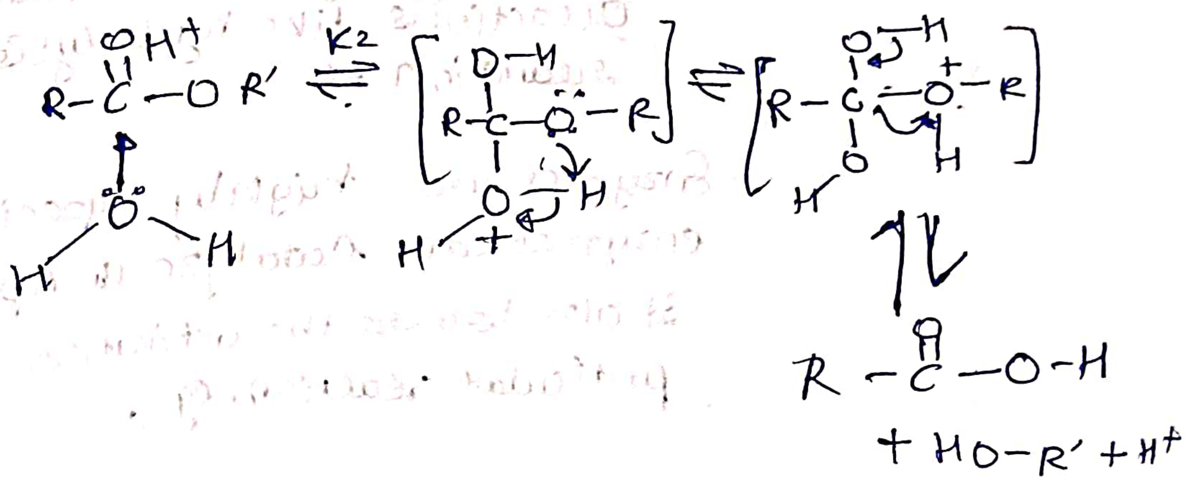
9. Hydrolysis of esters :-

↳ specific acid catalyzed rxn when the rxn rate is dependent on eqm for protonation of rxn.



$$R-\overset{O}{\overset{||}{C}}-O-R' + H_3O^+ \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} R-\overset{OH^+}{\overset{||}{C}}-O-R' + H_2O.$$

conjugate acid



$$Rate = K_2 [SH^+]$$

$$[SH^+] = \frac{K_1 K_2 [RCOOR][H^+]}{K_{-1} + K_2}$$

Enzymes (or biological catalyst) :-

Enzymes are highly complex, non-living nitrogeneous organic substances produced by living animals & plants.

They possess the incredible capacity in bringing about many complex reactions like hydrolysis, oxidation, reduction etc.

Enzymes are highly specific & each enzymes can catalyze a specific reaction. It also lowers the activation energy for a particular reaction. eg.

eg ① $$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastage}} \underset{\text{maltose}}{n(C_{12}H_{22}O_{11})}$$

② $$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zyamase}} 2C_2H_5OH + 2CO_2$$

③ $$NH_2CONH_2 + 2H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

④ $$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Ptaylin}} \underset{\text{Glucose}}{n(C_6H_{12}O_6)}$$

haracteristics of Enzymes :-

i) Enzymes are protein that can acts as enormously effective catalyst & can speed up the reaction by high factors of upto 10^{12}.

ii) They are highly specific & each enzymes catalyze a particular reaction. (Key & Lock)

iii) Enzymes are highly temp sensative. All enzymes reaction exhibits maximum efficiency at optimum temperature. Above this temperature the enzyme gets denatured, thereby losing its activity.

optimum temp : 288K ↔ 298K.
(15°C) ↔ (25°C)

For most enzymes the rxn rates increases upto 45°C and above 45°C thermal denaturation takes place. Above 55°C rapid denaturation destroys completely the catalytic activity of the enzyme protein.

iv) Enzyme catalyzed rxns are much more sensative to catalytic poison such as HCN, CS_2, H_2S etc. the inhibitors (or poisons) interact with the fn gp present on enzyme surface & often reduce or completely destroy the catalytic activity of the enzyme.

v) Activity of enzymes depends upon certain non-protein substances called co-enzymes.

vi) Enzymes loose their activity when exposed to UV radiation or in the presence of electrolyte

vii) The effect of PH on the rate of enzyme catalysed reaction is of complex nature. Usually the rate possess through a maximum as the pH increased (PH 5-7)

viii) Enzyme does not disturb the final state of eqm.

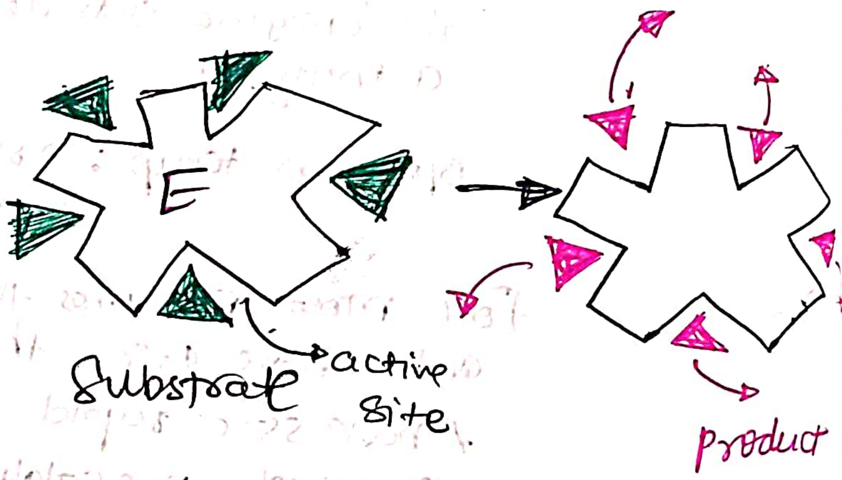
Mechanism & kinetic of enzyme catalysed reaction:-

L. Michaelis & Mary Menten proposed a mechanism for the kinetics of enzyme catalysed rxns which involves the following steps :-

Enzyme
↓
Complex Protein molecule

$$E + S \underset{K_1}{\overset{K_1}{\rightleftharpoons}} \boxed{ES}$$ Intermedia (fast)

$$ES \xrightarrow{K_2} P + E$$ (slow)



$$E_0 = \underset{\substack{\uparrow \\ \text{free enzyme}}}{E} + ES \Rightarrow E = E_0 - ES$$

(E available at that moment)

$$\frac{d[P]}{dt} = K_2 \underset{\substack{\downarrow \\ R.I \rightarrow \boxed{S.S.A}}}{[ES]}$$

$$\frac{d[ES]}{dt} = 0$$

$\frac{d[ES]}{dt} = 0$ ⇒ formation of [ES] = Decomposition of [ES]

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

$k_1[E][S] = +(k_{-1}+k_2)[ES]$

$k_1[E_0 - ES][S] = (k_{-1}+k_2)[ES]$

$k_1[E_0][S] - k_1[ES][S] = (k_{-1}+k_2)[ES]$

$k_1[ES][S] + (k_{-1}+k_2)[ES] = k_1[E_0][ES]$

$(k_1[S] + (k_{-1}+k_2))[ES] = k_1[E_0][S]$

$$\boxed{[ES] = \frac{k_1[E_0][S]}{k_1[S]+k_{-1}+k_2}}$$

$\Rightarrow \text{Rate} = \frac{d[P]}{dt} = k_2[ES]$

$\text{Rate} = \frac{d[P]}{dt} = \frac{k_1 k_2 [E_0][S]}{k_1[S]+(k_{-1}+k_2)}$

$\text{Rate} = \frac{k_2[E_0][S]}{[S]+\frac{(k_{-1}+k_2)}{k_1}}$

$K_m = \frac{k_{-1}+k_2}{k_1}$ → Michaelis constant

Men

$$\boxed{\text{Rate} = \frac{k_2[E_0][S]}{K_m+[S]}}$$

→ Michaelis-Menten Eqn

[S] → high

$[S] >> K_m$

$\text{Rate} = \frac{k_2[E_0]\cancel{[S]}}{\cancel{[S]}}$

$$\boxed{\text{Rate} = k_2[E_0]}$$

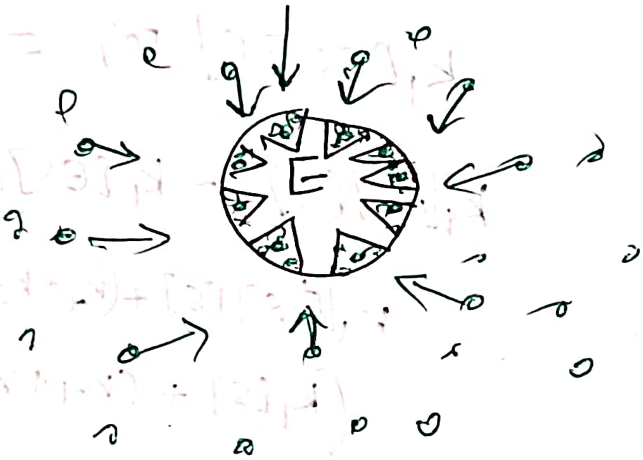
Rate = constant
zero order

[S] → Low

$$\text{Rate} = \frac{K_2 [E_0][S]}{K_m}$$

$$\text{Rate} \propto [S]^1$$

1st order

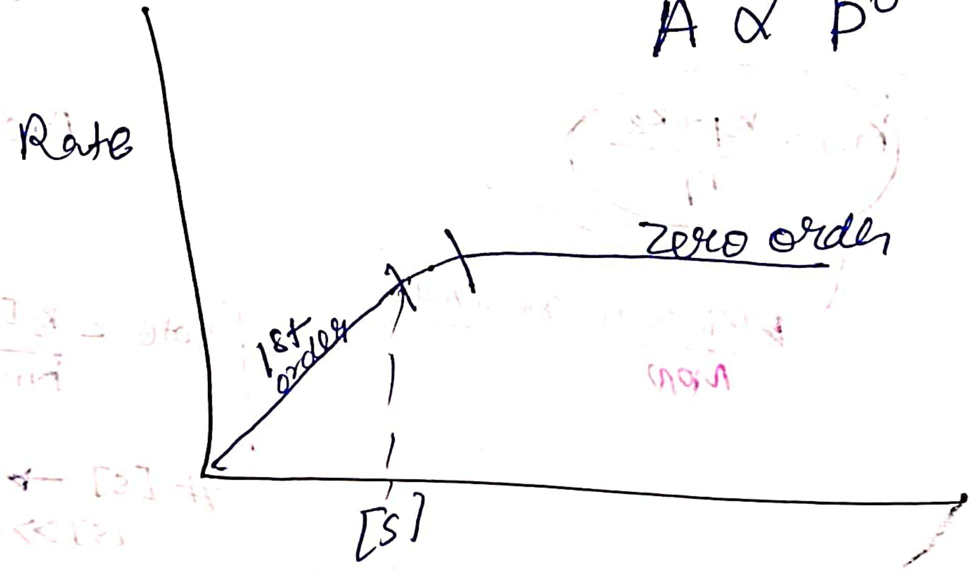


⇌ Adsorption

$A \propto P$

↓

$A \propto P^0$



when all the enzymes has reacted with the substrate at high concn, the rate of rxn will be maxm.

under this condn, no free enzyme will be remain

& hence,

$$[E_0] = [ES]$$

max Rate = $V_{max} = K_2 [ES] = K_2 [E_0]$

K_2 → turn over number of enzyme

⇓

No. of molecules converted in unit time by one molecule of enzyme.

Range : 100 - 1000 s^{-1} but can be $10^5 - 10^6 s^{-1}$

$$\boxed{\text{Rate} = \frac{V_{max}[S]}{K_m + [S]}}$$

Case-I if $K_m \gg [S]$

$$\text{Rate} = \frac{V_{max}[S]}{K_m} = k'[S]$$

(1st order rxn)

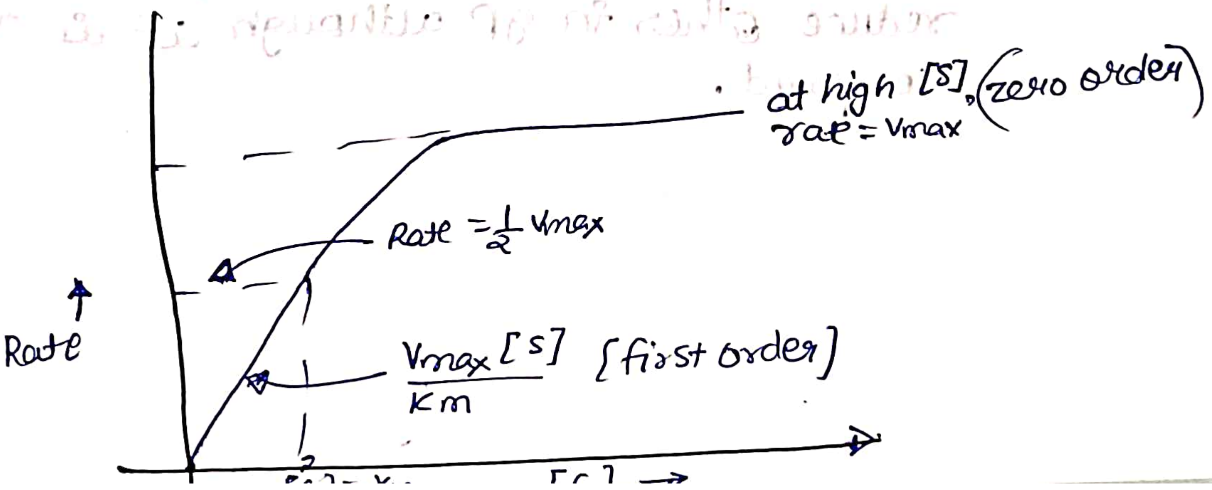
Case-II if $K_m \ll [S]$

$$\text{Rate} = \frac{V_{max}[S]}{[S]} = V_{max} = \text{constant}$$

(zero order)

Case-III if $K_m = [S]$

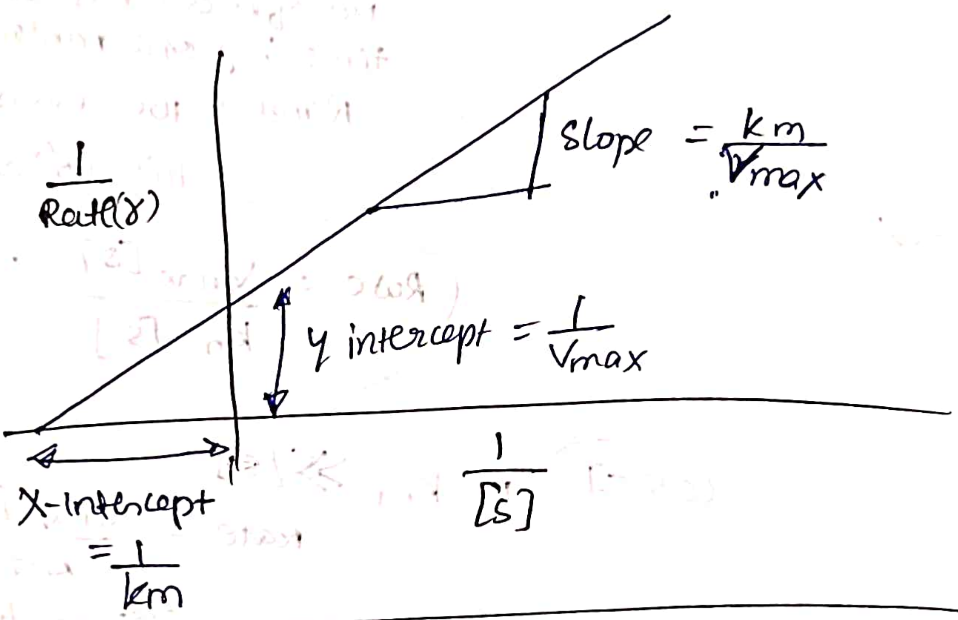
$$\text{Rate} = \frac{V_{max}[S]}{[S]+[S]} = \frac{V_{max}}{2}$$



Lineweaver - Burk method

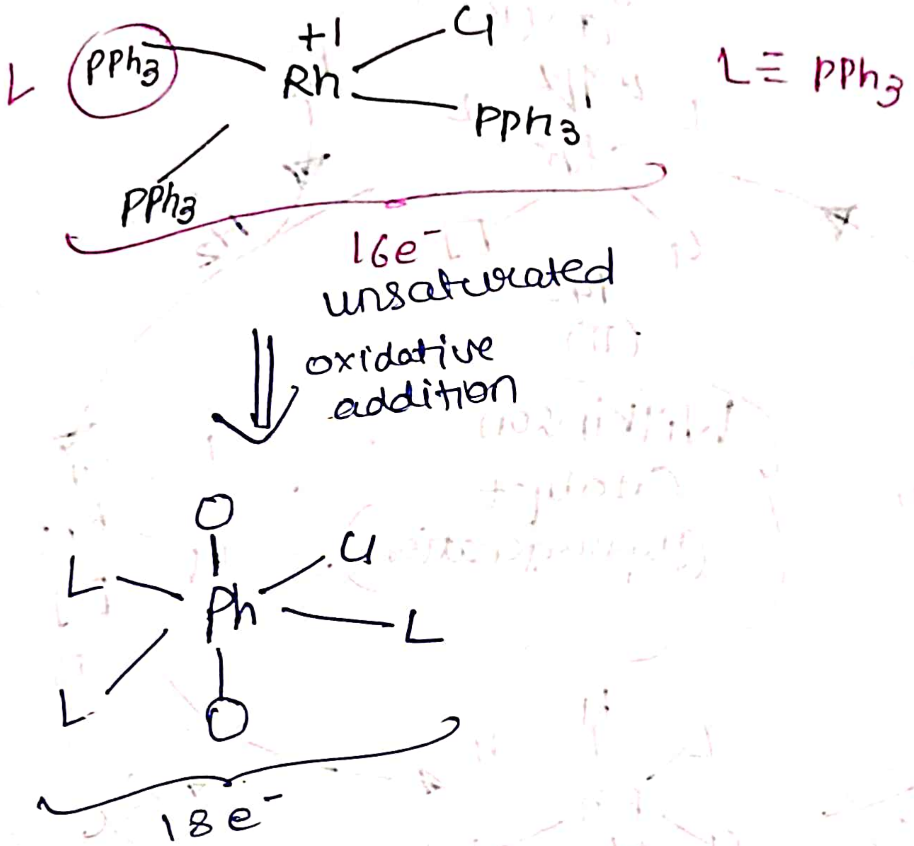
It is rather difficult to determine Vmax & (hence Km) directly from plot of rate vs [S]
It is possible by rearranging Michaelis-Menten eqn

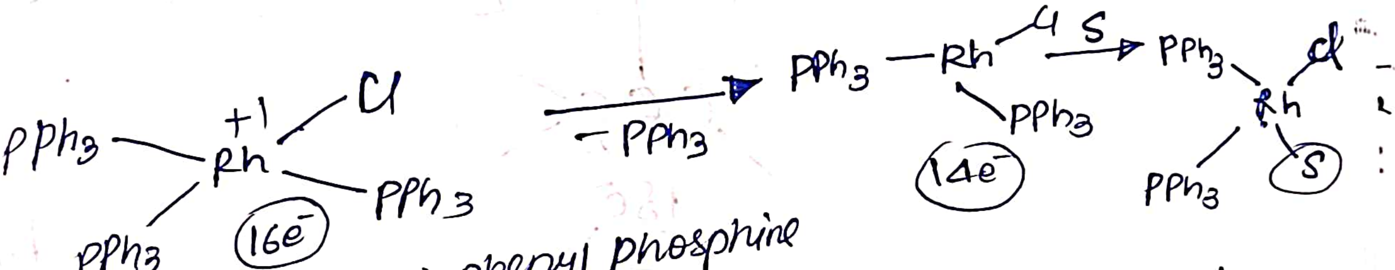
$$\frac{1}{Rate(r)} = \frac{Km + [S]}{Vm[S]} = \frac{Km}{Vmax[S]} + \frac{1}{Vmax}$$



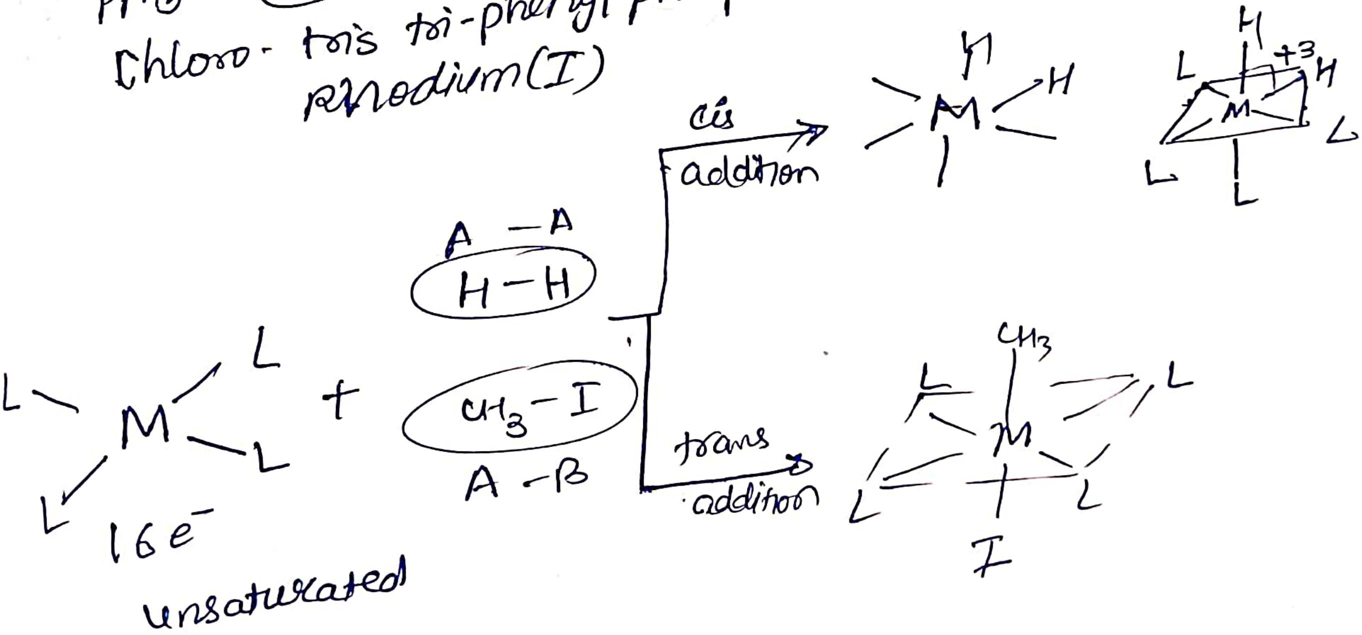
Hydrogenation reaction by Wilkinson's Catalyst $[PPh_3)_3 RhCl$

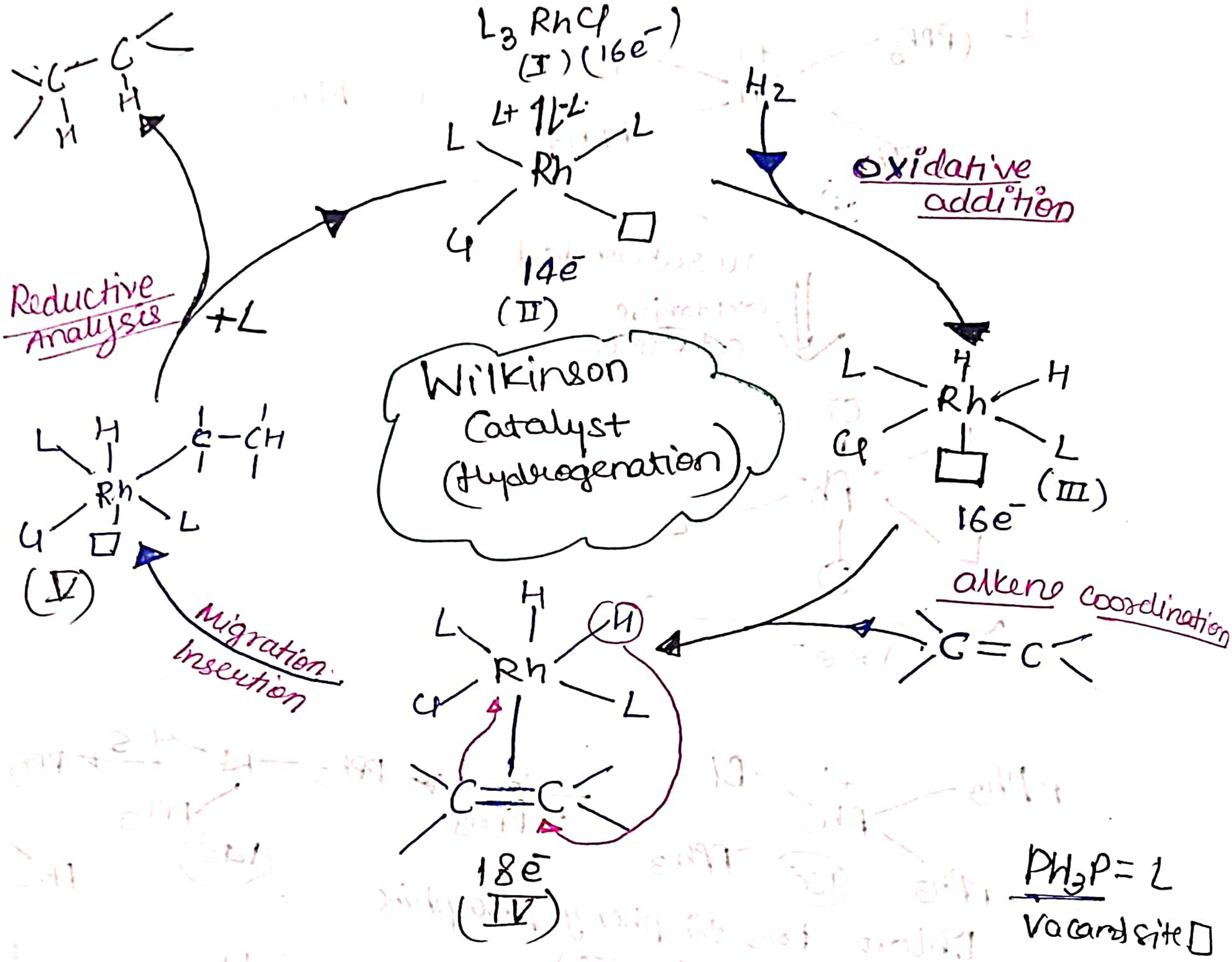
Tris-Triphenyl phosphine Rhodium Chloride $[(PPh_3)_3 RhCl]$ which is generally known as Wilkinson's catalyst acts as a homogeneous catalyst for the hydrogenation of alkenes & alkynes. The catalyst is not able to reduce other fn gp although it is very reactive compound.





Chloro- tris tri-phenyl phosphine rhodium(I)




L3RhCl
(I) (16e-)
L+ 1L-L
L
Rh
L
Cl
□
14e-
(II)
H2
oxidative addition
L
H
Rh
H
Cl
L
□
16e-
(III)
alkene coordination
C=C
H
L
Rh
H
Cl
L
C=C
18e-
(IV)
Migration Insertion
L
H
Rh
C-CH
Cl
□
L
(V)
Reductive Analysis
+L
C-C
H
H
Wilkinson
Catalyst
(Hydrogenation)
PH3P= L
Vacand site □

Phase Transfer Catalyst (PTC)

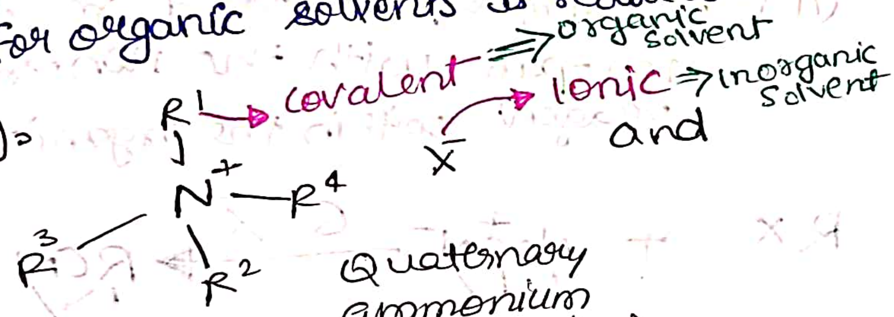
- It is type of catalyst which is generally used in a reaction in which one substance change there phase or we can say that one substance moves from one phase to another phase.

- The main role of this type of catalyst are to facilitate the migration of reactant from one phase to another.

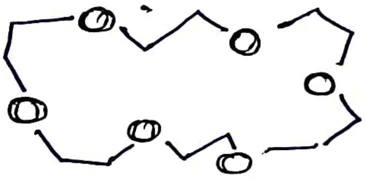
- The phase ~~ta~~ transfer catalysis (PTC) is a special form of heterogeneous catalysis

- Phase transfer catalysts are especially useful in green chemistry - by allowing the use of water, the need for organic solvents is reduced.

eg.



and



crown ether

Quaternary ammonium salts (Q^+X^-)

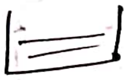
Example -

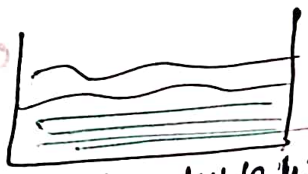
$$CH_3-(CH_2)_6-CH_2-Br + NaCN \xrightarrow[\left[Q^+X^-\right]]{PTC} CH_3-(CH_2)_6-CH_2-CN + NaBr$$

(Nonane-Nitrile)

1-Bromo octane ↓ Soluble in benzene

Sodium cyanide solid ↓ H_2O





organic solvent & inorganic solvent are not soluble with each other

organic solvent → Non-polar

inorganic solvent → Polar

(Like dissolve Like)

Types of Phase Transfer Catalyst

a. There are many phase Transfer Catalyst

b. such as Quaternary ammonium salt, phosphonium salt crown ether & Cryptand,

Mechanism of PTC

Fundamental processes :-

(i) Transfer of one reagent from its normal phase to the phase of other reagent.

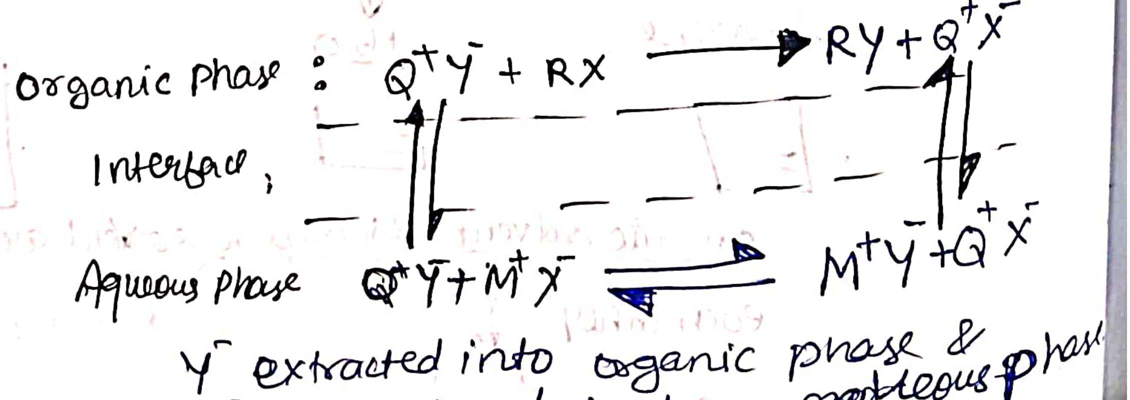
(ii) reaction of transferred reagent or ion-pair with the non-transferred reagent within the organic layer

$$RX + M^+Y^- \xrightarrow{Q^+X^-} RY + MX$$

eg. $$RCl + NaCN \xrightarrow{Q^+X^-} RCN + NaCl$$

RCl (Alkyl halide soluble in organic solvent, but insoluble in water)

NaCN (Inorganic salt soluble in water but insoluble in organic solvent)



Y^- extracted into organic phase & X^- is transferred back to aqueous phase

Applications of phase-Transfer catalyst :-

① PTC are not only used in organic chemistry but also a a broadly useful tool in several other areas of chemistry . ie. IOC, electrochemistry, photochemistry, heterocyclic chemistry, industrial chemistry, medicinal chemistry & especially polymer chemistry

(II) PTC can be used for synthesis process for ~~the~~ chemicals manufacturing

(III) PTC have great role in green chemistry.

* * *