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Engineering Chemistry-I (BS-109)

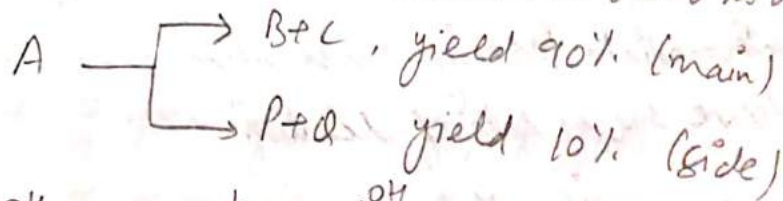
# Chemical Kinetics

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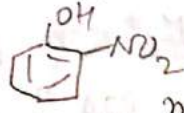
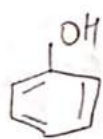
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→ Parallel reactions: Reactions undergo two or more independent reactions simultaneously. Each reaction gives a set of products. The reaction which gives major product is the main reaction & other is a side reaction.

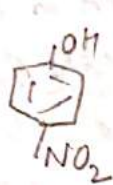


eg.



major

$\frac{dx}{dt} = k_1 [A]$



minor

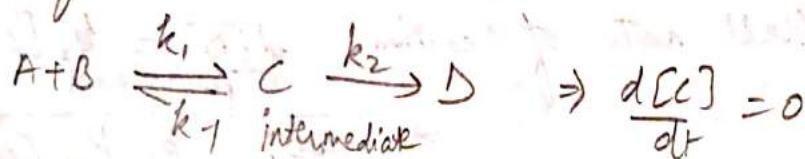
$\frac{dy}{dt} = k_2 [A]$

• Steady-state approximations: (SSA)

$(k_1 \neq k_2)$

→ It is used to estimate the overall reaction rate of a multi-step reaction wherein it assumes the rate of change of intermediate concentration as const.

→ It applies to the consecutive reactions with a slow first step and a fast second step ( $k_1 \ll k_2$ ) so that there is no accumulation of intermediate i.e. it is transformed into products as soon as it is formed.



Rate of react<sup>n</sup> W.R.T.C  $\Rightarrow \frac{d[C]}{dt} = k_1 [A][B] - k_{-1} [C] - k_2 [C] = 0$

$$\Rightarrow k_1 [A][B] = (k_{-1} + k_2) [C]$$

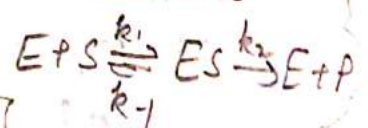
$$\Rightarrow [C] = \frac{k_1 [A][B]}{(k_{-1} + k_2)}$$

overall rate of react<sup>n</sup>:

$$\frac{d[D]}{dt} = k_2 [C]$$

$$\Rightarrow \boxed{\frac{d[D]}{dt} = \frac{k_1 k_2 [A][B]}{(k_{-1} + k_2)}}$$

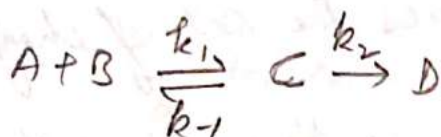
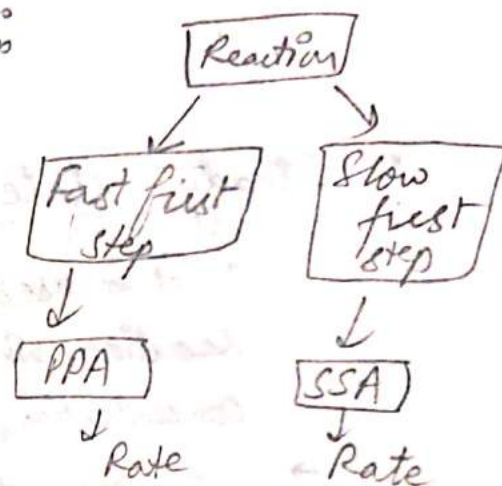
eg. in enzyme-catalyzed reactions





• Pre-equilibrium approximation: (PEA)

- Both steady state and pre-equilibrium approximations apply to intermediate forming consecutive reactions. They are used to solve for a rate of reaction.
- However, unlike the SSA, PEA requires the first step to be faster. This means PPA is an alternative method to solve the rate of reaction and is used under diff. cond<sup>n</sup>s than SSA
- In PPA, the reactants and intermediate are in eq<sup>m</sup>,  $\leq$  may not be necessary in SSA.



$$K_{eq} = \frac{[C]}{[A][B]} = \frac{k_1}{k_{-1}}$$

$$\Rightarrow [C] = \frac{k_1}{k_{-1}} [A][B]$$

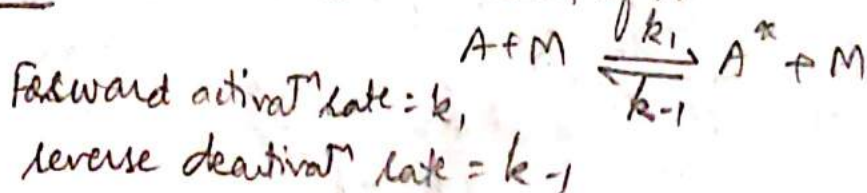
overall rate of reaction,  $\frac{d[D]}{dt} = k_2 [C] = k_2 \frac{k_1}{k_{-1}} [A][B]$

$$\Rightarrow \boxed{\frac{d[D]}{dt} = k_2 \cdot K_{eq} [A][B]}$$

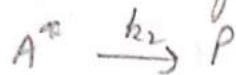
• Lindemann Theory:

- This theory forms the basis for all modern theories to explain successfully the observed first-order kinetics of many unimol. react<sup>n</sup>
- Proposed mechanism: For a react<sup>n</sup>  $A + M \rightarrow P$ , consists of 2 elementary steps:

Step-I: Bimolecular activation of A



Step 2: Unimolecular reaction of  $A^*$



Now,  $A^*$  is an energised molecule having sufficient vib<sup>l</sup> energy to form products

$$\text{rate of form<sup>n</sup> of } A^* = k_1 [A][M]$$

$$\text{rate of decomposition of } A^* = k_2 [A^*] + k_{-1} [A^*][M]$$

applying SSA,

$$\text{rate of change of conc of } A^* = \frac{d[A^*]}{dt} = \text{Rate of form<sup>n</sup> of } A^* - \text{rate of decomposition of } A^* = 0$$

$$0 = k_1 [A][M] - k_2 [A^*] - k_{-1} [A^*][M]$$

$$\Rightarrow k_1 [A][M] = (k_2 + k_{-1}[M]) [A^*]$$

$$\Rightarrow [A^*] = \frac{k_1 [A][M]}{k_2 + k_{-1}[M]}$$

$$\text{overall rate of react<sup>n</sup>} = \frac{d[P]}{dt} = k_2 [A^*]$$

$$\Rightarrow \boxed{\frac{d[P]}{dt} = \frac{k_1 k_2 [A][M]}{k_2 + k_{-1}[M]}}$$

Experimental findings:

Case I: at high pressure,  $k_{-1}[M] \gg k_2 \Rightarrow$  collisional deactivation of  $A^*$  is more likely

$$r = \frac{k_1 k_2}{k_{-1}} [A] \Rightarrow \text{first order reaction}$$

Case II: at low pressure,  $k_{-1}[M] \ll k_2$

$$r = k_1 [A][M] \Rightarrow \text{second order reaction}$$

Limitation:

- The bimolecular step takes no account of the energy dependence of activation; the internal degrees of freedom are completely neglected, and the theory consequently underestimates the rate of activation.



• Methods for the determination of the order of reaction.

①. Substitution method (using rate equation)

1<sup>st</sup> order:  $k = \frac{1}{t} \ln \frac{a}{a-x}$

2<sup>nd</sup> order:  $k = \frac{1}{t} \frac{x}{a(a-x)}$

3<sup>rd</sup> order:  $k = \frac{1}{2t} \left[ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$

To determine rate, a definite amount ( $a$ ) of reactant is taken and with time change 't', conc. is changed by 'x', which is estimated by chemical or mechanical analysis, i.e. ( $a-x$ ) can be calculated.

By knowing the values of ' $a$ ' and ' $a-x$ ' in the above rate law equations,  $k$  can be estimated and hence order of reaction.

Drawback: Laborious & complicated method.

②. Half-life method:

1<sup>st</sup> order:  $t_{1/2} = \frac{0.693}{k}$  (fixed); 2<sup>nd</sup> order:  $t_{1/2} = 1/ak$

3<sup>rd</sup> order:  $t_{1/2} = 1/(a^2k)$

In separate sets of experiments, if diff conc. are taken and  $t_{1/2}$  are measured, then order can be easily determined.

If  $t_{1/2}$  varies inversely with the in. conc  $\Rightarrow$  react<sup>n</sup> is of 2<sup>nd</sup> order  
(plot  $t_{1/2}$  vs  $1/a$  : straight line)

If  $t_{1/2}$  vs  $1/a^2$  gives st. line  $\Rightarrow$  3<sup>rd</sup> order

③. Van't Hoff's differential method:

Let the order of reaction be ' $n$ '

for 1<sup>st</sup> set of experiment, in. conc. =  $C_1$

2<sup>nd</sup> " " " , in. conc. =  $C_2$

So, rate of reaction for two experiments will be:

$$R_1 = -\frac{dc_1}{dt} = k C_1^n$$

$$R_2 = -\frac{dc_2}{dt} = k C_2^n$$

Taking log both sides

$$\log R_1 = \log k + n \log C_1$$

$$\log R_2 = \log k + n \log C_2$$

$$n = \frac{\log R_1 - \log R_2}{\log C_1 - \log C_2}$$

⇒ Order can be determined if  $R_1$  &  $R_2$  are known

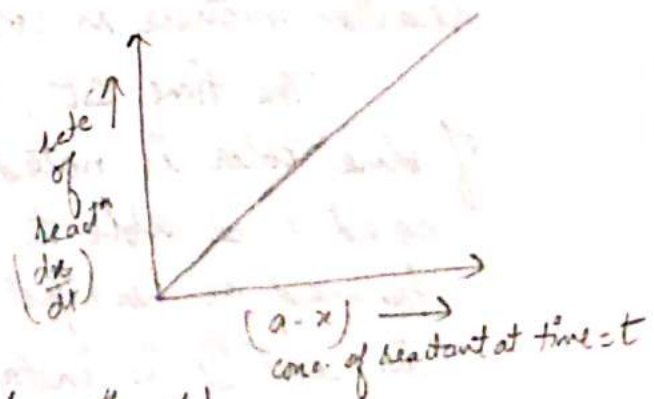
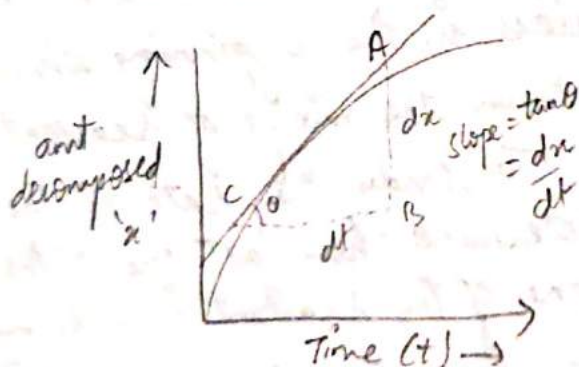
④ Graphical method:

Plotting time 't' vs 'a function of conc', we can obtain the order of react<sup>n</sup>

(a) Plot of  $\log C$  vs  $t \rightarrow$  st. line  $\Rightarrow$  1<sup>st</sup> order

(b)  $1/C$  vs  $t \rightarrow$  st. line  $\Rightarrow$  2<sup>nd</sup> order

(c)  $1/C^2$  vs  $t \rightarrow$  st. line  $\Rightarrow$  3<sup>rd</sup> order



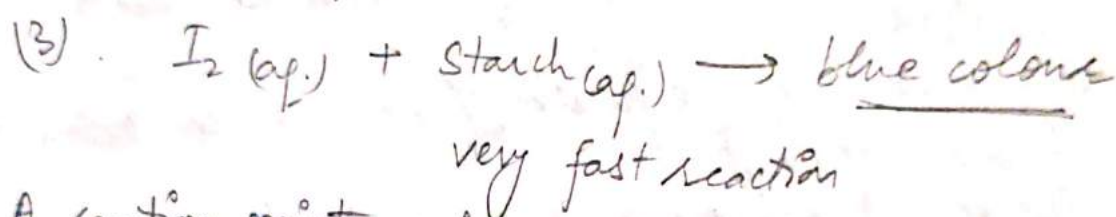
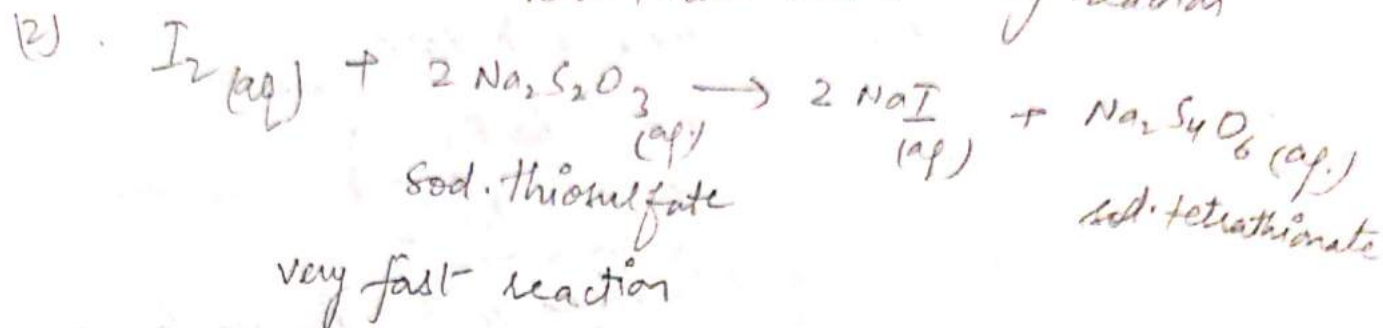
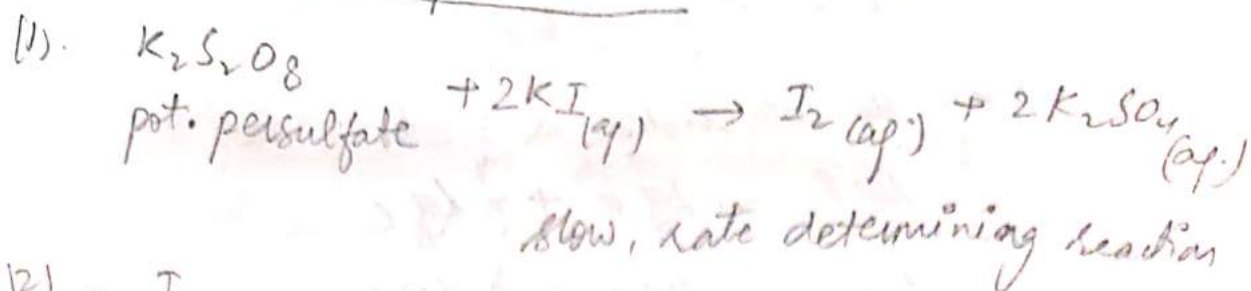
• CLOCK REACTION: (under differential method)

In case of some reactions, time taken for the colour change of the reaction mixture can be used for determining initial rate. Such self-indicating reactions are known as clock reactions.

eg -  $I_2$  clock reaction.



→ Iodine Starch complex reactions :



A reaction mixture is prepared using pot. persulfate and  $KI$  in a higher conc. and sod. thiosulfate is added in much lower conc. A drop of starch is also present in the reaction mixture. The reaction mixture is colorless in the beginning which turns blue.

The time  $\Delta t$ , between the mixing of reactants and appearance of blue color is noted. To study the rate of the react (1), we need to be able to determine how fast one of the products is formed or how fast one of the reactant is consumed.  $I_2$  liberated in react (1) is instantaneously retransformed to  $I^-$  &  $S_4O_6^{2-}$ . The blue starch iodine complex becomes visible after complete consumption of  $Na_2S_2O_3$ .

$$\text{Rate} = k [KI]^m [K_2S_2O_8]^n \Rightarrow \log(\text{rate}) = \log k + m \log [KI] + n \log [K_2S_2O_8]$$

(Vst)

→ Plot of  $\log(Vst)$  vs  $\log[KI]$  is made using  $\Delta t$  value obtained by varying  $[KI]$  and keeping  $[K_2S_2O_8]$  const. → slope of st. line gives 'm'.  
 → Sim. plot of  $\log(1/\Delta t)$  vs  $\log[K_2S_2O_8]$  by varying  $[K_2S_2O_8]$  and keeping  $[KI]$  const. gives 'n'.  
Experimentally obs. =  $m = n = 1$  → overall order = 2

In this laboratory exercise, we will measure the Rate Constant  $k$  for the oxidation of Iodide ( $\text{I}^-$ ) by Peroxysulfate ( $\text{S}_2\text{O}_8^{2-}$ ).



This reaction is referred to as a Clock Reaction because the progress of (Eq. 1) is monitored by a secondary Clocking reaction which consumes the product  $\text{I}_2$  as it is produced and triggers a color change when the Clocking Reagent is itself completely consumed. For this purpose, we use Thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) as the Clocking Reagent to reduce the  $\text{I}_2$ :



As long as any Thiosulfate Ion is present, none of the Iodine produced in (Eq. 1) remains; it is consumed as quickly as it is produced. (This, of course, requires that (Eq. 2) proceed very rapidly. This is in fact the case.) As soon as the Thiosulfate is used up, Iodine will begin to appear in the solution. The presence of Iodine is then dramatically detected by the formation of a blue Starch-Iodine molecular complex and the reaction is said to “Clock” at this point. (Actually, the starch molecules complex with  $\text{I}_3^-$  which is formed by a reaction between  $\text{I}_2$  and  $\text{I}^-$ .) We can set the Clock Point by simply adding differing amounts of Thiosulfate Ion to the solution.

The Rate at which a chemical reaction proceeds is typically influenced by the amount of each reactant present and the temperature of the reaction vessel. And, typically, this relationship between the Reaction Rate and Reagent Concentration takes a simple form known as the Rate Law:

$$\text{Rate} = k [\text{A}]^n [\text{B}]^m \quad (\text{Eq. 3})$$

where  $A$  and  $B$  are generic reacting Species,  $k$  is a reaction specific proportionality constant known as the Rate Constant, and  $n$  and  $m$  are the Reaction Order. The Rate Law parameters  $k$ ,  $n$  and  $m$  must be determined experimentally.