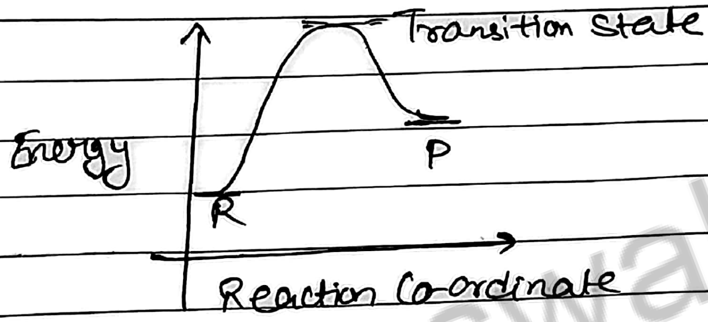
Mechanism of Reaction

On basis of Mechanism, Reactions are of two types

i) Simple Reactions / Elementary Reaction / Single step

⇒ No Reaction Intermediate

Reactant ⟶ Product



There is only one step & hence that step is rate determining step (rds)

i) Unimolecular

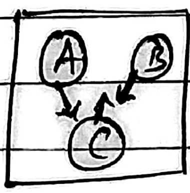
$A \longrightarrow P$

ii) Bimolecular

$A + B \longrightarrow P \qquad 2A \longrightarrow P$

iii) Trimolecular $\quad A+B+C \longrightarrow P \;|\; 3A \longrightarrow P \;|\; 2A+B \longrightarrow$

Molecularity greater than 3 is very rare



Probability of 3 molecules colliding simultaneously is rare & hence $M > 3$ is not observed for example $N_2 + 3H_2 \longrightarrow 2NH_3$

Molecularity $= 4$ X $\Rightarrow$ Complex Reaction

$H_2 + I_2 \longrightarrow 2HI$ (simple)

Molecularity $= 2$

Rate $= k[H_2]^1[I_2]^1$

order $= 2$

$2A + B \longrightarrow$ Products (simple)

Molecularity $= 3$

Rate $= k[A]^2[B]^1$

order $= 3$

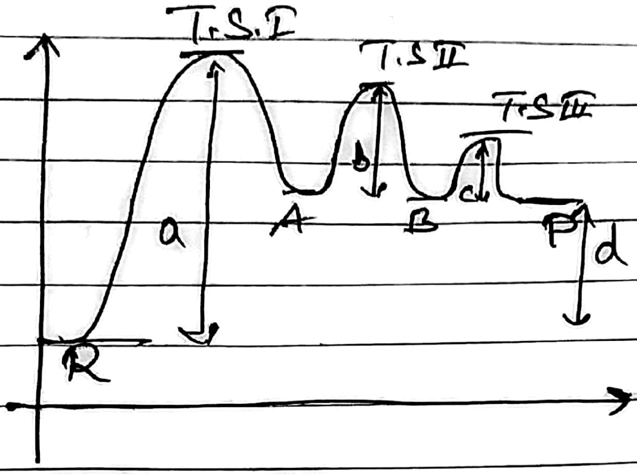
$A + 2B \longrightarrow$ Products

rate $= k[A]^2[B]^{1/2}$ Simple ??

NO rate should be $k[A]^1[B]^2$ for simple reaction

Complex Reaction (Multi-step)

⇒ There will be Intermediate/s



$R \rightarrow \cancel{A}$ Step 1

$\cancel{A} \rightarrow \cancel{B}$ Step 2

$\oplus$ $\cancel{B} \rightarrow P$ Step 3

$R \rightarrow P$

a → Activation energy (Ea) for $R \rightarrow A$

b → " " " for $A \rightarrow B$

c → " " " " $B \rightarrow P$

d → Heat of Reaction

As c is the smallest of a, b, c

hence Activation energy for $B \rightarrow P$ is minimum ⇒ fastest step

similarly a is the largest of a, b, c

hence Activation energy for $R \rightarrow A$ is maximum ⟹ slowest step (rds) each step of a Complex Reaction is an elementary step

⇒ overall Molecularity of any Complex Reaction is not defined, Molecularity for each step can be determined

⇒ order is decided from slowest step (rds)

<u>Case I</u>: when rds (slow step) is given

① $2A + 3B \longrightarrow A_2B_3$

<u>Mechanism is given</u>

$M = 2$ $\quad A + B \xrightarrow{K_1} \cancel{AB}$ Step 1 (slow)

$M = 2$ $\quad \cancel{AB} + B \xrightarrow{K_2} \cancel{AB_2}$ Step 2 (fast)

$M = 3$ $\quad \cancel{AB_2} + A + B \xrightarrow{K_3} A_2B_3$ Step 3 (fast)

rate Law $= K_1[A]^1[B]^1$

order $= 2$

(2) Note: If slowest step (rds) involves Intermediate

$$2A + 3B \longrightarrow A_2B_3$$

Mechanism

M = 2 $\quad A + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} AB$ (fast)

M = 2 $\quad AB + B \xrightarrow{K_3} AB_2$ (slow)

M = 3 $\quad AB_2 + A + B \xrightarrow{K_4} A_2B_3$ (fast)

rate = $K_3 [AB][B]$ $\quad$ But rate Law में [AB] Intermediate नहीं आएगा। अब क्या करें?

Assume the first step to be reversible
(Most of the times it will be reversible in question itself)

$$A + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} AB \qquad K_{eq} = \frac{K_1}{K_2} = \frac{[AB]}{[A][B]}$$

$$[AB] = \frac{K_1}{K_2} \times [A][B]$$

rate = $K_3 [AB][B]$

rate = $\dfrac{K_3 K_1}{K_2} [A][B]^2 = K_{eff} [A][B]^2$

order = 3 $\quad K_{eff} = \dfrac{K_3 K_1}{K_2}$

Q) $2O_3 \longrightarrow 3O_2$ for the following reaction Mechanism is given. Calculate effective rate constant and order of reaction

Mechanism:

$$O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O \quad \text{(fast)}$$

$$O + O_3 \xrightarrow[k_3]{} 2O_2 \quad \text{(slow)}$$

Solution

$$rate = k_3[O][O_3]$$

But [O] is Intermediate

$$O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$K_{eq} = \frac{k_1}{k_2} = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{k_1}{k_2} \times \frac{[O_3]}{[O_2]}$$

$$\text{rate} = k_3[O][O_3]$$

$$= \frac{k_3 k_1}{k_2}[O_3]^2[O_2]^{-1}$$

$$= k_{eff}[O_3]^2[O_2]^{-1}$$

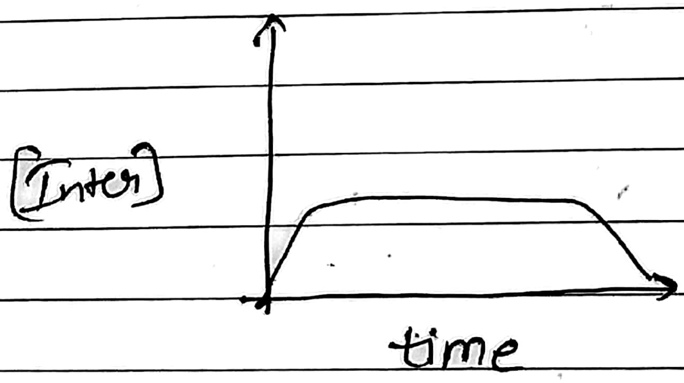
$$\text{order} = 2-1 = 1$$

$$k_{eff} = \frac{k_3 k_1}{k_2}$$

Case II : When rds is not given

<u>Steady State Approximation</u>

Intermediates are formed & used instantaneously so most of the time there concentration is constant (Steady)



at steady state $\frac{d[\text{Inter}]}{dt} = 0$