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$$X(g) \xrightarrow{2\times10^{-3}} B \qquad 100$$

$$X(g) \xrightarrow{3\times10^{-2}} C \qquad 1500$$

1600

$= 30\times10^{-3}$

$$\frac{k_1}{k_2} = \frac{1}{15}$$

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

$$100 = 1600\, e^{-32\times10^{-3}\times t}$$

$$t_{1/2}\times 4$$

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Case - I

$k_2 >> k_1$

$$A \xrightarrow{k_1} \cancel{I \xrightarrow{k_2}} P$$

$$A \xrightarrow{k_1} P$$

$$a-x \qquad\qquad x$$

$$[P] = [A]_0 \{1 - e^{-k_1 t}\}$$

RDS: having lowest rate constant

Using steady state cond^n for 'I'

$$A \xrightarrow[k_1[A]]{k_1} I \xrightarrow[k_2[I]]{k_2} P$$

$k_1[A] = k_2[I]$

Let 'I' is in S.S

RoA of I = RoD of I

$$k_1[A] = k_2[I]$$

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

for Steady state of intermediate $k_2 >> k_1$

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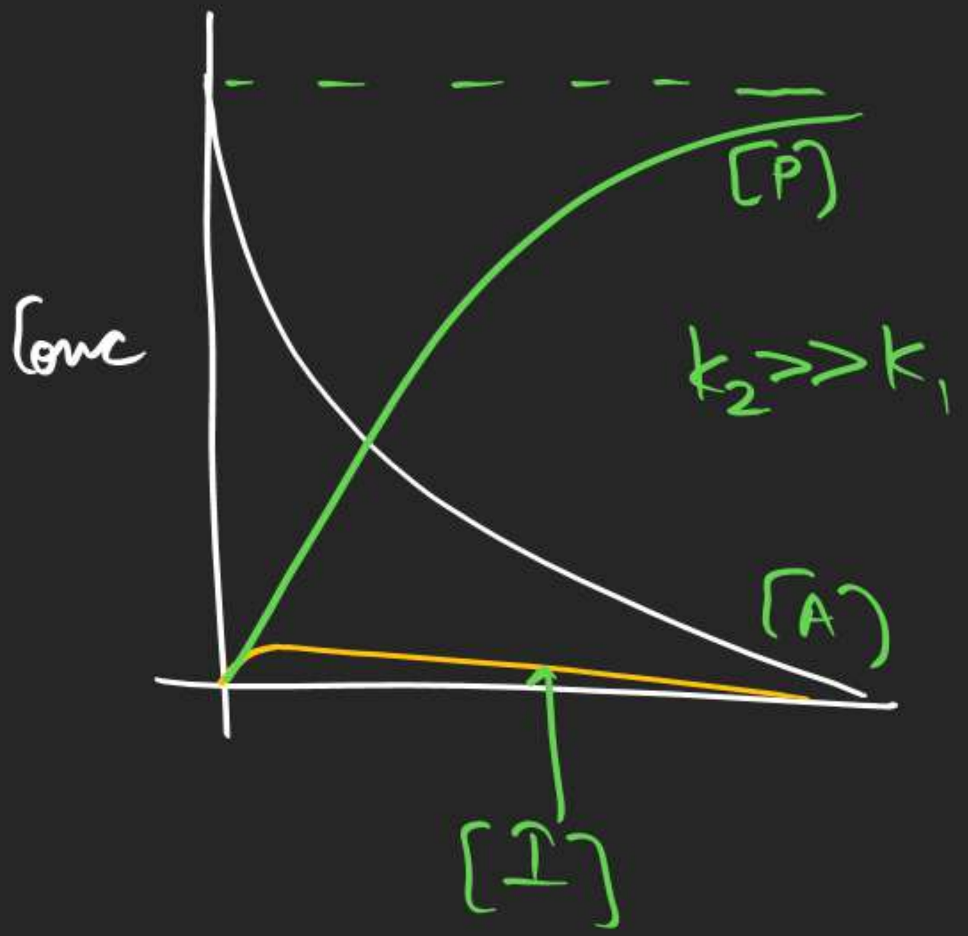


Case-II if $k_1 >> k_2$

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

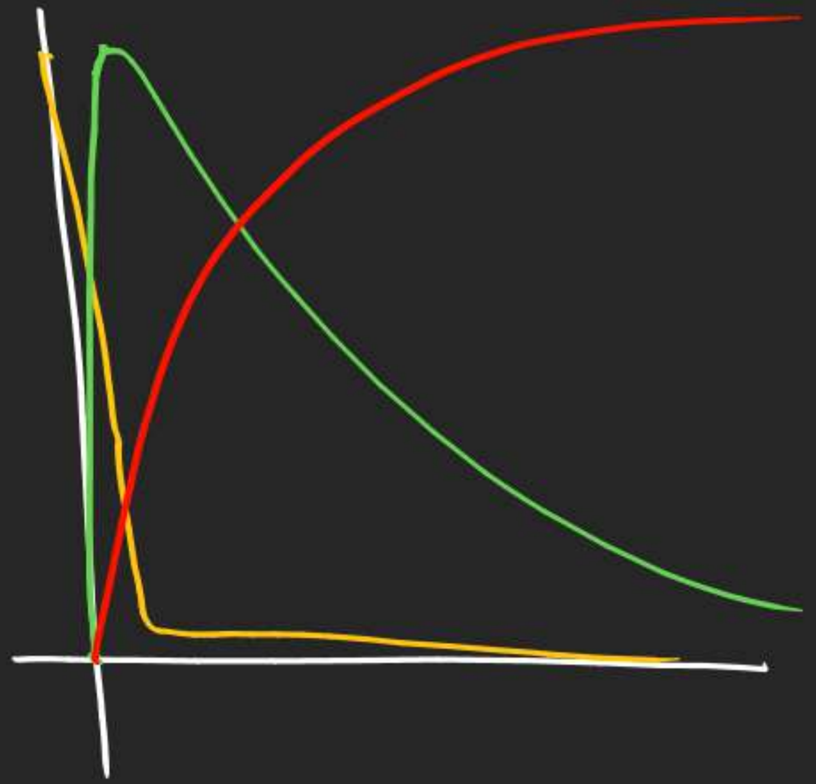
$$[I] = [A]_0\, e^{-k_2 t}$$

$t = 0 \quad [I] = [A]_0$

$$\cancel{A \xrightarrow{k_1}} I \xrightarrow{k_2} P$$

$\cancel{[A]_0}$ $\quad [A]_0$

$$[P] = [A]_0\left[1 - e^{-k_2 t}\right]$$



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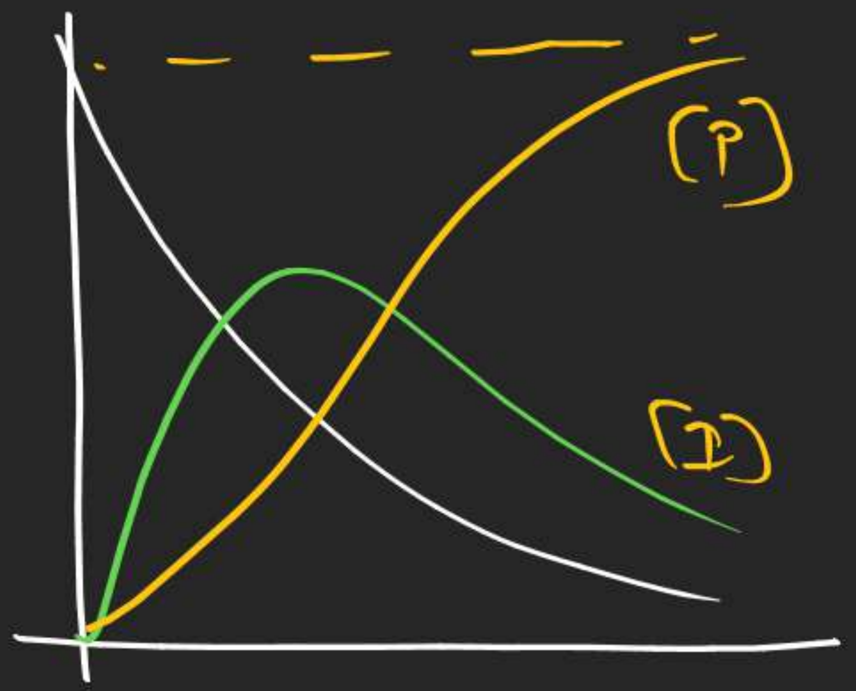
Case-III : $\rightarrow$ $k_1 = k_2$

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

([I] conc will not be const)

$$[I] = k_1 t [A]_0 e^{-k_1 t}$$



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Rate law for complex Rxn :→

Ex. 1 $2NO_2 + F_2 \xrightarrow{RoR} 2NO_2F$

Mech

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \quad (\text{slow})$$

$$NO_2 + F \xrightarrow{k_2} NO_2F \quad (\text{fast})$$

$$\frac{d[NO_2F]}{dt} = ?$$

Using RDS method

RoR = Rate of RDS

$$\frac{1}{2}\frac{d[NO_2F]}{dt} = k_1[NO_2][F_2]$$

Using Steady state method

Since $k_2 >> k_1$

'F' will be in steady state

RoA = RoD

$$k_1[NO_2][F_2] = k_2[NO_2][F]$$

$$\Rightarrow \frac{d[NO_2F]}{dt} = k_1[NO_2][F_2] + k_2[NO_2][F]$$

$$= 2k_1[NO_2][F_2]$$

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Q. $2O_3 \xrightarrow{RoR} 3O_2$

Mech

$O_3 \xrightarrow{k_1} O_2 + O$ (slow)

$O_3 + O \xrightarrow{k_2} 2O_2$ (fast)

RoR = Rate of RDS

$$\frac{1}{3}\frac{d[O_2]}{dt} = k_1[O_3]$$

$$\frac{d[O_2]}{dt} = 3k_1[O_3]$$

Using s. state for 'O'

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

———————— x ————————

$$\frac{d[O_2]}{dt} = k_1[O_3] + 2k_2[O_3][O]$$

$$= k_1[O_3] + 2k_1[O_3]$$

$$= 3k_1[O_3]$$

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Ex. 2 $2NO + O_2 \longrightarrow 2NO_2$

Mech $2NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (fast eqlb^m)

$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (slow)

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2}$$

Since it is fast eqlb^m, it can be used at any time

$$\frac{1}{2}\frac{d[NO_2]}{dt} = k_2\underbrace{[N_2O_2]}[O_2]$$

$$= \frac{k_2 k_1}{k_{-1}}[NO]^2[O_2]$$

$$= k[NO]^2[O_2]$$

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Molecularity :→

0 - I

70, 71, 74

5 - I

52 - 55

42 - 44