$$v = k[A] \qquad A \longrightarrow P$$

$$A + B \longrightarrow P$$

$$v = k[A][B]$$

$$\nu_A A + \nu_B B \longrightarrow \nu_p P$$

-ve | +ve | fractional | zero

$$v = k[A]^a [B]^b \ldots [P]^p$$

Isolation method

$$v = k' [A]^a \qquad v = k'' [B]^b$$

pseudo first order reaction

$$k [ester][H_2O] = k' [ester]$$

Method of initial rates

$$v = k[A]^{\alpha}$$

$$v_0 = k[A]_0^{\alpha}$$

$$\log v_0 = \log k + \alpha \log [A]_0$$

$$\nu_A A + \nu_B B \longrightarrow \nu_C C + \nu_D D$$

$$v = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{\nu_C}\frac{d[C]}{dt} = \frac{1}{\nu_D}\frac{d[D]}{dt}$$

extent of reacn.

$$\xi = \frac{n_{t,J} - n_{0,J}}{n_J} \qquad \frac{1}{V}\frac{d\xi}{dt}$$

(x_i)

$\Delta n / n$

$$A \longrightarrow P$$

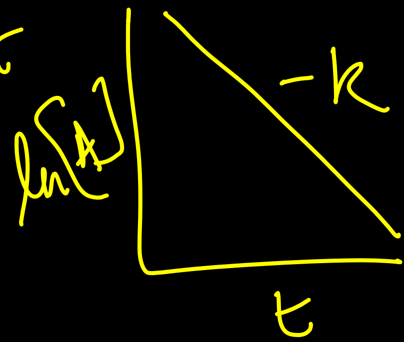
$$v = -\frac{d[A]}{dt} = k[A]$$

$$[A] = [A]_0\, e^{-kt}$$

$$[A]_0 / 2$$

$$t_{1/2} = \ln 2 / k$$

$$\ln[A] = \ln[A]_0 - kt$$



$$\frac{0.693}{k}$$

Second Order reaction

$$A \longrightarrow P$$

$$\frac{d[A]}{dt} = -k[A]^2$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

n^{th} order $A \longrightarrow P$

$$t_{1/2} = \frac{1}{k[A]_0^{n-1}}$$

$$A + B \longrightarrow P$$

$$\frac{d[A]}{dt} = -k[A][B] = -k\left([A]_0 - x\right)\left([B]_0 - x\right)$$

$$\ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = \left([B]_0 - [A]_0\right)kt$$

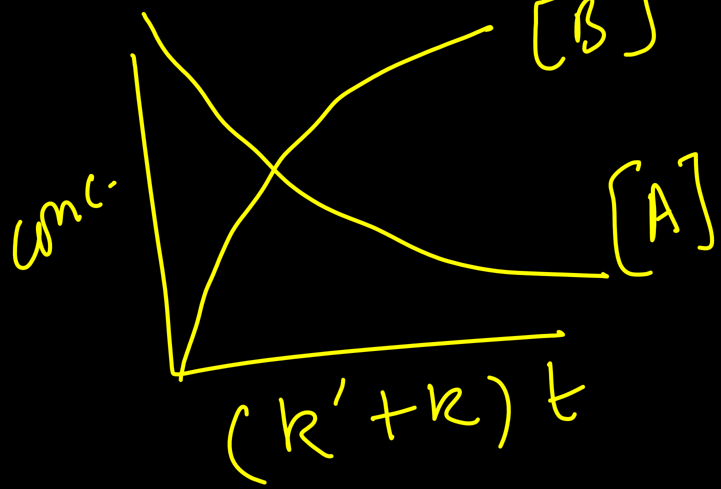
$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B \qquad [A]_0 \qquad [B]_0 = 0$$

$$[A] + [B] = [A]_0$$

$$\frac{d[A]}{dt} = -k[A] + k'[B]$$

$$= -(k+k')[A] + k'[A]_0$$

$$[A] = \frac{k' + k e^{-(k+k')t}}{k'+k} \quad [A]_0$$



At $t = \infty$

$$[A]_{eq} = \frac{k' [A]_0}{k' + k}$$

$$[B]_{eq} = [A]_0 - [A]_{eq} = \frac{k [A]_0}{k' + k}$$

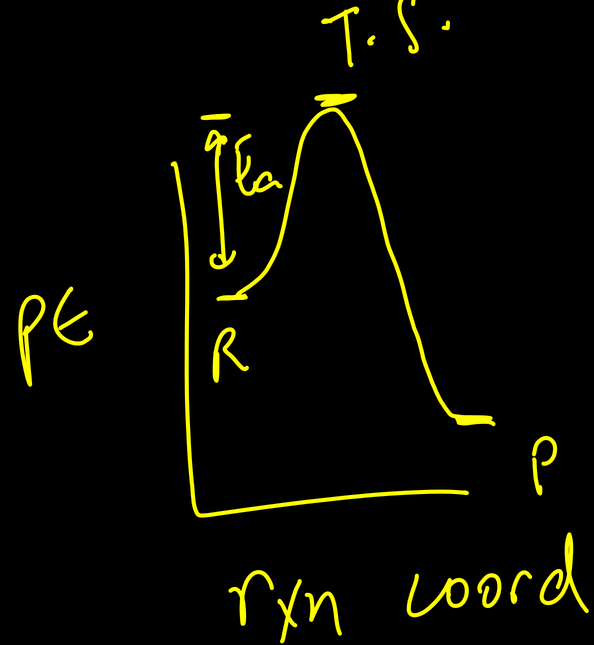
$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k}{k'}$$

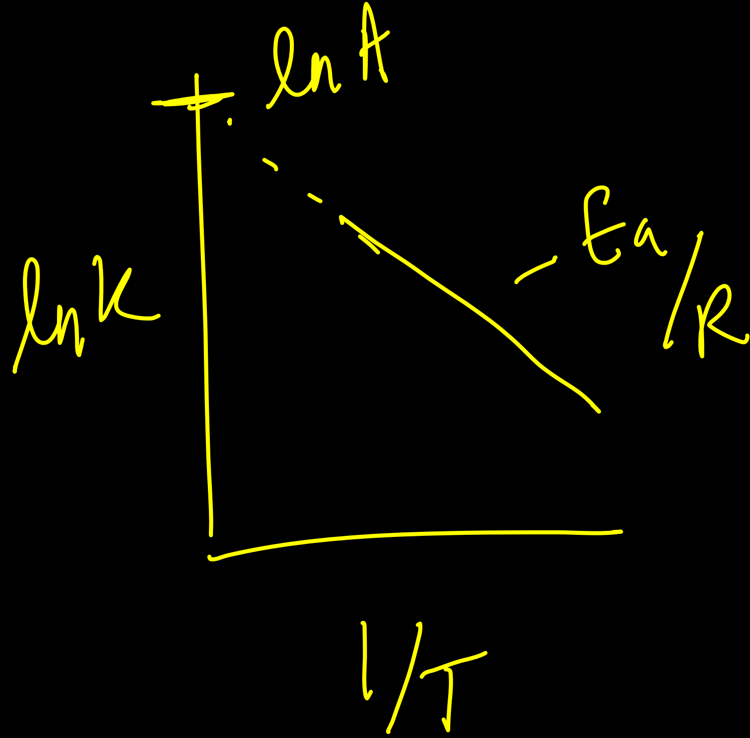
$$k [A]_{eq} = k' [B]_{eq}$$

Temperature dependence

Arrhenius Eqn.

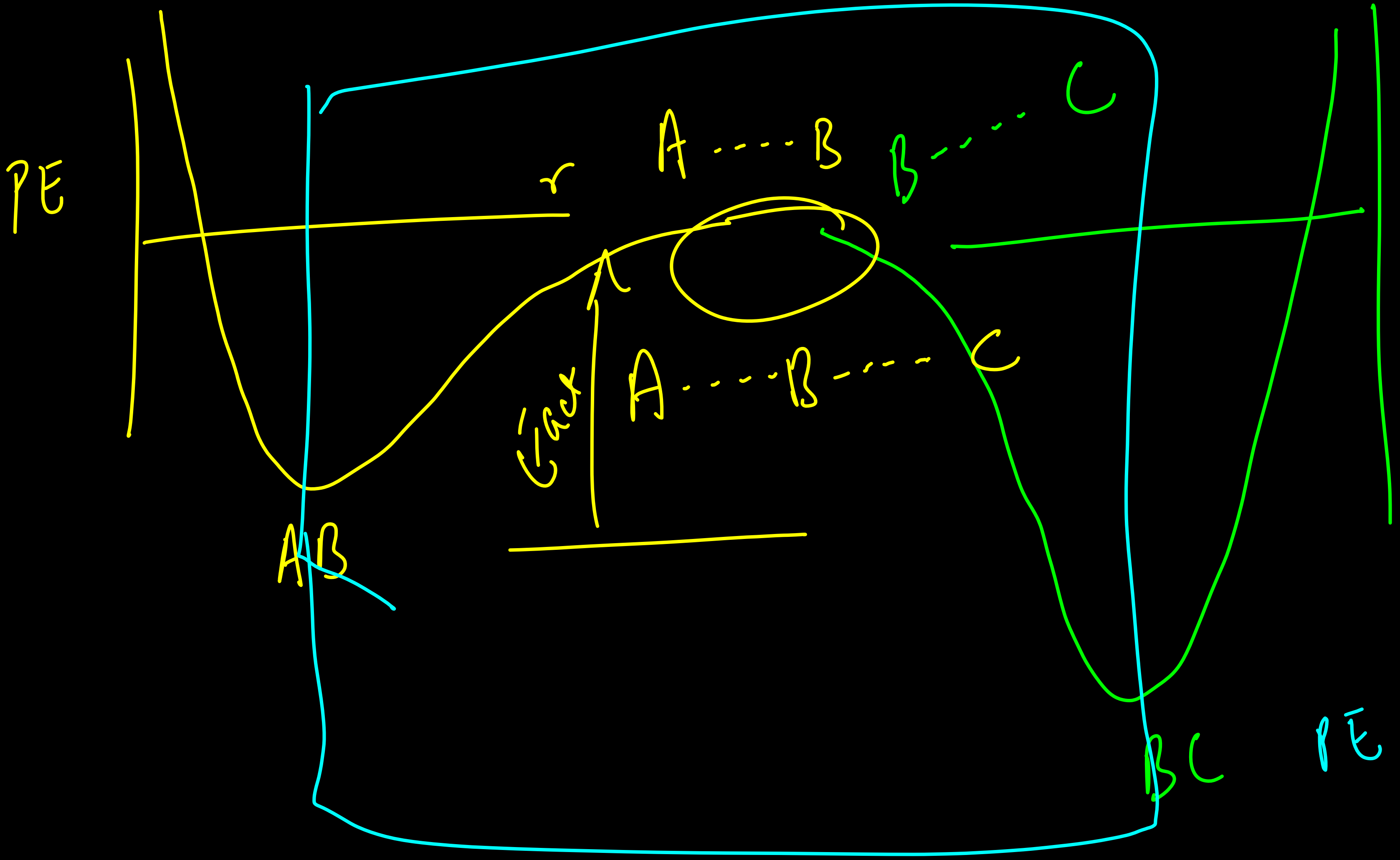
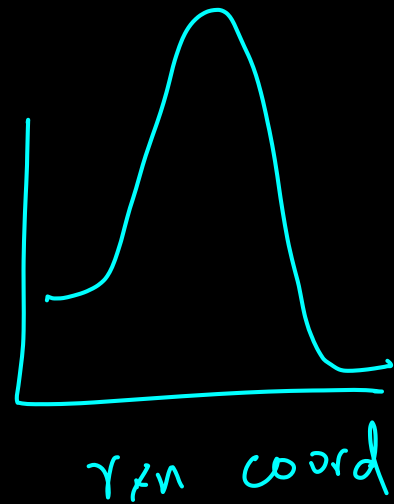
$$\ln k = \ln A - \frac{E_a}{RT}$$





A

r


PE
r
A ... B
B - - C
Eact
A ... B --- C
AB
BC

PE
rxn coord

Elementary Reactions

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$ ← complex rxn

$$Br^{\cdot} + H_2 \longrightarrow HBr + H^{\cdot}$$ ← elementary step

Unimolecular

$$A \longrightarrow B \qquad \frac{d[A]}{dt} = -k[A]$$

Bimolecular

$$A + B \longrightarrow C \qquad \frac{d[A]}{dt} = -k[A][B]$$

$$r = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]}$$

Consecutive elementary reactions

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

$$A \xrightarrow{k_a} I$$

$$I \xrightarrow{k_b} P$$

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

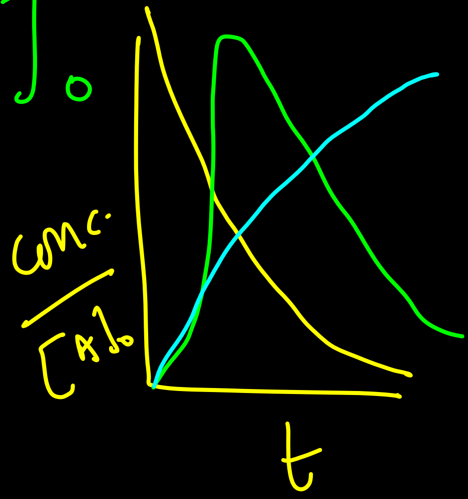
$$[A]_0 = [A] + [I] + [P]$$

$$\frac{d[I]}{dt} = k_a[A] - k_b[I]$$

$$\frac{d[P]}{dt} = k_b[I]$$

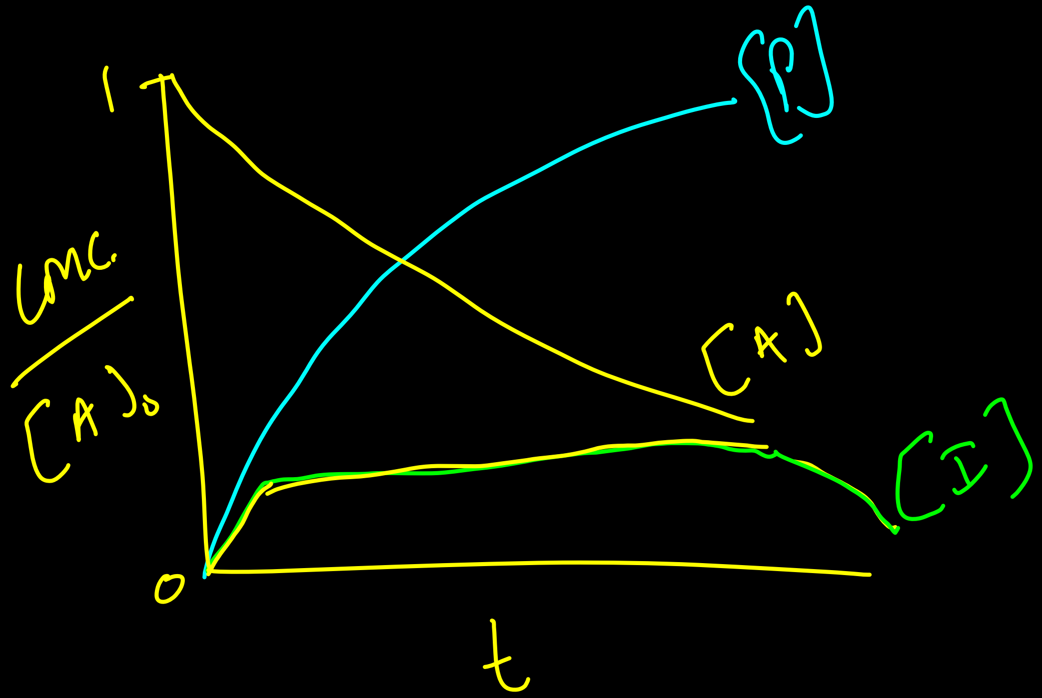
$$[A] = [A]_0 \, e^{-k_a t}$$

$$[I] = \frac{k_a}{k_b - k_a}\left(e^{-k_a t} - e^{-k_b t}\right)[A]_0$$



$$[P] = [A]_0 - [A] - [I]$$

$$= \left\{1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_b - k_a}\right\}[A]_0$$



Steady-State approx

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

$k_b >> k_a$

$$\frac{d[I]}{dt} = 0 \qquad k_a[A] = k_b[I]$$

$$\frac{d[P]}{dt} = k_a[A]$$

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