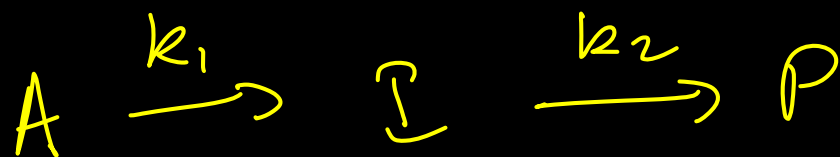
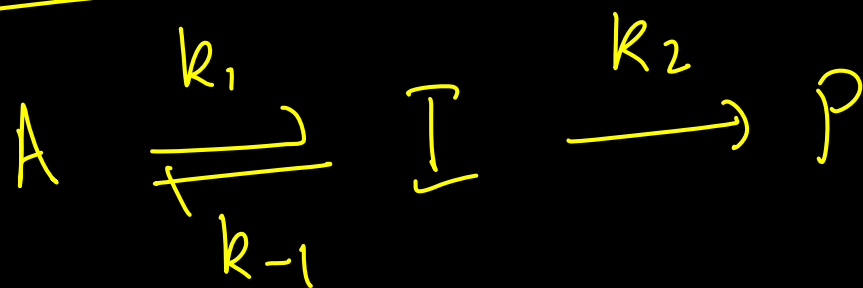


Steady State Approx.



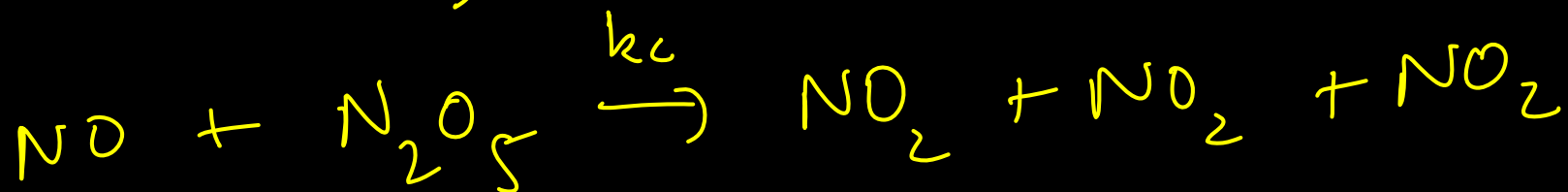
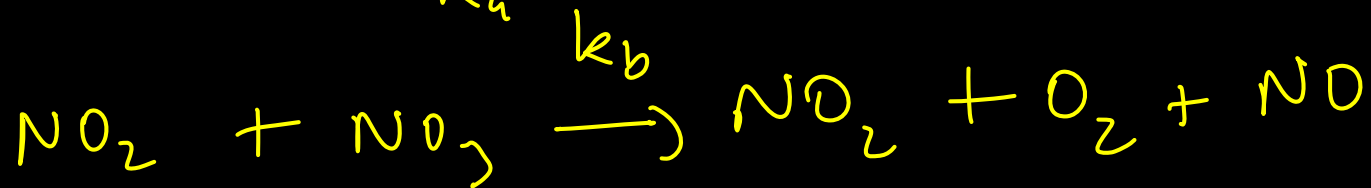
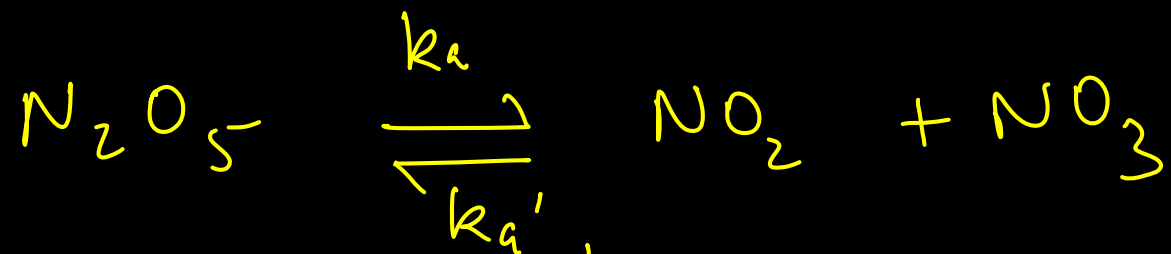
$$k_2 \gg k_1$$

Pre-Equilibrium



$$k_{-1} \gg k_1, k_2$$

$$K_{eq} = \frac{[I]_{eq}}{[A]_{eq}}$$



$$\frac{d[\text{O}_2]}{dt} = k_b [\text{NO}_2] [\text{NO}_3]$$

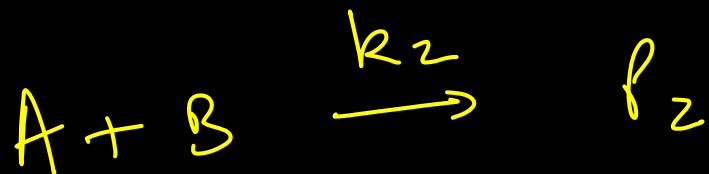
$$\frac{d[\text{NO}_3]}{dt} = 0 = k_a [\text{N}_2\text{O}_5] - k_a' [\text{NO}_2] [\text{NO}_3] - k_b [\text{NO}_2] [\text{NO}_3]$$

$$[\text{NO}_2] [\text{NO}_3] = k_a [\text{N}_2\text{O}_5] / (k_b + k_a')$$

$$\frac{d[O_2]}{dt} = \frac{k_b k_a [N_2O_5]}{k_b + k_a'} = k_{eff} [N_2O_5]$$

fast eq. $[NO_2][NO_3] = \frac{k_a [N_2O_5]}{k_a'}$

$$\frac{d[O_2]}{dt} = \frac{k_b k_a [N_2O_5]}{k_a'} = k_{eff} [N_2O_5]$$

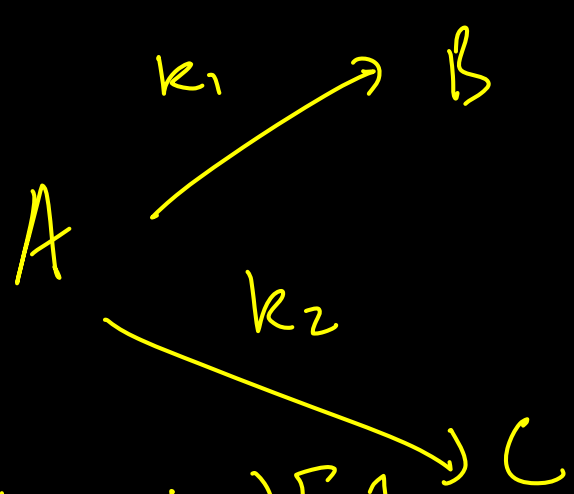


If react. reaches eq. \rightarrow thermodynamically favoured product

$$\frac{d[P_1]}{dt} = k_1 [A][B] \quad \frac{d[P_2]}{dt} = k_2 [A][B]$$

$k_1/k_2 \rightarrow$ kinetically controlled product

parallel reactions



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

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

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

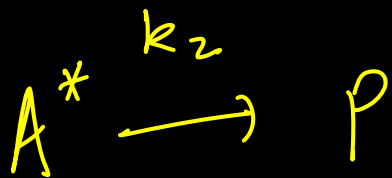
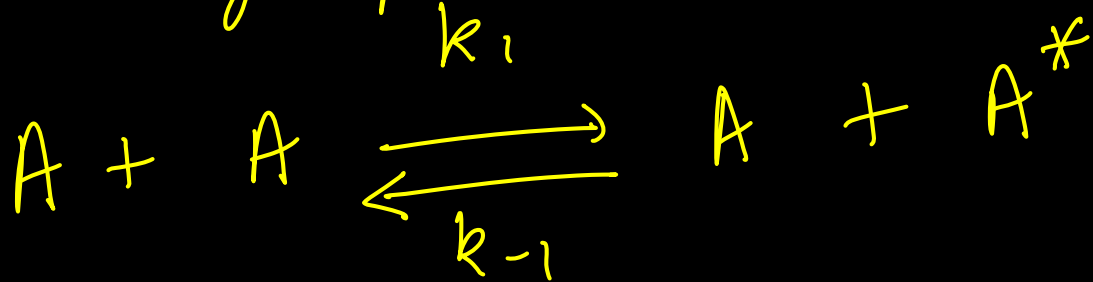
Branching ratio

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

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

Lindemann - Hinshelwood mechanism

Unimolecular gas phase reactions



$$\frac{d[A^*]}{dt} = 0 = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*]$$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2}$$

$$k_{-1}[A][A^*] \quad k_2[A^*]$$

$$\frac{d[P]}{dt} = k_1[A]^2 \quad \text{if } k_2 \gg k_{-1}[A]$$

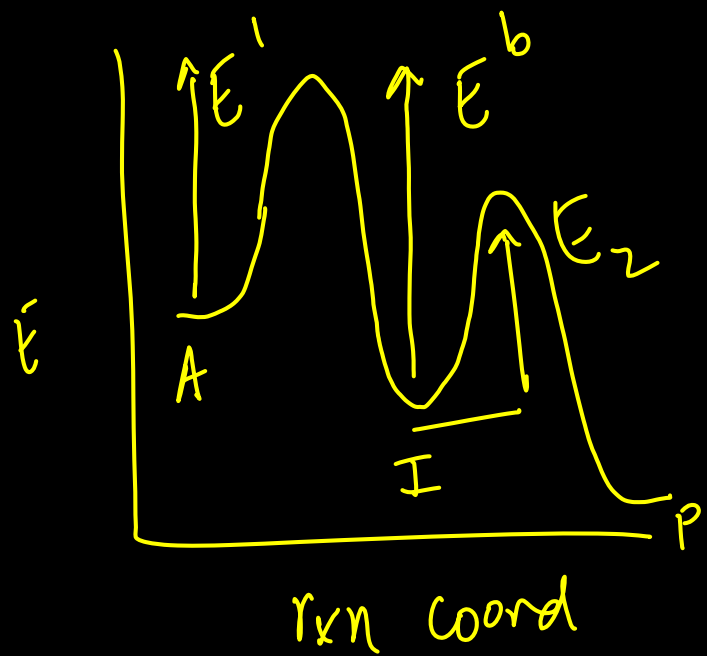
$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1}} [A] \quad \text{if } k_2 \ll k_{-1}[A]$$

$$k_{\text{app}} = \frac{k_1 k_2 [A]}{k_{-1}[A] + k_2}$$

$$\frac{d[P]}{dt} = k_{\text{eff}} [A]$$

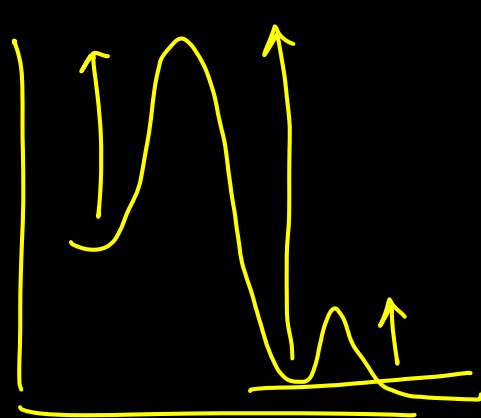
$$\frac{1}{k_{\text{eff}}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1} \frac{1}{[A]}$$

Plot $1/k_{\text{eff}}$ vs. $\frac{1}{[A]}$

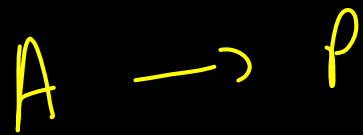


$$E^1 + E^2 - E^b \quad +ve \quad E_a$$

$$k = A e^{-E_a/RT}$$



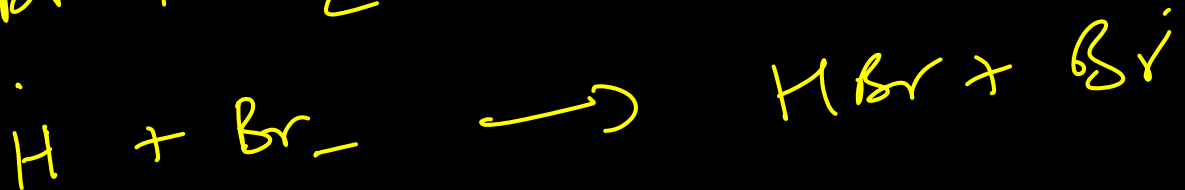
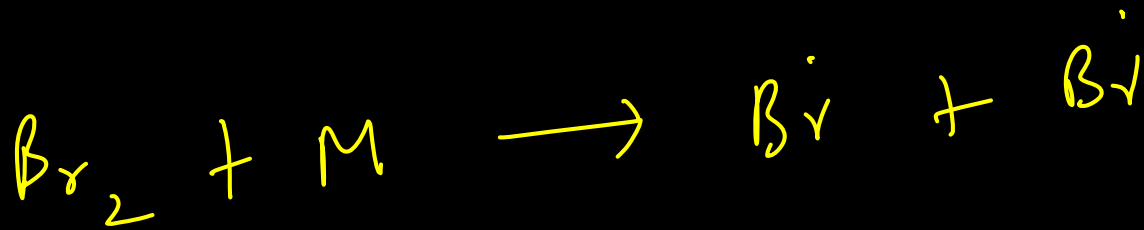
-ve E_a



$$v = k [A] [P]$$

autocatalytic

Initiation
step



} propagation



— retardation



$$\frac{d[\text{HBr}]}{dt}$$

1. F

9. T

(vi) entropy

volume

2. F

10. F

(vii) zero

3. F

(i) Attractive

4. F

(ii) volume Temperature

5. F

(iii) C_v T

6. F

(iv) volume

7. T

8. F

(v) a/v^2 or $\frac{RT}{v-b} - p$