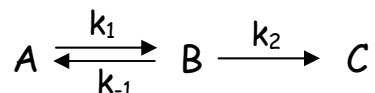


Complex Reactions and Mechanisms (continued)

IV) Steady State and Equilibrium Approximations

a) Steady State Approximation

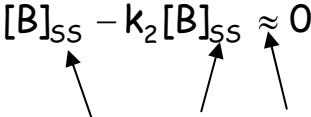


Assume that $[B]$ is small and slowly varying

e.g. $\frac{d[B]}{dt} \approx 0$ and $(k_2 + k_{-1}) \gg k_1$

$[B]$ reaches a steady state concentration $[B]_{ss}$ and remains there

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B]_{ss} - k_2[B]_{ss} \approx 0$$



Steady State approximation

Solving... $[B]_{ss} = \frac{k_1[A]}{k_{-1} + k_2}$

So $-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]_{ss}$

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

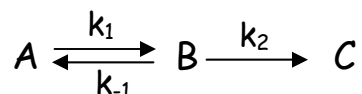
$$\boxed{\frac{d[C]}{dt} = k_2[B]_{SS} = \frac{k_1 k_2 [A]}{k_{-1} + k_2} = -\frac{d[A]}{dt}}$$

Looks like $A \xrightarrow{k'} C$ (first order) with $k' = \frac{k_1 k_2}{k_{-1} + k_2}$

****Necessary Condition for use of Steady State Approximation****

- i) Data must be taken after B has built up to a steady state value.
- ii) $(k_2 + k_{-1}) \gg k_1 \Rightarrow [B]_{SS}$ is small

b) Equilibrium Approximation



Assume $k_2 \ll k_{-1}$ and k_1

That is... $B \xrightarrow{k_2} C$ is the rate limiting step.

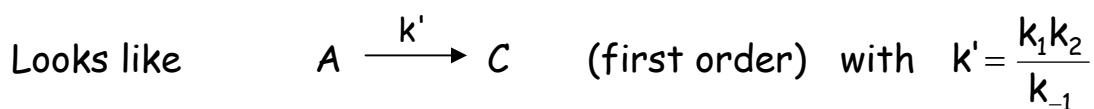
Then... A and B quickly come into equilibrium, while C slowly builds up.

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

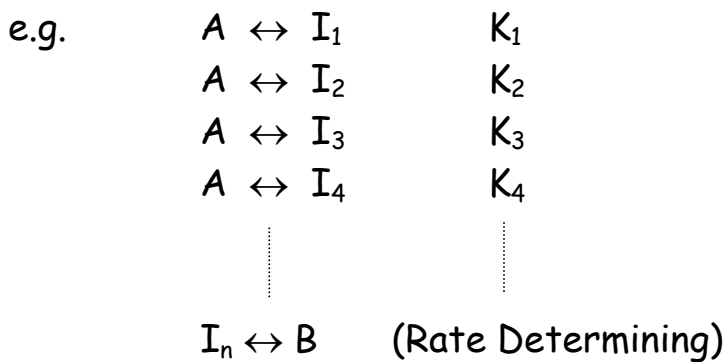
Equilibrium approximation

$$\text{So... } \frac{d[C]}{dt} = k_2[B] = k_2 K_{eq}[A] = \frac{k_1 k_2}{k_{-1}} [A]$$

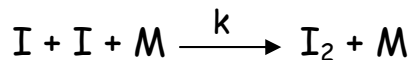
$$\text{Or, } \boxed{\frac{d[C]}{dt} = \frac{k_1 k_2}{k_{-1}} [A]}$$



In general, for a mechanism with multiple pre-equilibria...

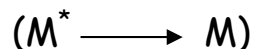
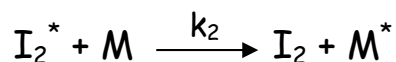
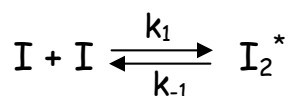


$$\boxed{\frac{d[B]}{dt} = k_n [I_n] = k_n \left[\prod_{i=1}^n K_i \right] [A]}$$

Examples:**A) Apparent Termolecular Reactions (Reaction Chaperones)**

M is a rare gas molecule or the wall of the reaction vessel

Mechanism:



where $(k_2 + k_{-1}) \gg k_1$, that is the Steady State approximation!

$$\text{So } \frac{d[I_2^*]}{dt} = k_1[I]^2 - k_{-1}[I_2^*]_{ss} - k_2[I_2^*]_{ss}[M] \approx 0$$

Steady State approximation

$$\text{Solving... } [I_2^*]_{ss} = \frac{k_1[I]^2}{k_{-1} + k_2[M]}$$

$$\text{And ... } \boxed{\frac{d[I_2]}{dt} = k_2[I_2^*]_{ss}[M] = k_2[M] \frac{k_1[I]^2}{k_{-1} + k_2[M]}}$$

Limiting Cases

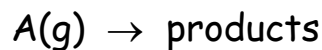
$$\text{i) } k_2[M] \gg k_{-1} \quad \text{then} \quad \frac{d[I_2]}{dt} = k_1[I]^2$$

(high pressure) second order

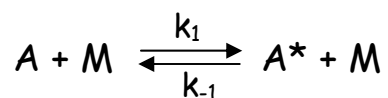
$$\text{ii) } k_2[M] \ll k_{-1} \quad \text{then} \quad \frac{d[I_2]}{dt} = \frac{k_1 k_2}{k_{-1}} [M][I]^2$$

(low pressure) third order

B) Gas decomposition (Lindemann Mechanism)



Mechanism:



M is a rare gas molecule and/or A,



So... $(k_2 + k_{-1}) \gg k_1$, Steady State approximation again.

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*]_{ss}[M] - k_2[A^*]_{ss} \approx 0$$

Steady State approximation

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

$$\boxed{-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_2[A^*]_{ss} = \frac{k_1k_2[A][M]}{k_{-1}[M] + k_2}}$$

Limiting Cases

i) High pressure (1 bar) $k_{-1}[M] \gg k_2$

$$-\frac{d[A]}{dt} = \frac{k_1k_2}{k_{-1}}[A] = k_\infty[A] \quad (1^{\text{st}} \text{ order})$$

ii) Low pressure ($\sim 10^{-4}$ bar) $k_{-1}[M] \ll k_2$

$$-\frac{d[A]}{dt} = k_1[A][M] \quad (\text{if } M \equiv A, \text{ then } 2^{\text{nd}} \text{ order in } A)$$