Lecture 36: Steady State

Steady State, Lindemann Mechanism

What is steady state?

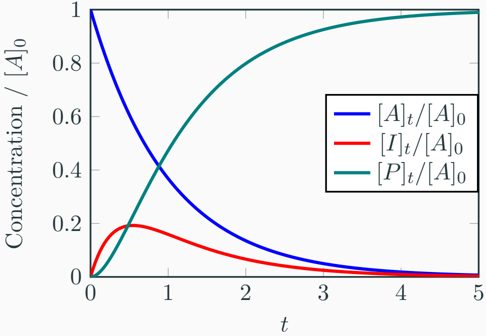
Steady State Approximation

Assumes the concentration of intermediates remains constant

$$\frac{d[I]}{dt} = 0$$

Use steady state when not told slow/fast in mechanism

$$[P]_t = [A]_0 \left[1 + \frac{1}{k_1 - k_2} \left(k_2\, e^{-k_1 t} - k_1\, e^{-k_2 t} \right) \right]$$



Example: Steady State

Find the rate law for the reaction $2\,\mathrm{A} \longrightarrow \mathrm{C}$ with the following proposed mechanism:

$$2\,\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

Steady state on B:

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

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

Rate of formation of C:

$$\frac{d[C]}{dt} = v(t) = k_2[B] = \frac{k_1 k_2[A]^2}{k_{-1} + k_2}$$

Example: Steady State

Consider the limits steady state approximation

$$2\,\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

$$v(t) = \frac{k_1 k_2 [A]^2}{k_{-1} + k_2}$$

Step 1 slow

$$2\,\mathrm{A} \xrightarrow{k_1} \mathrm{B}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

$$v(t) = \frac{k_1 k_2 [A]^2}{\cancel{k_{-1}} + k_2} = k_1 [A]^2$$

Step 2 slow

$$v(t) = k_2 [B]$$

$$k_1 [A]^2 = k_{-1} [B] \implies [B] = \frac{k_1}{k_{-1}} [A]^2$$

$$v(t) = \frac{k_1 \cdot k_2}{k_{-1}} [A]^2$$

$$v(t) = \frac{k_1 k_2 [A]^2}{k_{-1} + \cancel{k_2}} = \frac{k_1 \cdot k_2}{k_{-1}} [A]^2$$

Lindemann Mechanism

Models gas phase decomposition, explains why seemingly unimoleclar (first order) processes appear second order

$$\mathrm{A} + \mathrm{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{P}$$

Steady state on activated complex A^*:

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

Solve for $[A^*]$:

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

Rate law:

$$v(t) = k_2[A^*] = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2}$$

Limiting Cases of Lindemann Mechanism

$$v(t) = k_2[A^*] = \frac{k_1 k_2 [A][M]}{k_{-1}[M] + k_2}$$

$$\text{Case 1: } k_2 \gg k_{-1}[M] \quad \Longrightarrow \quad v = k_1[A][M]$$

$$\text{Case 2: } k_2 \ll k_{-1}[M] \quad \Longrightarrow \quad v = \frac{k_1 k_2}{k_{-1}}[A]$$

Unimolecular decomposition can be either first or second order, depending on relative rates

Example: Double Steady State

Consider the reaction:

$$\mathrm{H_2} + \mathrm{Br_2} \longrightarrow 2\,\mathrm{HBr}$$

Proposed mechanism:

$$\mathrm{Br_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,\mathrm{Br}^\bullet$$

$$\mathrm{Br}^\bullet + \mathrm{H_2} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{HBr} + \mathrm{H}^\bullet$$

$$\mathrm{H}^\bullet + \mathrm{Br_2} \xrightarrow{k_3} \mathrm{HBr} + \mathrm{Br}^\bullet$$

Steady state on intermediates $(\mathrm{Br}^\bullet, \mathrm{H}^\bullet)$:

$$\frac{d[\mathrm{H}^\bullet]}{dt} = k_2[\mathrm{Br}^\bullet][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}^\bullet] - k_3[\mathrm{H}^\bullet][\mathrm{Br_2}] = 0$$

$$\frac{d[\mathrm{Br}^\bullet]}{dt} = k_1[\mathrm{Br_2}] - k_{-1}[\mathrm{Br}^\bullet]^2 - k_2[\mathrm{Br}^\bullet][\mathrm{H_2}] + k_{-2}[\mathrm{HBr}][\mathrm{H}^\bullet] + k_3[\mathrm{H}^\bullet][\mathrm{Br_2}] = 0$$

Example: Double Steady State

Add to cancel terms:

$$k_1[\mathrm{Br_2}] - k_{-1}[\mathrm{Br^\bullet}]^2 = 0 \implies [\mathrm{Br^\bullet}] = \sqrt{\frac{k_1[\mathrm{Br_2}]}{k_{-1}}}$$

Solve for intermediate $\mathrm{H^\bullet}$:

$$\begin{aligned}
\frac{d[\mathrm{H^\bullet}]}{dt} &= k_2[\mathrm{Br^\bullet}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H^\bullet}] - k_3[\mathrm{H^\bullet}][\mathrm{Br_2}] = 0 \\
k_2[\mathrm{Br^\bullet}][\mathrm{H_2}] &= [\mathrm{H^\bullet}]\left(k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]\right) \\
[\mathrm{H^\bullet}] &= \frac{k_2[\mathrm{Br^\bullet}][\mathrm{H_2}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]} \\
&= \frac{k_2\sqrt{\frac{k_1[\mathrm{Br_2}]}{k_{-1}}}[\mathrm{H_2}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}
\end{aligned}$$

Example: Double Steady State

$$\mathrm{Br_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,\mathrm{Br^\bullet}$$

$$\mathrm{Br^\bullet} + \mathrm{H_2} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{HBr} + \mathrm{H^\bullet}$$

$$\mathrm{H^\bullet} + \mathrm{Br_2} \xrightarrow{k_3} \mathrm{HBr} + \mathrm{Br^\bullet}$$

Rate of formation of HBr:

$$v(t) = k_2[\mathrm{Br^\bullet}][\mathrm{H_2}] + k_3[\mathrm{H^\bullet}][\mathrm{Br_2}] - k_{-2}[\mathrm{H^\bullet}][\mathrm{HBr}]$$

Substitute $[\mathrm{H^\bullet}] = \dfrac{k_2\sqrt{\frac{k_1[\mathrm{Br_2}]}{k_{-1}}}[\mathrm{H_2}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}$ and $[\mathrm{Br^\bullet}] = \sqrt{\dfrac{k_1[\mathrm{Br_2}]}{k_{-1}}}$:

$$v(t) = k_2\left(\sqrt{\frac{k_1[\mathrm{Br_2}]}{k_{-1}}}\right)[\mathrm{H_2}] + k_3\left(\frac{k_2\sqrt{\frac{k_1[\mathrm{Br_2}]}{k_{-1}}}[\mathrm{H_2}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}\right)[\mathrm{Br_2}] - k_{-2}\left(\frac{k_2\sqrt{\frac{k_1[\mathrm{Br_2}]}{k_{-1}}}[\mathrm{H_2}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}\right)[\mathrm{HBr}]$$

Example: Double Steady State

Factor and simplify:

$$v(t) = k_2\sqrt{\frac{k_1}{k_{-1}}}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}\left[1 + \frac{k_3[\mathrm{Br_2}] - k_{-2}[\mathrm{HBr}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}\right]$$

$$= k_2\sqrt{\frac{k_1}{k_{-1}}}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}\frac{2k_3[\mathrm{Br_2}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}$$

$$\boxed{v(t) = \frac{2k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}}$$