Lecture 36: Detailed Balance

Detailed Balance, Relating k to K_c

Detailed Balance

$$\mathrm{A} + \mathrm{B} \underset{\mathrm{k_{-1}}}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{C} + \mathrm{D}$$

Forward and reverse rates are equal at equilibrium (detailed balance):

$$v_1(t) = v_{-1}(t)$$
$$k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} = k_{-1}[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}$$

Rearrange:

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}}} = K_c$$

Detailed Balance, multiple steps

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{P}$$

Detailed balance for each elementary equilibrium:

$$K_{c,1} = \frac{k_1}{k_{-1}} = \frac{[\mathrm{I}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}$$

$$K_{c,2} = \frac{k_2}{k_{-2}} = \frac{[\mathrm{P}]_{\mathrm{eq}}}{[\mathrm{I}]_{\mathrm{eq}}}$$

Multiplying gives overall equilibrium:

$$K_{c,\mathrm{overall}} = K_{c,1} K_{c,2} = \frac{[\mathrm{P}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}$$

$$K_c = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

Example: Detailed Balance

Overall Reaction:

$$CO + Cl_2 \longrightarrow Cl_2CO$$

Proposed mechanism:

$$Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl \qquad \text{(Step 1)}$$

$$Cl + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ClCO \qquad \text{(Step 2)}$$

$$ClCO + Cl_2 \xrightarrow{k_3} Cl_2CO + Cl \qquad \text{(Step 3)}$$

$$2\,Cl \xrightarrow{k_4} Cl_2 \qquad \text{(Step 4)}$$

Reactant: CO, Cl_2. Product: Cl_2CO. Catalyst: none. Intermediate: Cl, ClCO

Example: Detailed Balance

$$\mathrm{Cl_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,\mathrm{Cl} \qquad \text{(fast eq)}$$

$$\mathrm{Cl} + \mathrm{CO} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{ClCO} \qquad \text{(slow eq)}$$

$$\mathrm{ClCO} + \mathrm{Cl_2} \xrightarrow{k_3} \mathrm{Cl_2CO} + \mathrm{Cl} \qquad \text{(fast)}$$

$$2\,\mathrm{Cl} \xrightarrow{k_4} \mathrm{Cl_2} \qquad \text{(fast)}$$

Fast step after slow equilibrium makes equilibrium one-directional

$$v(t) = k_2[\mathrm{Cl}][\mathrm{CO}]$$

$$k_1[\mathrm{Cl_2}] = k_{-1}[\mathrm{Cl}]^2$$

$$[\mathrm{Cl}] = \sqrt{\frac{k_1}{k_{-1}}[\mathrm{Cl_2}]}$$

$$v(t) = k_2\sqrt{\frac{k_1}{k_{-1}}[\mathrm{Cl_2}]}\,[\mathrm{CO}]$$

Fast equilibrium before the slow step:

$$K_{c,1} = \frac{[\mathrm{Cl}]^2}{[\mathrm{Cl_2}]}$$

$$[\mathrm{Cl}] = \sqrt{K_{c,1}[\mathrm{Cl_2}]}$$

$$v(t) = k_2\sqrt{K_{c,1}[\mathrm{Cl_2}]}\,[\mathrm{CO}]$$

Calculus derivation of one-directional equilibrium

Fast step after slow equilibrium makes equilibrium one-directional

Pathway 1:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P}$$

Pathway 2:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{P}$$

$A \longrightarrow I \longrightarrow P$

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

Concentrations as function of time:

$$\frac{d[A]}{dt} = -k_1[A] \implies [A]_t = [A]_0\, e^{-k_1 t}$$

$$\frac{d[I]}{dt} = k_1[A] - k_2[I]$$

$$\frac{d[P]}{dt} = k_2[I]$$

Substitute $[A]_t = [A]_0 e^{-k_1 t}$, rearrange:

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

Inverse product rule:

$$\frac{d}{dt}\left([I]\, e^{k_2 t}\right) = k_1[A]_0\, e^{(k_2 - k_1)t}$$

$$[I]\, e^{k_2 t} = k_1[A]_0 \int e^{(k_2 - k_1)t}\, dt$$

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

$[I]_0 = 0 \implies C = -\dfrac{k_1[A]_0}{k_2 - k_1}$, divide by $e^{k_2 t}$

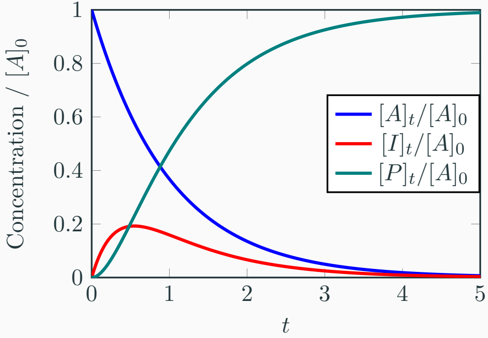
Analytical Solutions

Concentrations as function of time:

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

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

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



Derivation of $[P]_t$

Conservation of Mass:

$$[A]_0 = [A]_t + [I]_t + [P]_t \implies [P]_t = [A]_0 - [A]_t - [I]_t$$

Substitute and simplify:

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

What if $k_2 \gg k_1$?

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

$$k_1 - k_2 \approx -k_2$$
$$k_2\, e^{-k_1 t} \gg k_1\, e^{-k_2 t}$$

$$[P]_t \approx [A]_0 \left(1 - e^{-k_1 t}\right)$$

Fast step after slow equilibrium makes equilibrium one-directional

Pathway 1:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k_2} \mathrm{P}$$

Pathway 2:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{P}$$