

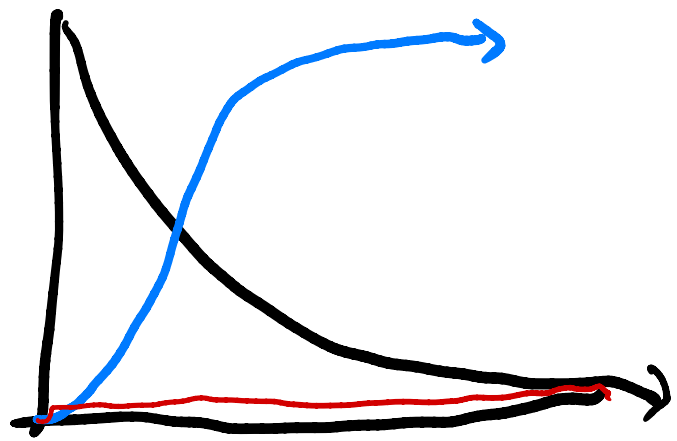
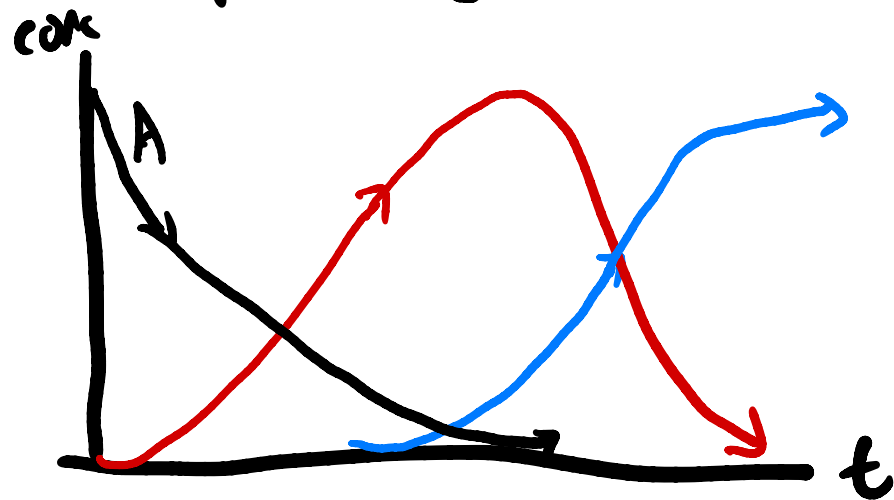
Steady state approximation

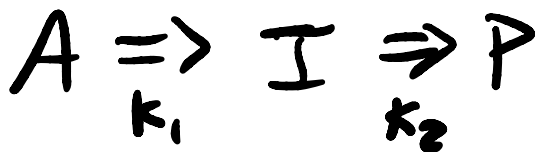


$$k_1 \gg k_2$$

(also applies for reversible reactions)

$$k_2 \gg k_1$$





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

$$\frac{d[I]}{dt} = k_1[A] - k_2[I] \approx 0 \Rightarrow [I]_{ss} = \frac{k_1[A]}{k_2}$$

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

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

$$\frac{d[I]}{dt} = k_1[A] - k_2[I] \approx 0 \Rightarrow [I]_{ss} = \frac{k_1[A]}{k_2}$$

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

$$[I]_{ss} = \frac{k_1 e^{-k_1 t} [A]_0}{k_2}$$

$$\frac{d[I]_{ss}}{dt} = \frac{-k_1^2 e^{-k_1 t} [A]_0}{k_2} \Rightarrow \frac{k_1^2 [A]_0}{k_2} \text{ small}$$

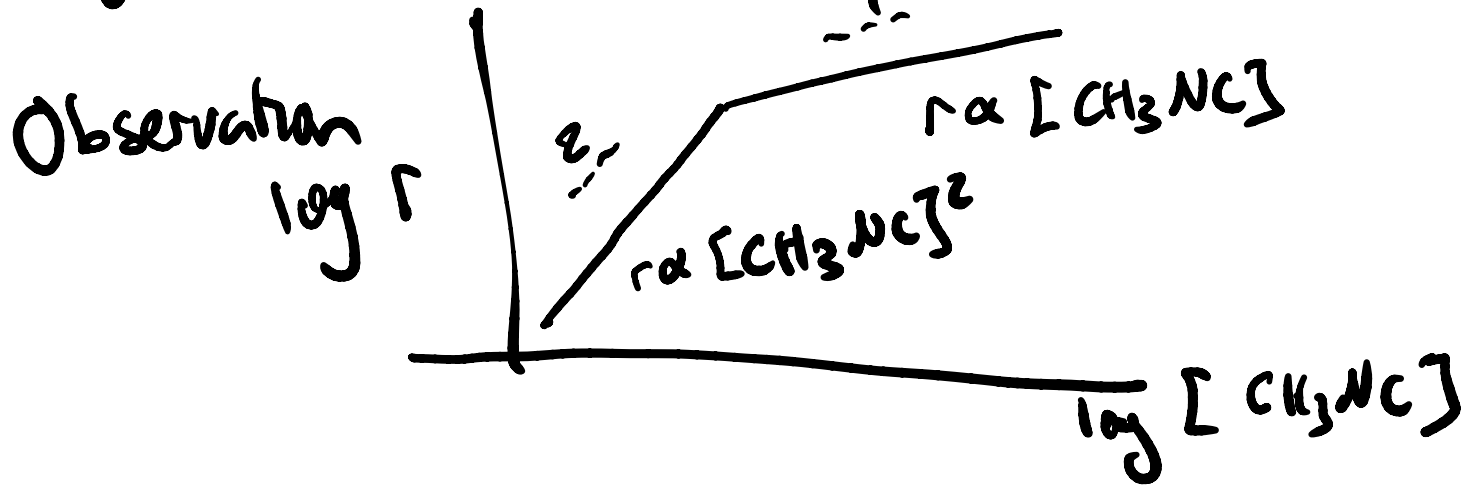
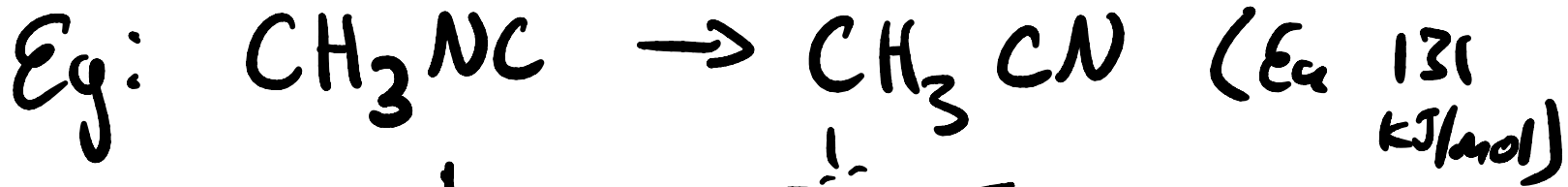
$$\frac{d[P]}{dt} = k_1 [A] = k_1 [A]_0 e^{-k_1 t}$$

$$\begin{aligned} [P](x) &= \int_0^x dt k_1 [A]_0 e^{-k_1 t} \\ &= [A]_0 (1 - e^{-k_1 t}) \end{aligned}$$

equation for single step reaction

Lindemann Mechanism

Molecule gets activated by collision
with another molecule





$$[A^*] \approx 0$$

$$\frac{d[A^*]}{dt} \approx 0$$

$$\frac{d[A^*]}{dt} = -k_f^{(2)} [A^*] - k_b [A^*] [M] + k_f^{(1)} [A] [M] \approx 0$$

$$\frac{d[A]^*}{dt} = -k_f^2 [A]^* - k_b [A]^* [M] + k_f' [A][M] \approx 0$$

$$[A]^* = \frac{k_f' [A][M]}{k_f^2 + k_b [M]}$$

$$= k_{obs} [A] \quad \uparrow \quad \frac{k_f' k_f^2 [M]}{k_f^2 + k_b [M]}$$

$$\frac{d[B]}{dt} = k_f^2 [A]^* = \frac{k_f^{(1)} k_f^{(2)} [A][M]}{k_f^{(2)} + k_b [M]}$$

$$\frac{d[B]}{dt} = k_{\text{obs}} [A] \quad \left(\text{Explains } \text{CH}_3\text{NC} \right)$$

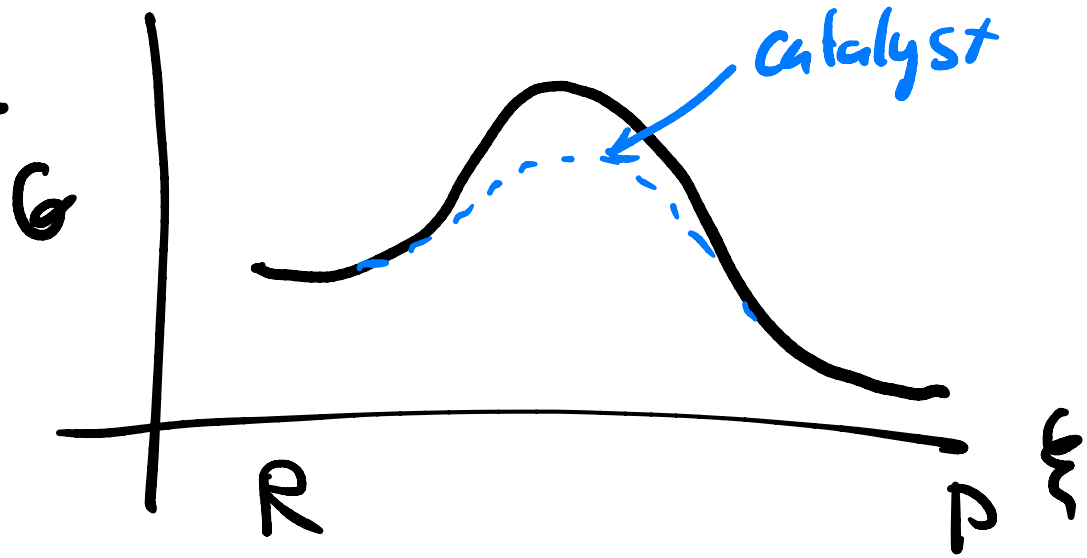
$$k_{\text{obs}} = \frac{k_f' k_f^2}{(k_f^2 + k_b [M])} [M]$$

at large $[M]$, $k_{\text{obs}} \approx \frac{k_f' k_f^2}{k_b}$

(lot of deactivation)

for small $[M]$, $k_{\text{obs}} \approx k_f' [M]$

Catalysis



- Add but doesn't get used up
- different reaction path

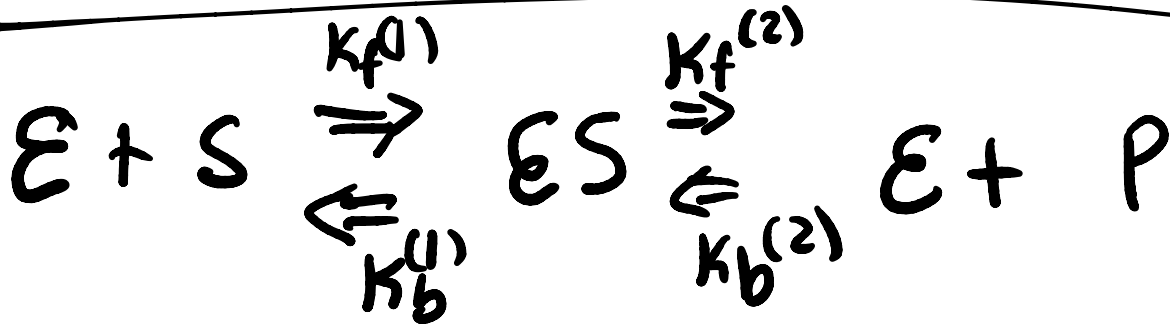
Homogeneous catalyst, mixed in
Enzymes

Heterogeneous (different phase)

usually a metal surface

Enzyme: biomolecule acts catalyst

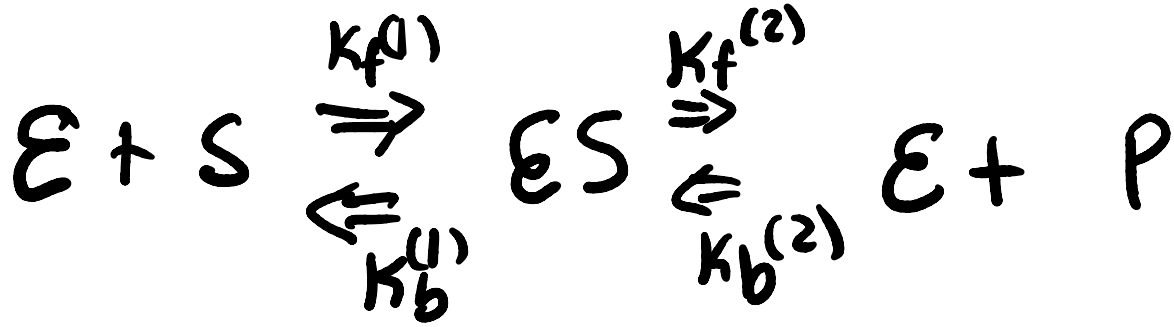
Michaelis-Menten Scheme



$$\frac{d[E]}{dt} = -k_f^{(1)} [E][S] + k_f^{(2)} [ES] + k_b^{(1)} [ES] - k_b^{(2)} [E][P]$$

$$\frac{d[S]}{dt} = -k_f^{(1)} [E][S] + k_b^{(1)} [ES]$$

$$\frac{d[P]}{dt} = k_f^{(2)} [ES] - k_b^{(2)} [P][E]$$



$$\frac{d[ES]}{dt} = k_f^{(1)} [E][S] - k_b^{(1)} [ES] - k_f^{(2)} [ES] + k_b^{(2)} [E][P] = 0$$

Assumption $[S] \gg [E]$

Enzyme conserved

$$[E]_0 = [ES] + [E]$$

$$[E] = [E]_0 - [ES]$$

rate, $-d[S]/dt$

$$\text{rate} = \frac{(k_f^{(1)} k_f^{(2)} [S] - k_b^{(1)} k_b^{(2)} [P]) [E]_0}{k_f^{(1)} [S] + k_b^{(1)} + k_b^{(2)} [P] + k_f^{(2)}}$$

Initial rate

$$[S] = [S]_0$$

$$[P] \approx 0$$

$$= \frac{k_f^{(2)} [E]_0 [S]_0}{[S]_0 + k_M}$$

$$k_M = \frac{k_f^{(2)} + k_b^{(1)}}{k_f^{(1)}}$$