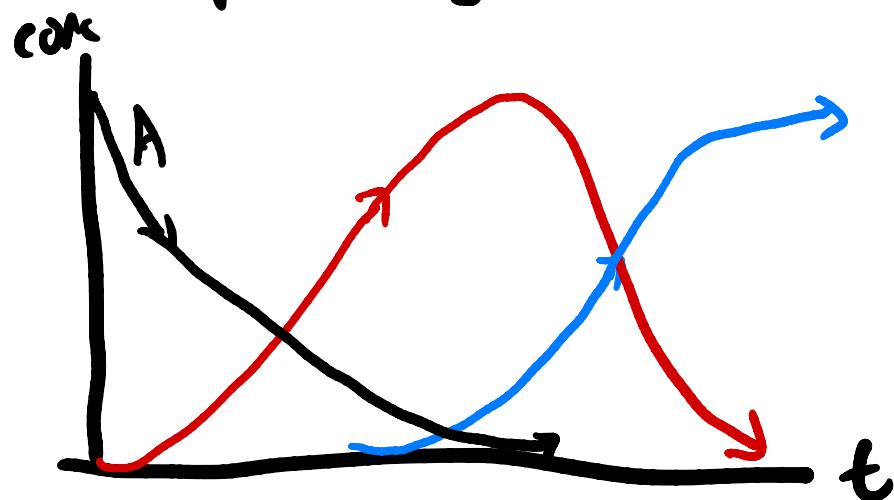


Steady state approximation

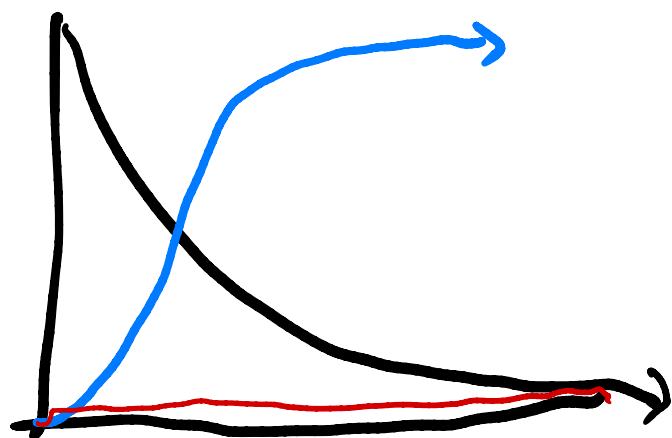


(also applies for reversible reactions)

$$k_1 \gg k_2$$



$$k_2 \gg k_1$$





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

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

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

$$\frac{d[A]}{dt} = -k_1 [A] \Rightarrow [A] = [A_0] e^{-k_1 t}$$

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

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

$$[I]_{ss} = \frac{k_1 e^{-k_1 t}}{k_2} [A_0] \quad \frac{d[I]_{ss}}{dt} = -\frac{k_1^2}{k_2} e^{-k_1 t} [A_0] \Rightarrow \frac{k_1^2 [A_0]}{k_2} \text{ small}$$

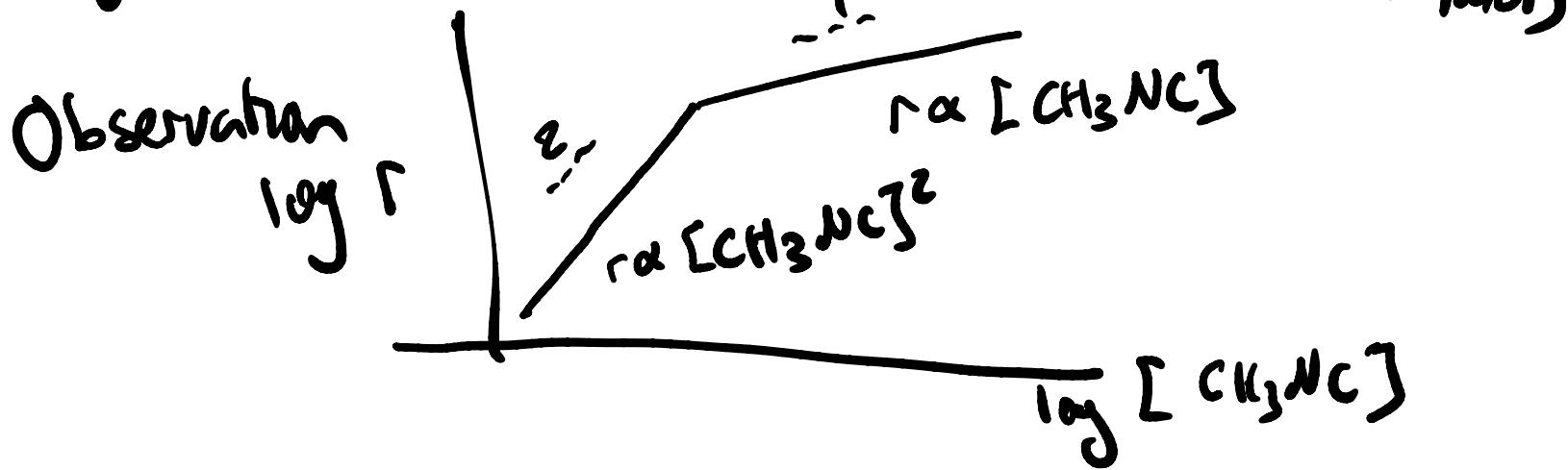
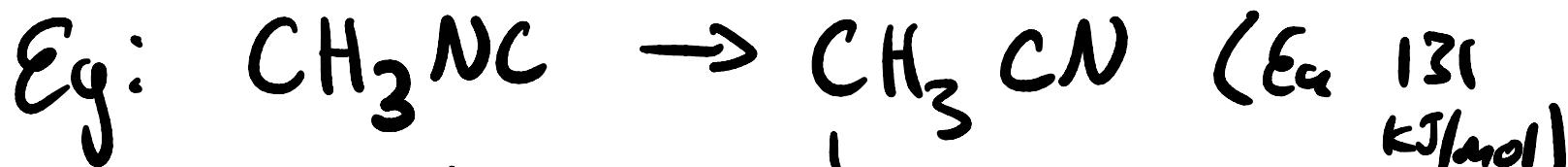
$$\frac{d[P]}{dt} = k_1[A] = k_1[A]_0 e^{-k_1 t}$$

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

equation for single step reaction

Lindemann Mechanism

Molecule gets activated by collision with another molecule





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

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

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

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

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

$$\frac{d[B]}{dt} = k_f^2 [A]^* = \frac{k_f^{(1)} k_f^{(2)} [A][M]}{k_f^{(3)} + k_b[M]}$$

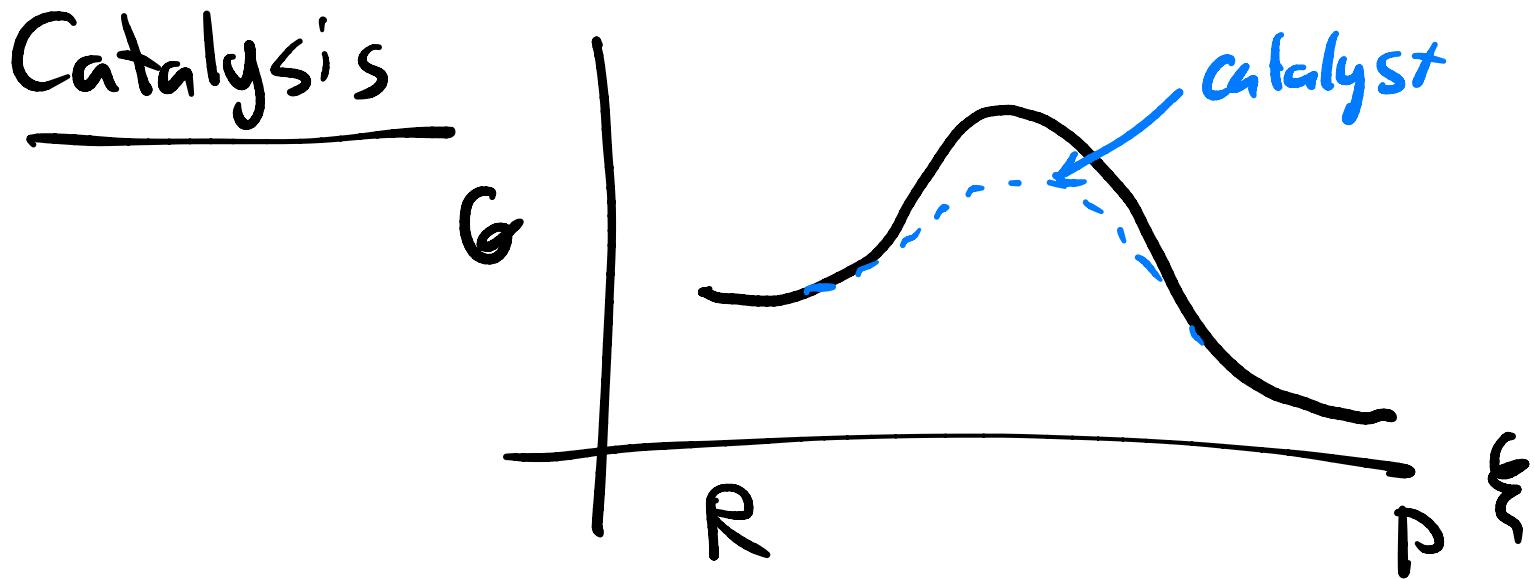
$$= \frac{k_f' k_f^2 [M]}{k_f^2 + k_b[M]}$$

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

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

at large $[M]$, $k_{obs} \approx \frac{k_p' k_f^2}{k_b}$
 (lot of deactivation)

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



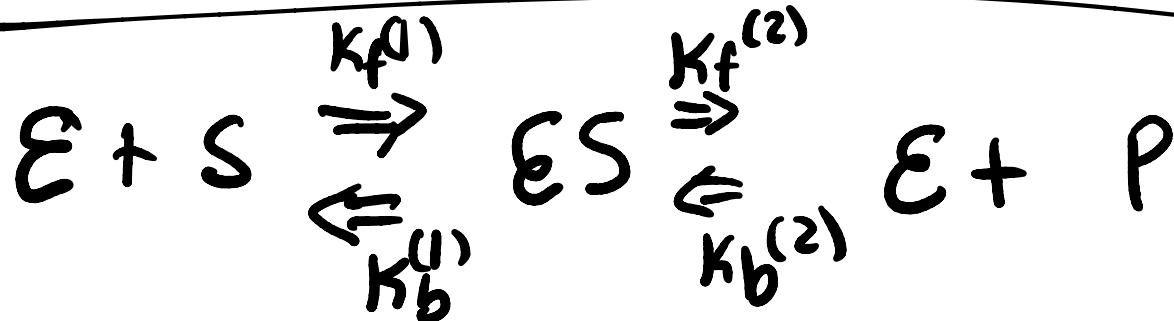
- Add but doesn't get used up
- different reaction path

Homogeneous catalyst mixed in
Enzymes

Heterogeneous (different phase)
usually a metal surface

Enzyme: biomolecule acts catalyst

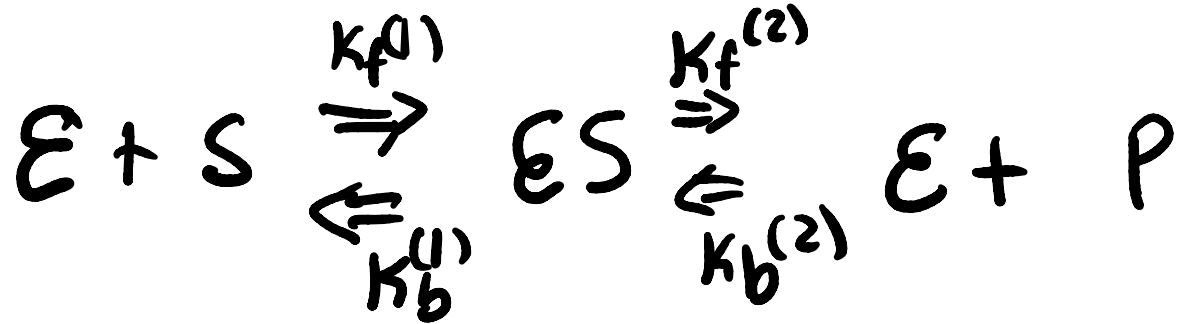
Michaelis-Menten Scheme



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

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

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



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

Assumption $[S] \gg [E]$

Enzyme conserved $[E]_0 = [ES] + [E]$
 $[E] = [E]_0 - [ES]$

$$\text{rate} = -d[S]/dt$$

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

Initial rate $[S] = [S]_0$
 $[P] \approx 0$

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

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