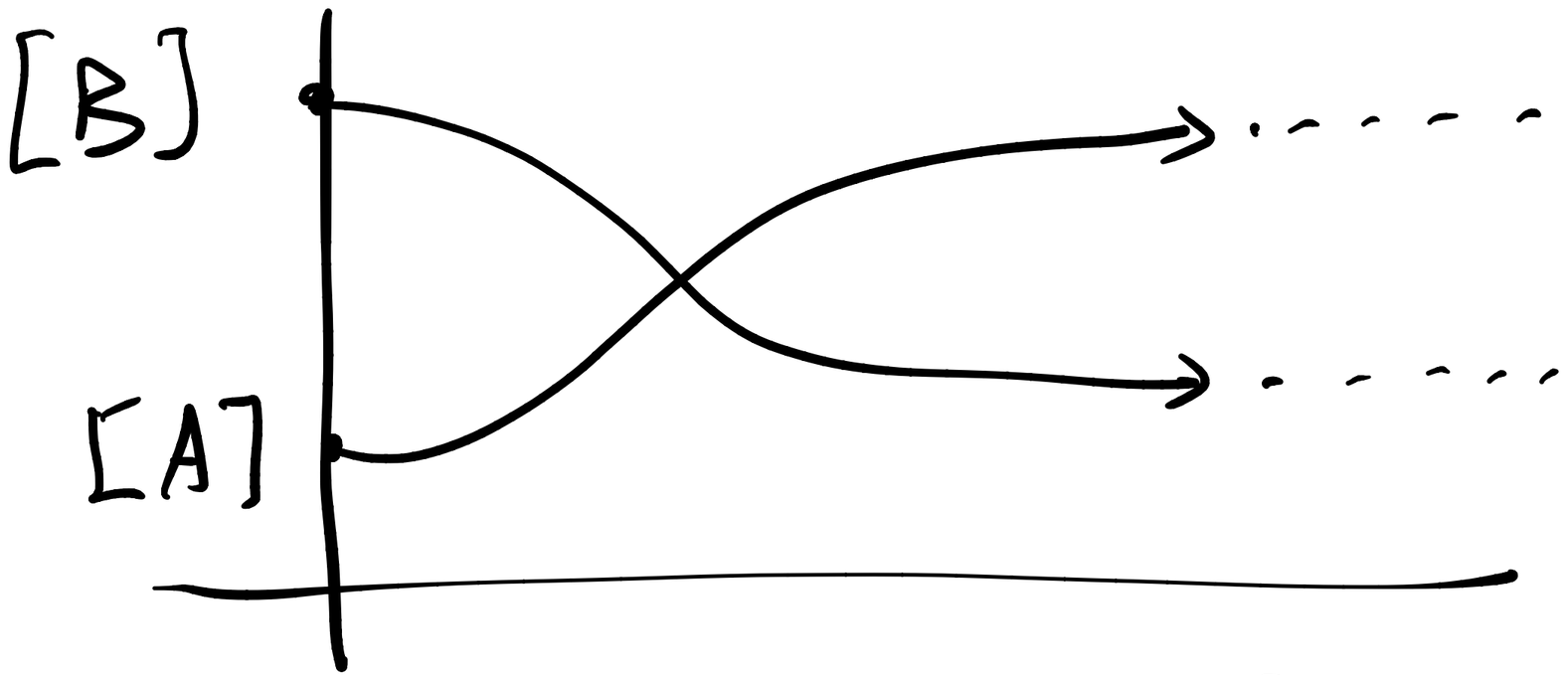
Previously Relaxation methods to get Rate Constants

Desired

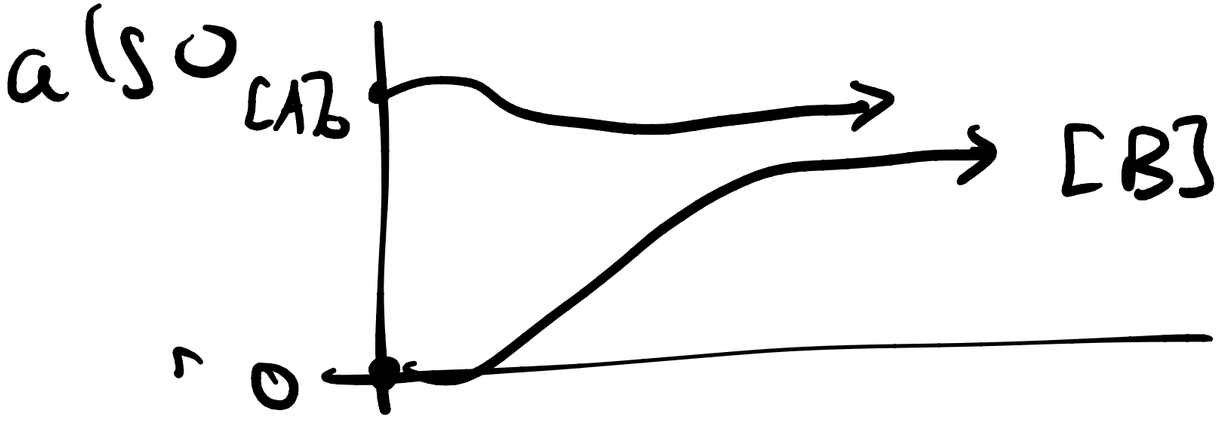
$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$[A] - [A]_{eq} = ([A]_0 - [A]_{eq}) e^{-(k_f + k_b)t}$$



$f_{:1}$ $k_f + k_b$

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f}{k_b}$$



Relaxation experiment

① let it go to eq.

② change conditions (P, T)

What happens in a T-jump experiment

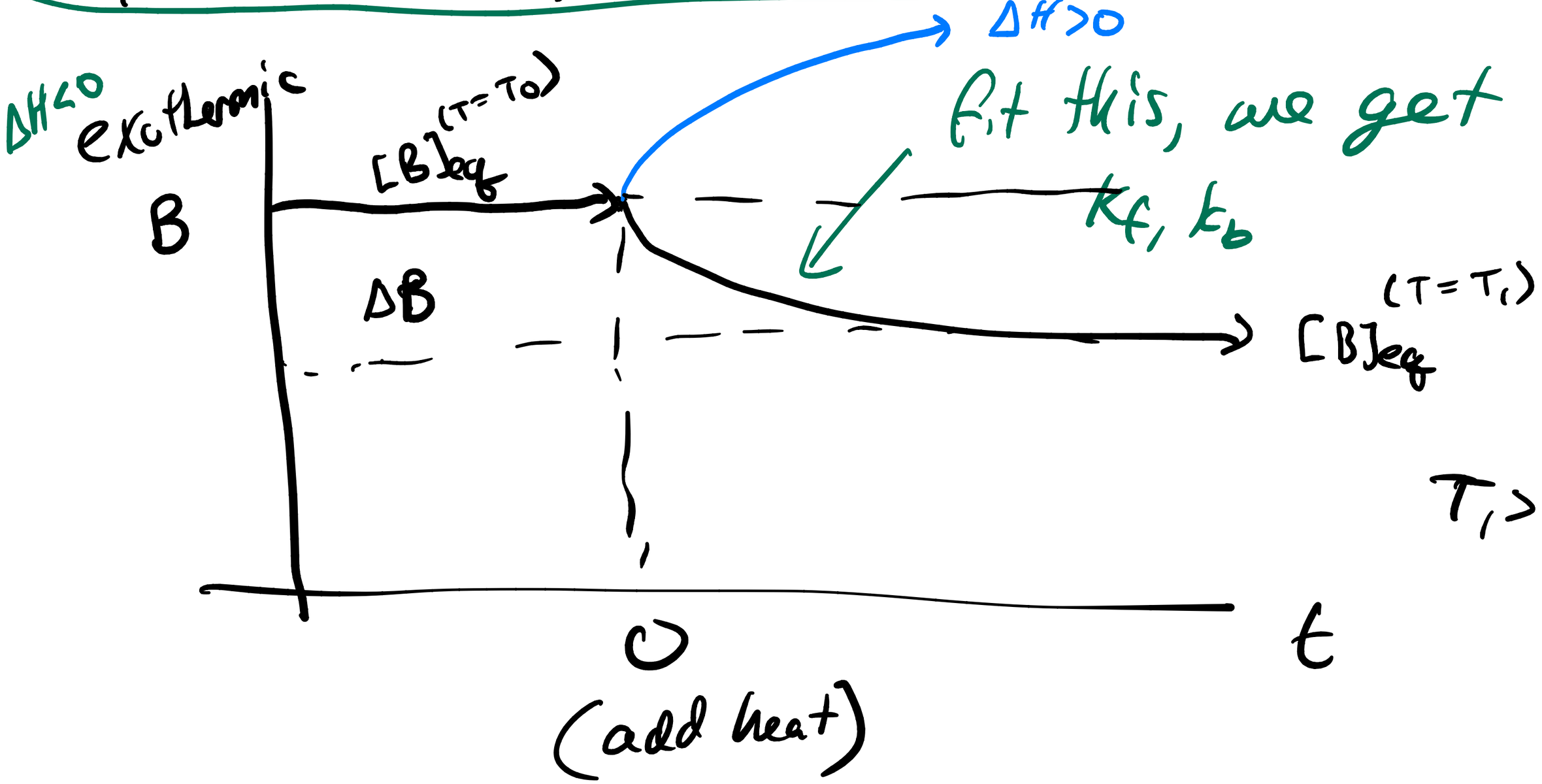
$$K_{eq} = e^{-\Delta G^\circ/RT} = e^{\left(-\Delta H^\circ/RT + \frac{\Delta S^\circ}{R}\right)}$$

$\Delta H^\circ < 0$ exothermic

$A \rightleftharpoons B$ (t q)

expect more A less B

for $\Delta H° > 0$, opposite



$$\Delta A(t) = [A] - [A]_{eq}^{T_1}$$

$$\Delta B(t) = [B] - [B]_{eq}^{T_1}$$

$$\frac{d\Delta B}{dt} = -(k_f + k_b)\Delta B$$

$$\Delta B = \Delta B(0)\, e^{-t(k_f + k_b)}$$

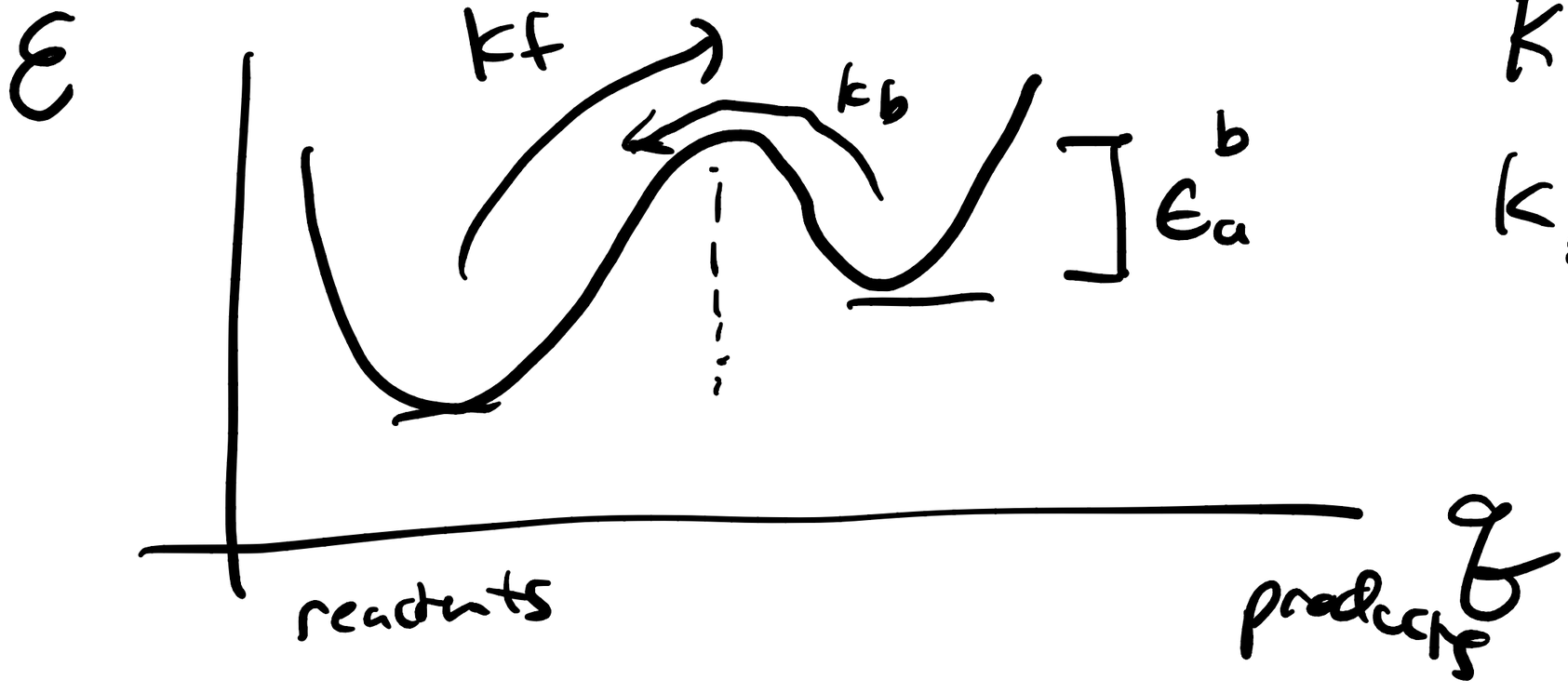
assume k_f, k_b don't change with temperature

Temperature dependence of rate constants

$$K = A e^{-E_a/k_B T}$$ (Arrhenius' Law)

E_a ↑ activation energy

TS



$$k_f = A e^{-E_a^f/k_B T}$$

$$k_b = B e^{-E_a^b/k_B T}$$

Get E_a?

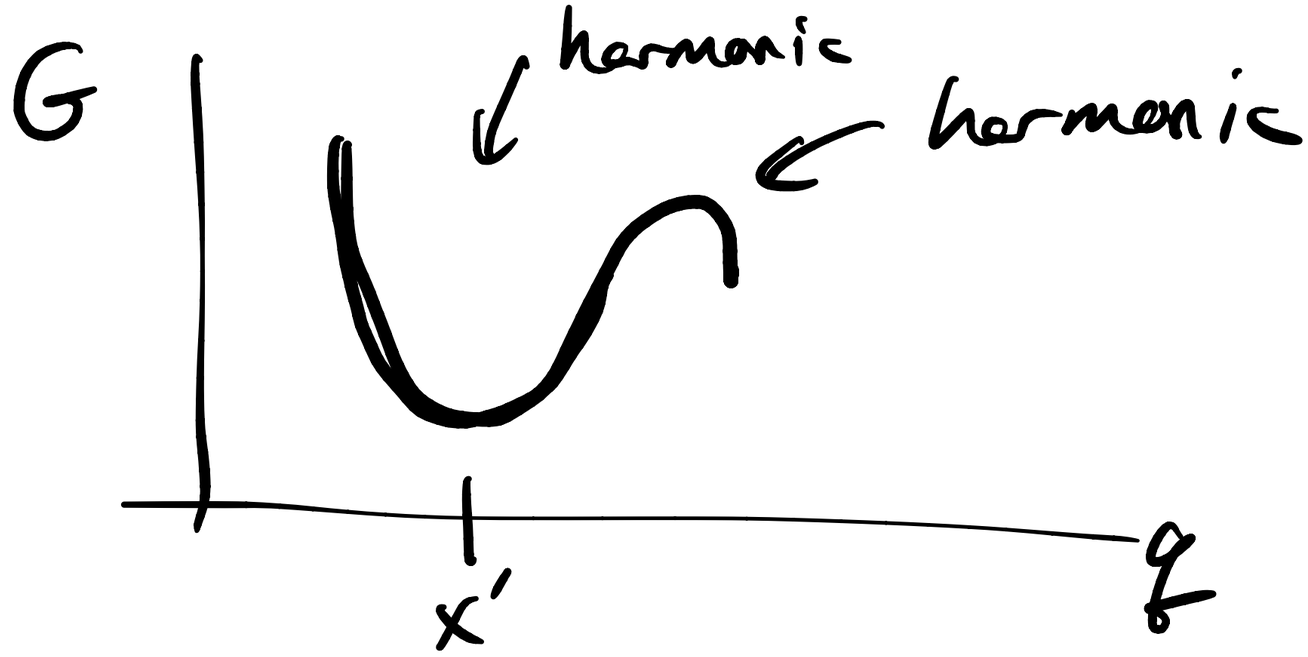
plot $\ln k$ vs $\frac{1}{k_B T}$, slope is $-E_a$

Sometimes, not a straight line

$$k = a\, T^m e^{-E_a/k_B T}$$

prefactor depends on how fast things can move in the reaction, & how fast barrier is crossed

An example: Kramers' theory



$$U_{well}(x) = \frac{1}{2}k(x-x')^2$$

$$= \frac{1}{2}m\omega^2(x-x')^2$$

ω ← frequency

$$k = \frac{\omega_{well}\,\omega_{barrier}}{2\pi}\,\frac{D}{k_B T}\,e^{-\Delta\bar{G}^{\ddagger}/RT}$$

Reaction Mechanisms

Story of elementary reactions
combine to give overall mechanism

often Reactants → I → Products

Elementary reaction is one with
no intermediates (we don't think)

Direct interactions between reactants

$$aA + bB \Rightarrow P$$

$$r = k[A]^a[B]^b \quad (\dots)$$

combine these and, some steps hidden

$$A + B \rightleftharpoons C$$

vs

$$A + x \rightleftharpoons Ax$$

$$Ax + B \rightleftharpoons C + x$$

Detailed Balance

@ Equilibrium, forward & reverse rates of all elementary reactions are equal

$$aA + bB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

$$r_f = k_f [A]_{eq}^{a} [B]_{eq}^{b}$$

$$r_b = k_b [C]_{eq}^{c} [D]_{eq}^{d}$$

) equal, for every elementary reaction

$$k_f [A]_{eq}^{a} [B]_{eq}^{b} = k_b [C]_{eq}^{c} [D]_{eq}^{d} \rightsquigarrow \boxed{K_{eq}^{i} = \frac{k_f^{i}}{k_b^{i}}}$$

D.B. links mechanism steps

$$A \rightleftharpoons B \qquad (1)$$

$$A + C \rightleftharpoons B + C \qquad (2) \quad \leftarrow \text{catalysis}$$

@ eq $\quad r_f^1 = r_b^1 \qquad k_f^1 [A]_{eq} = k_b^1 [B]_{eq}$

$r_f^2 = r_b^2 \qquad k_f^2 [A]_{eq} [C]_{eq} = k_b^2 [B]_{eq} [C]_{eq}$

divide equations:

$$\frac{k_f^1}{k_f^2} = \frac{k_b^1}{k_b^2}$$

Can get same condition

$$r_f^1 + r_f^2 = r_b^1 + r_b^2$$

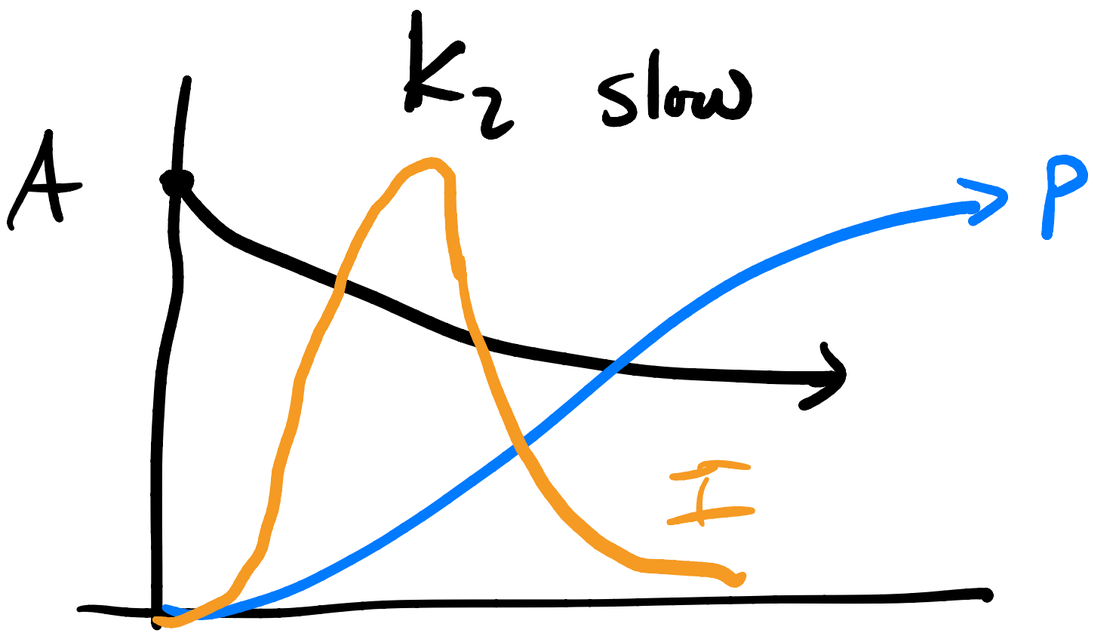
How can we tell if there is an intermediate ...

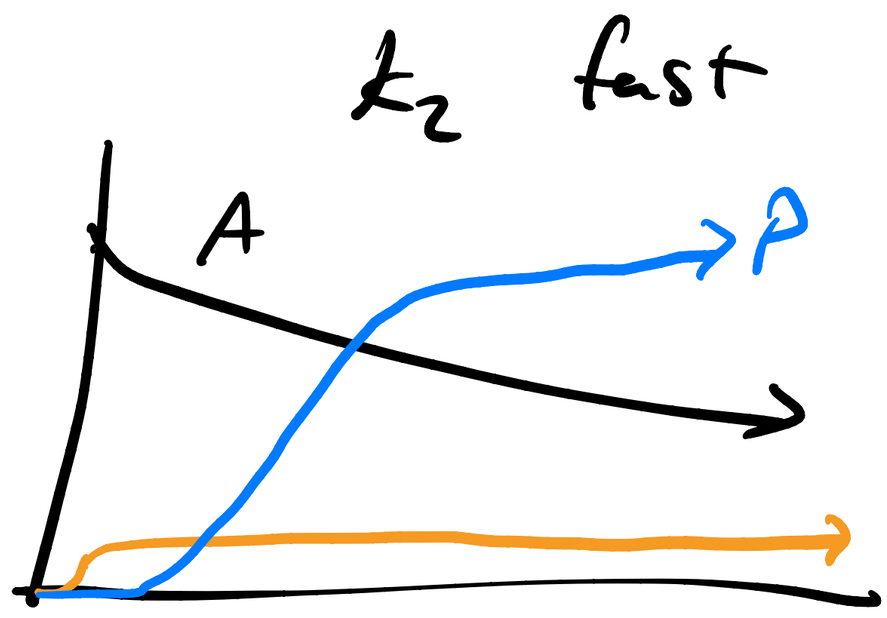
$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

vs

$$A \xrightarrow{k_3} P$$

can't detect





Next time:

Approximation: Steady state for the intermediate

$$\frac{d[I]}{dt}^{ess} = 0 = k_f'[A] - k_b'[I]_{ss} + k_f^2[I]_{ss}$$

$$A \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} I \xrightarrow{k_f^2} P$$