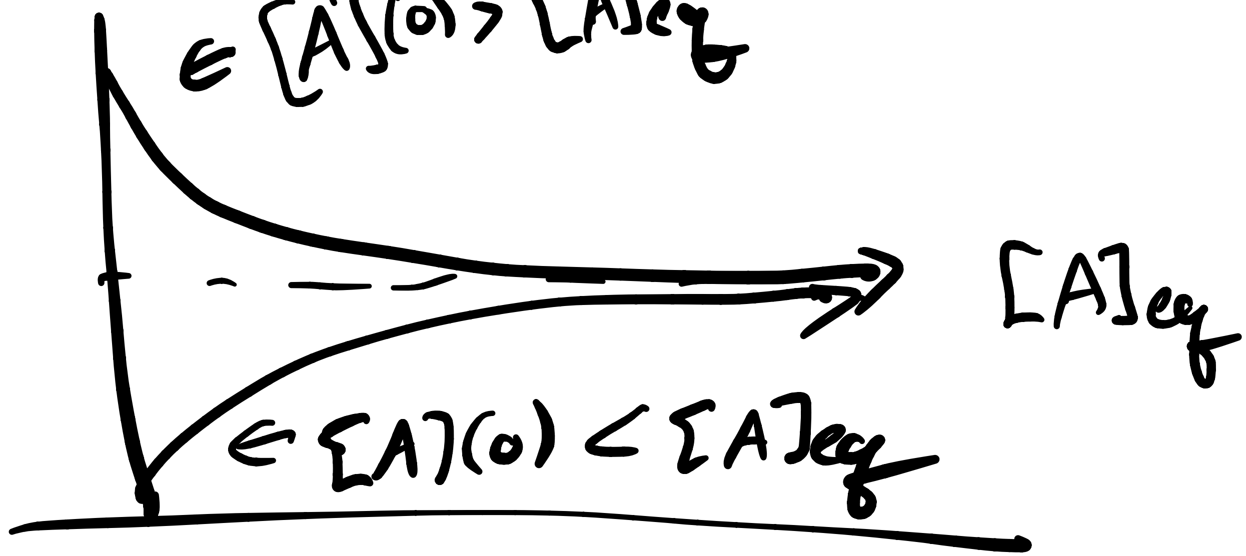
Finishing reaction mechanisms

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B \qquad r = -\frac{1}{\nu_i}\frac{d[i]}{dt}$$

$$\frac{d[A]}{dt} = -k_f[A] + k_b[B] = -r(t)$$

$$\frac{d[B]}{dt} = -k_b[B] + k_f[A] = r(t)$$



$$[A](t) - [A]_{eq} = \left([A](t=0) - [A]_{eq}\right)e^{-\nu t}$$

$$[A](t) = [A]_{eq} + \left([A](0) - [A]_{eq}\right)e^{-\nu t}$$

$$\nu = \underline{(k_f + k_b)}$$

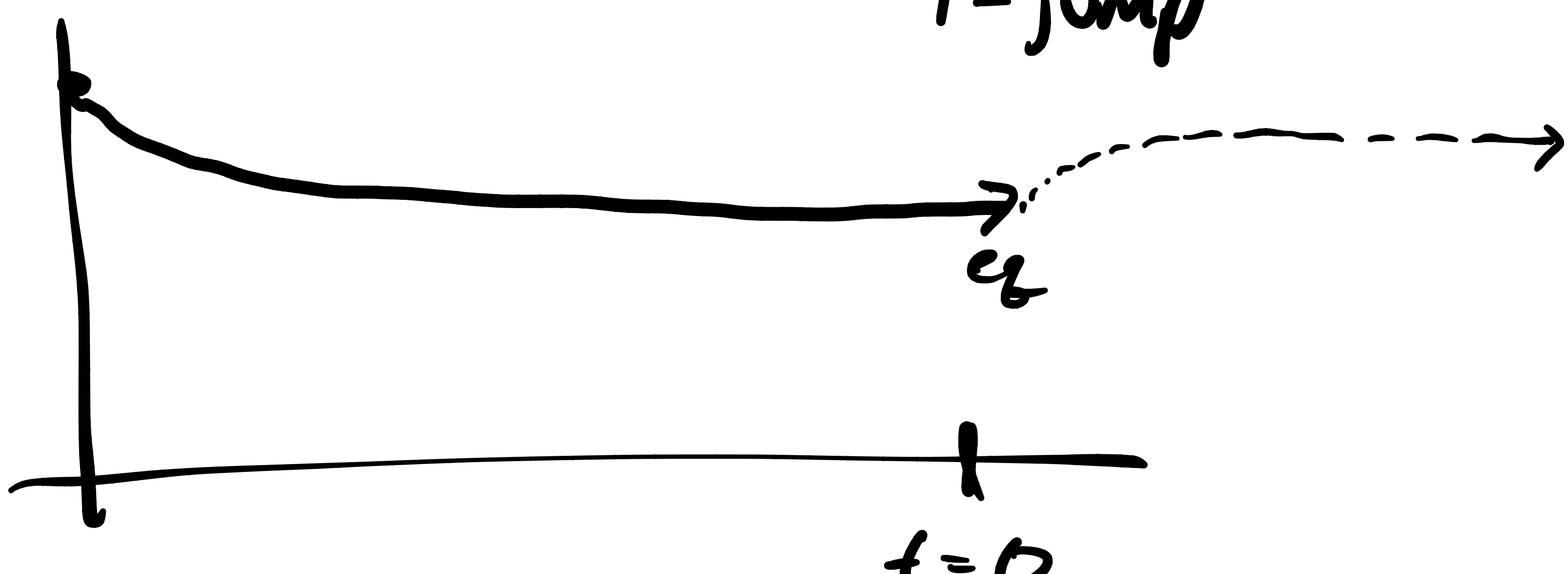
How determine mechanism

→ excess of species (not feasible)

→ method of initial rates (doesn't work for slow mixing)

→ method of relaxation

T-jump



what happens to eq constant

$$K_{eq} = \frac{[B]}{[A]} = e^{-\Delta \bar{G}^\circ / RT}$$

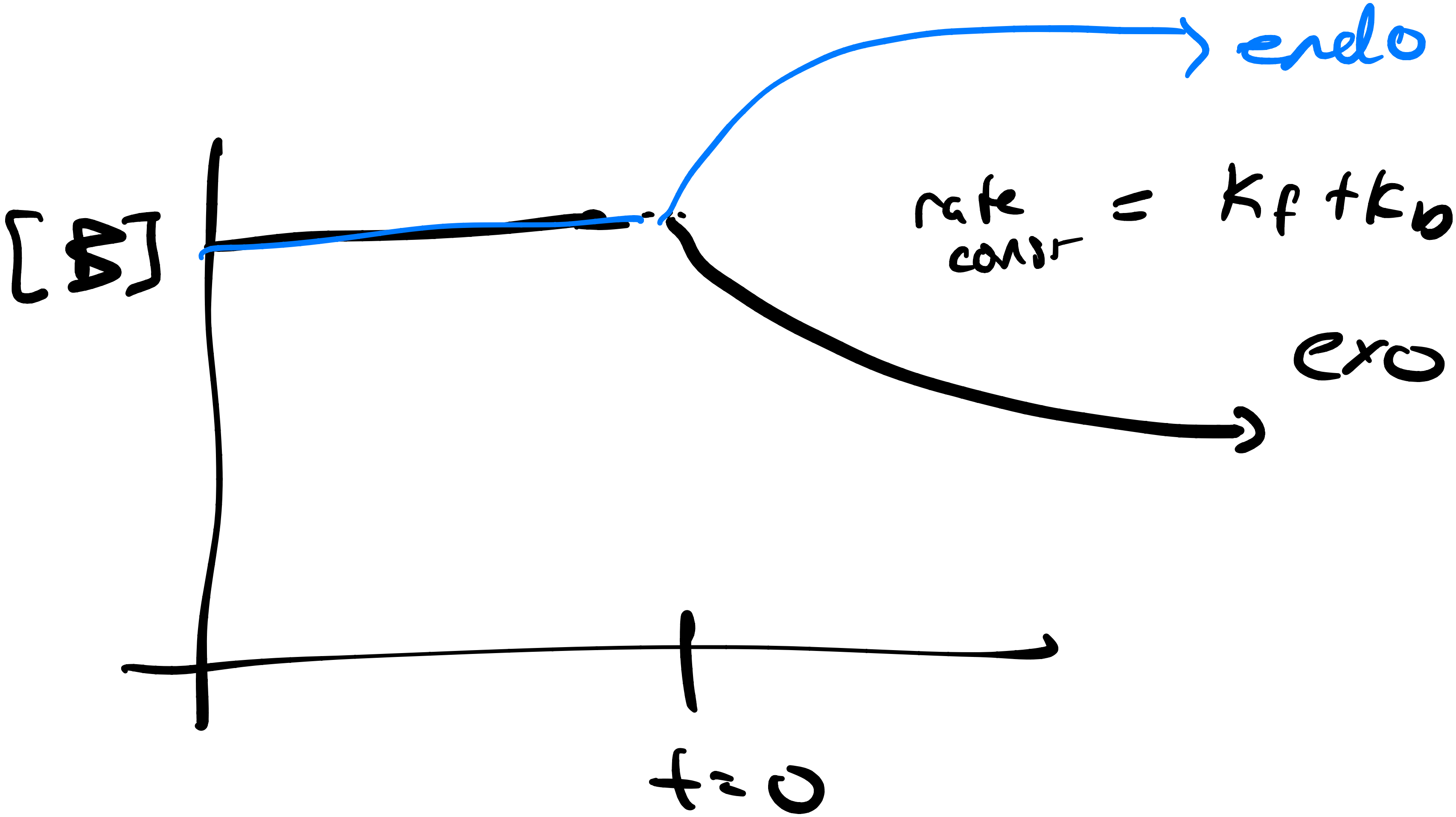
$$= e^{-\frac{\Delta \bar{H}^\circ}{RT} + \frac{\Delta \bar{S}^\circ}{R}}$$

if $\Delta \bar{H}^\circ < 0$ exothermic

$A \rightleftarrows B + q$, $T \uparrow$ favor reactants

if $\Delta \bar{H}^\circ > 0$

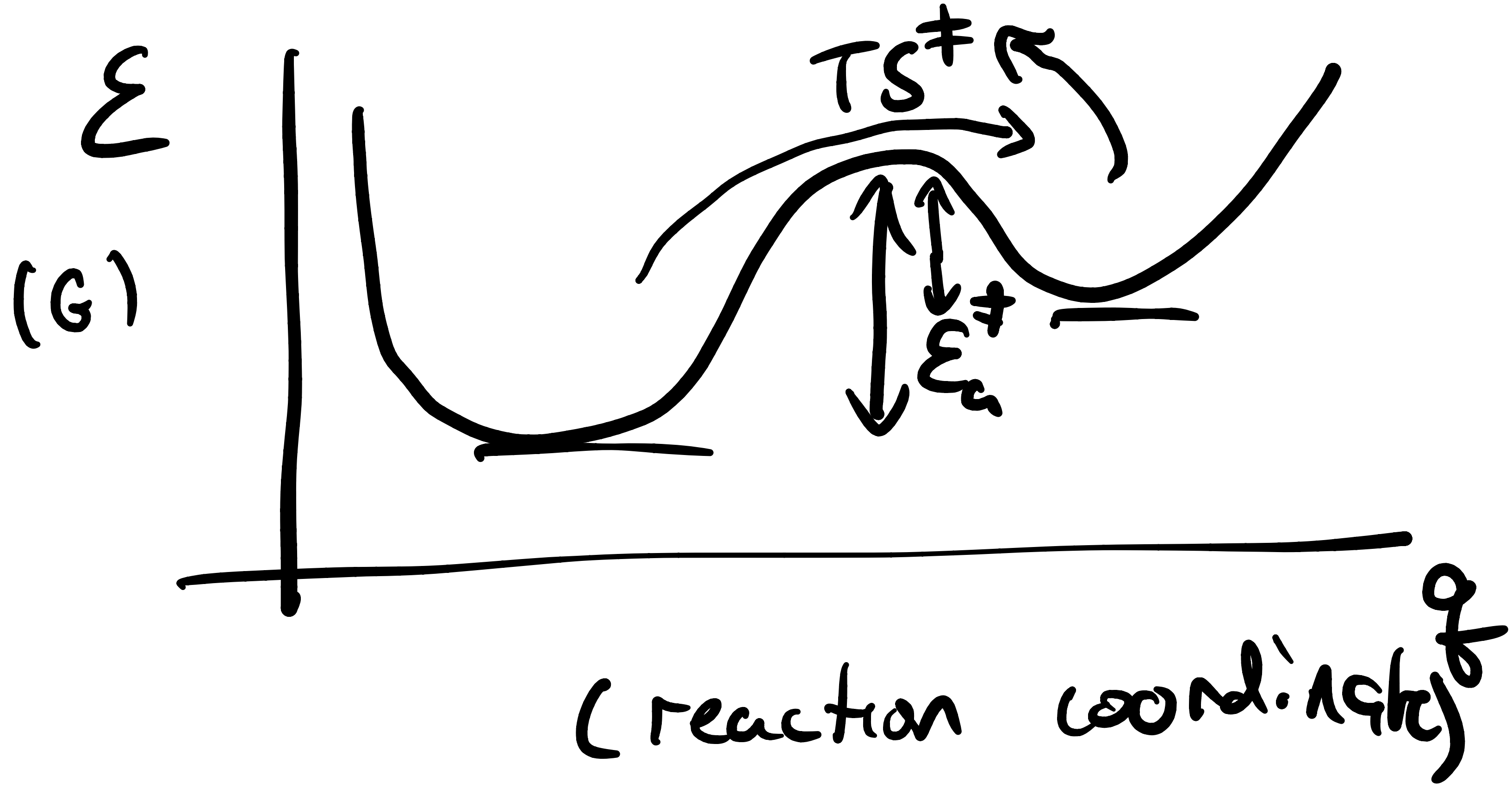
$q + A \rightleftarrows B$ $T \uparrow$ favors products



[B]
endo
rate const = $k_f + k_b$
exo
t=0

Temperature dependence of rate constants

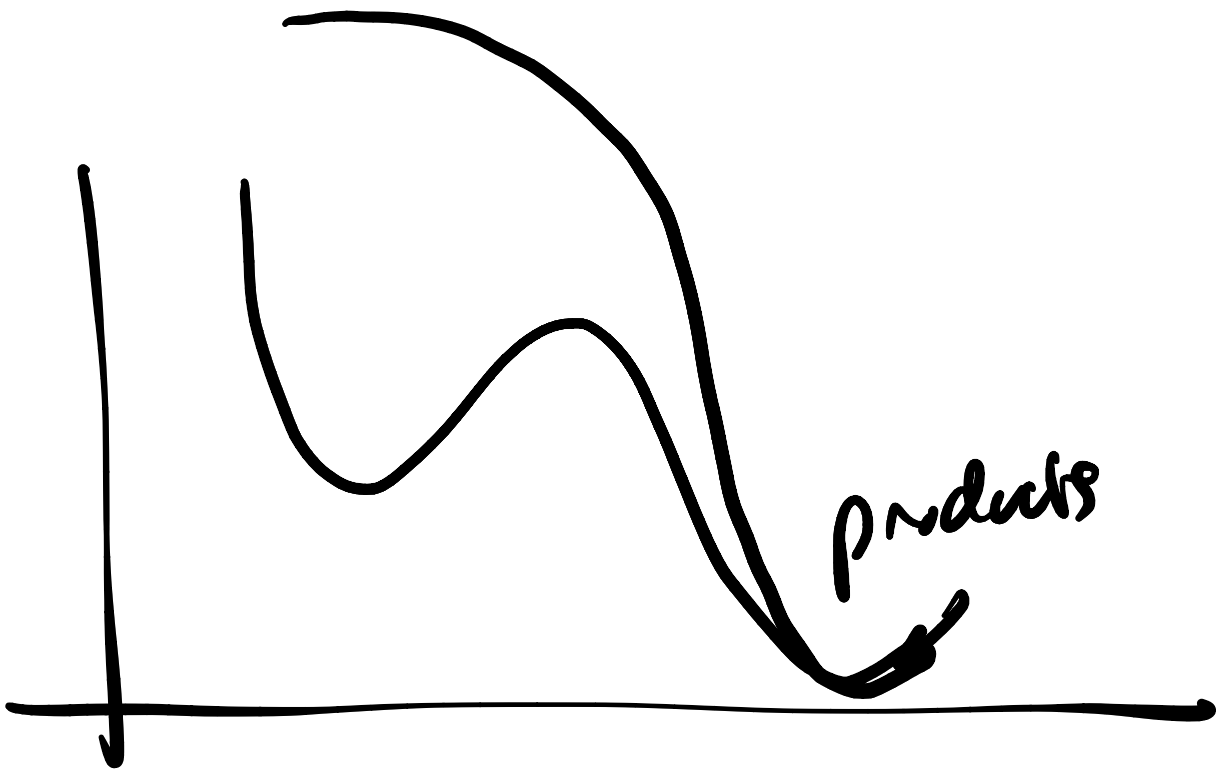
typically is slow reactions at low temperatures

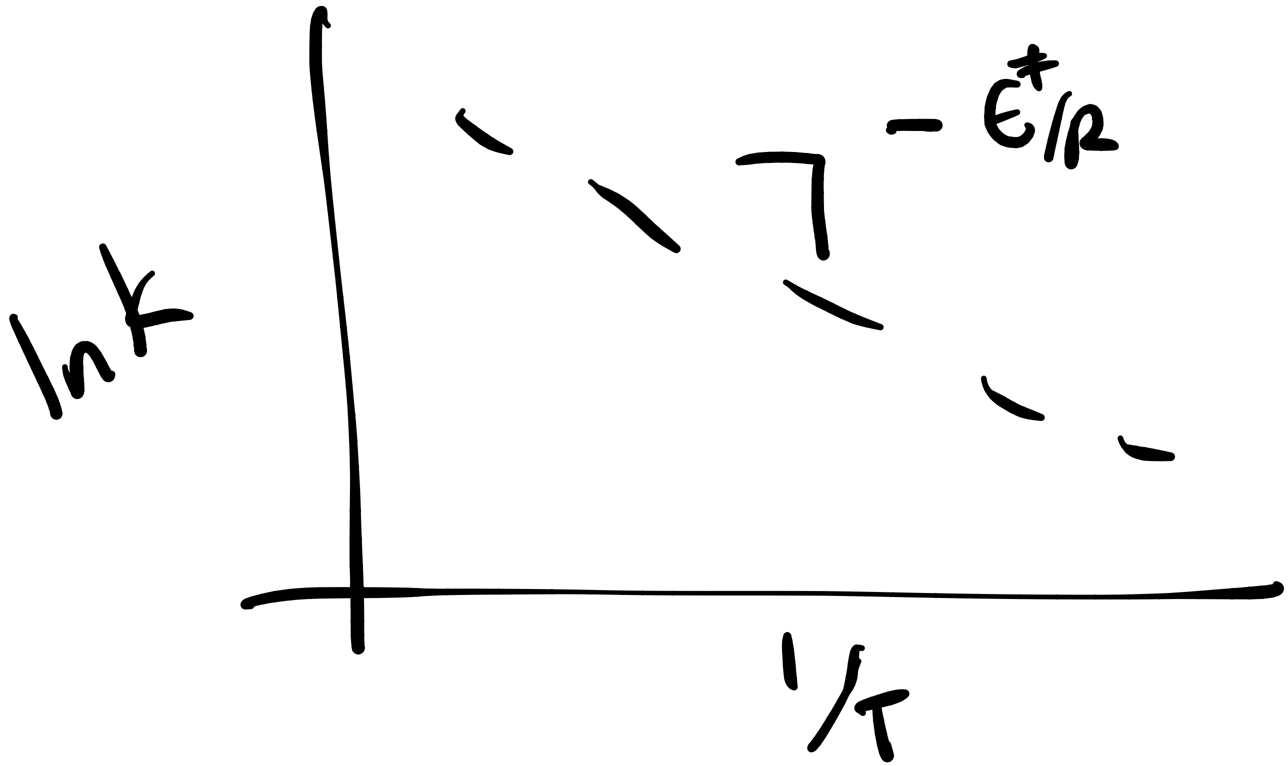


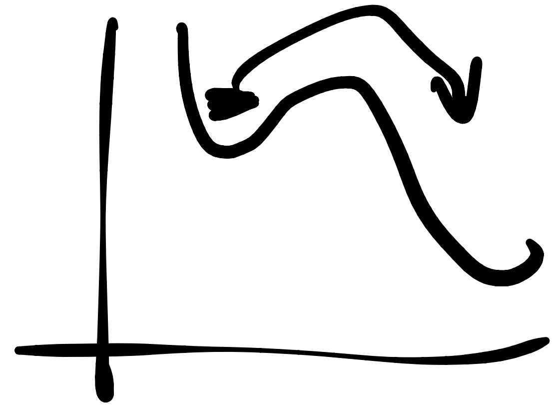
$$K = e^{-\Delta G / RT}$$

$$k_f = A e^{-\varepsilon_f^{\ddagger}/RT} \quad \text{(Arrhenius)}$$

$$k_b = B e^{-\varepsilon_b^{\ddagger}/RT}$$







in fact $k = aT^{m} e^{-\epsilon^{\ddagger}/RT}$

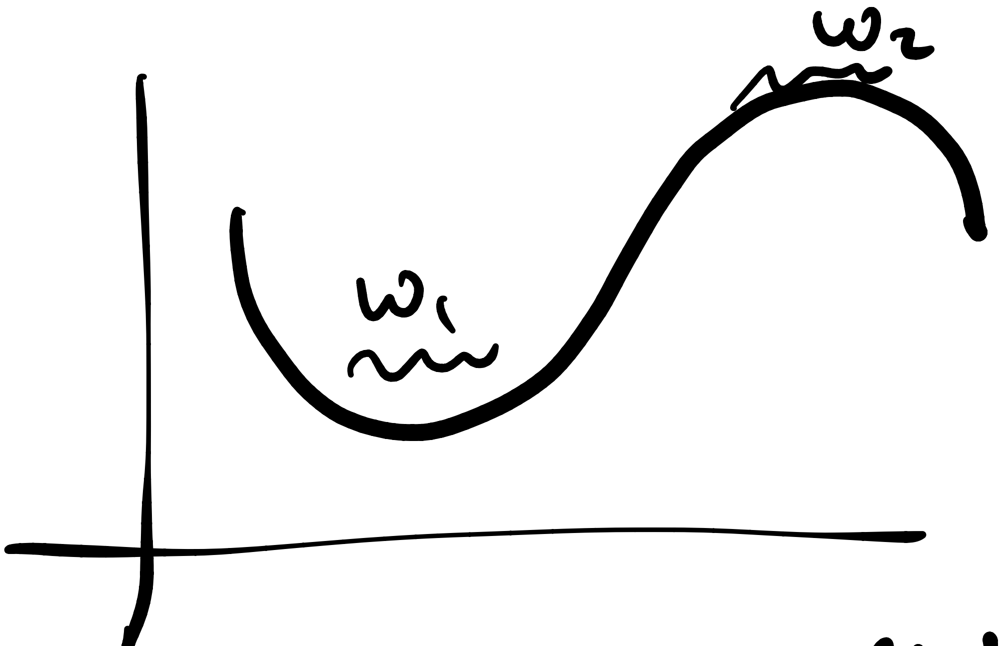
m could be 1, $1/2$, $-1/2$

not straight line above

(28-8)

<u>example</u> Kramer's theory

$$\text{rate} = \frac{\omega_1 \omega_2}{2\pi} \frac{KT}{D} e^{-\Delta F^{\ddagger}/RT}$$



→ how fast you move in basin

→ " " " cross barrier

Ch 29 Reaction mechanisms

Elementary reactions

$$aA + bB \to C$$

$$\text{rate forward} = K[A]^a[B]^b \cdot \text{etc}$$

direct collisions

Can be many hidden steps

different rate laws emerge

<u>Key principle</u>: Detailed balance

rates of all elementary reactions are balanced @ equilibrium

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

$$\text{rate } f = k_f^i [A]^a [B]^b$$

$$\text{rate } b = k_b^i [C]^c [D]^d$$

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

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

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

$$K_{eq} = k_f / k_b$$

if you know $k_f + k_b$

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

then you know all 3 quantities

Detailed balance links steps in reactions

$$A \underset{k_b^1}{\overset{k_f^1}{\rightleftharpoons}} B$$

(catalyst)

$$A + C \underset{k_b^2}{\overset{k_f^2}{\rightleftharpoons}} B + C$$

$$r_f^1 = r_b^1 \qquad r_f^2 = r_b^2$$

$$k_f^1 [A]_{eq} = k_b^1 [B]_{eq}$$

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

$$\Rightarrow \quad k_f^2 / k_f^1 = k_b^2 / k_b^1$$

Intermediates

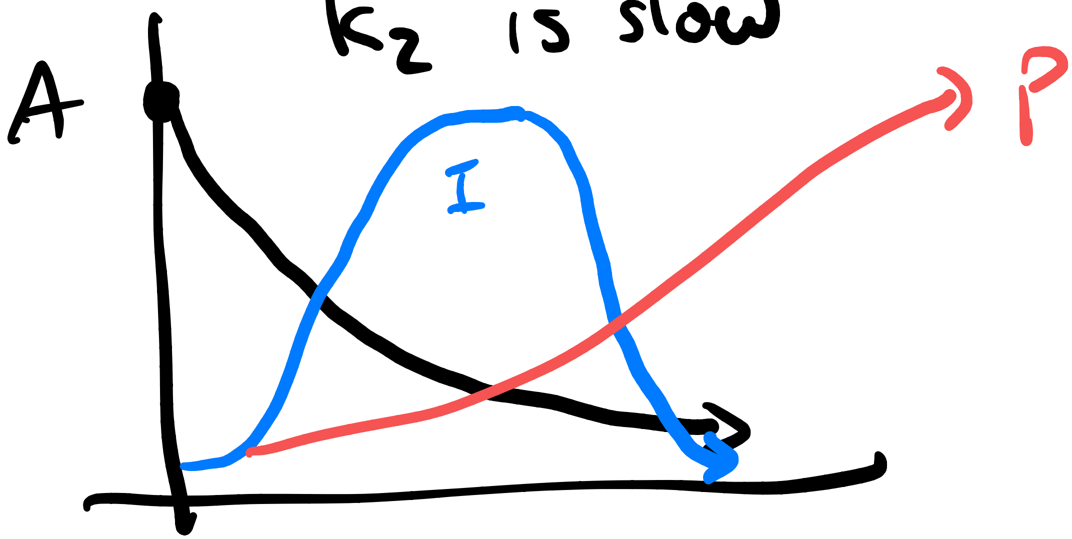
how do you know

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P_{roduct}$$

$$A \xrightarrow{k_3} P$$

can't distinguish

k_2 is slow



k_2 fast