Rate laws

$$r(t) = k [A]^{M_A} [B]^{M_B} \cdots$$

initial rates method

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$
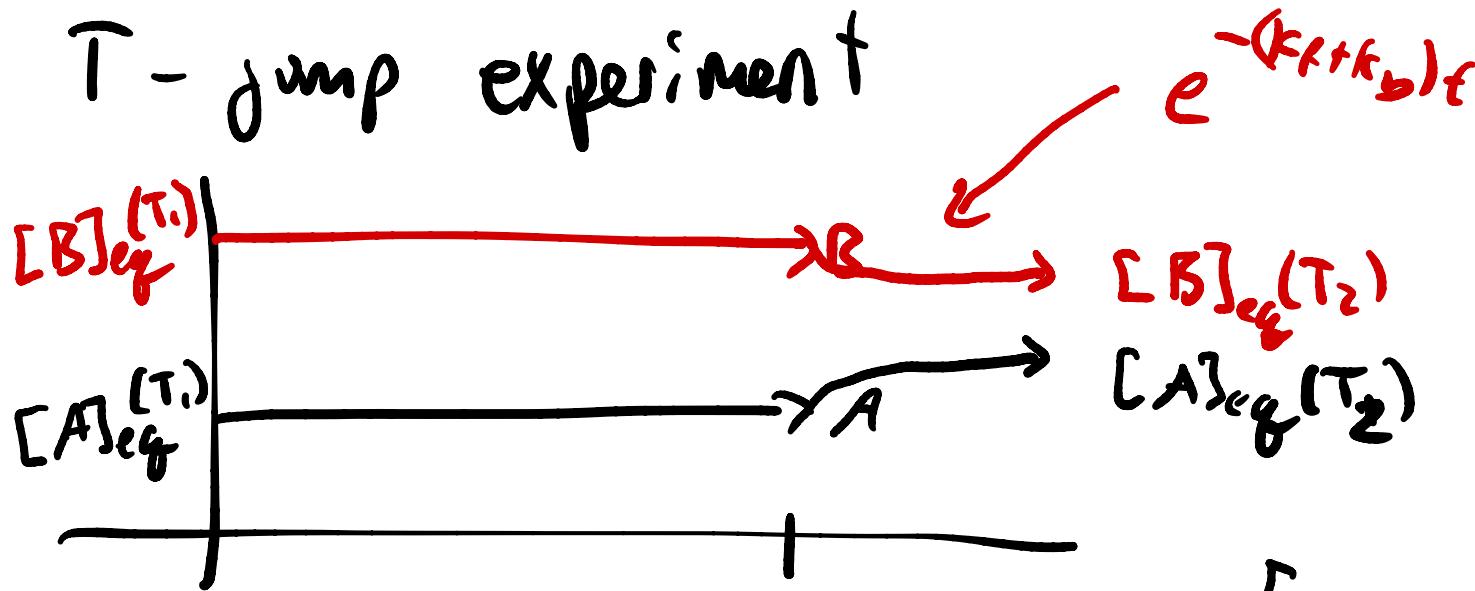
$$k_{rxn} = k_f + k_b$$
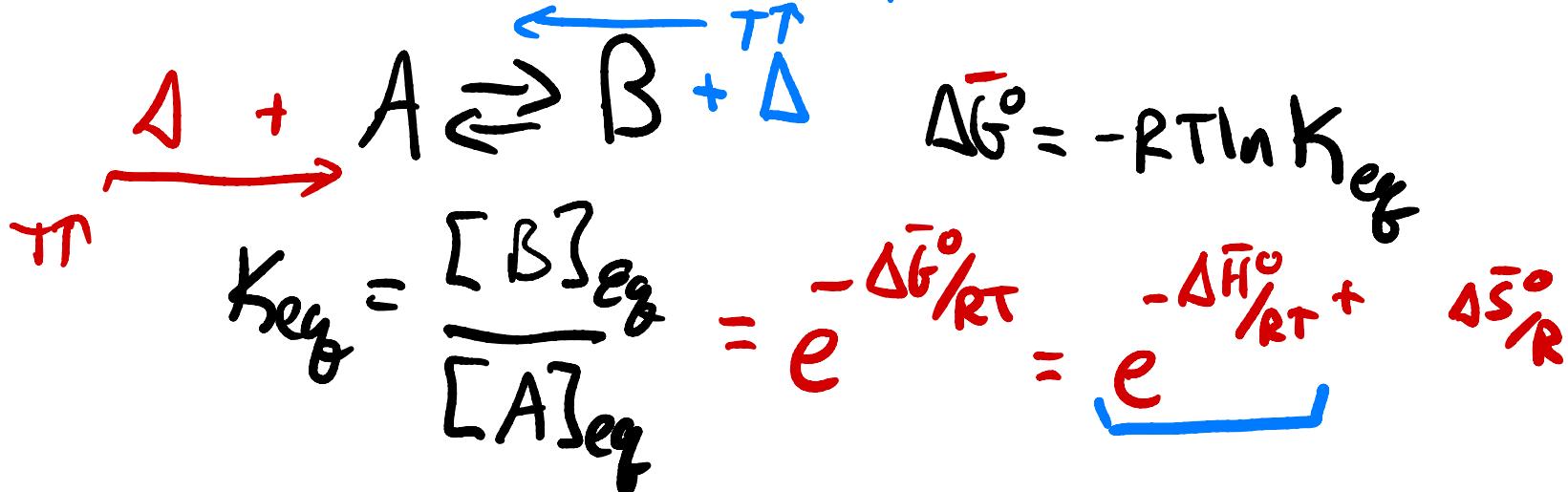
fit to equation

T - jump experiment

$e^{-(k_f + k_b)t}$

$[B]_{eq}^{(T_1)}$ ──────────→ B ───────→ $[B]_{eq}(T_2)$

$[A]_{eq}^{(T_1)}$ ──────────→ A ───────→ $[A]_{eq}(T_2)$

change to T_2

[Onsager regression hypothesis]

relaxation to equilibrium follows same rate law as the reaction

$$\Delta + A \rightleftharpoons B + \Delta$$

$$\Delta G^0 = -RT \ln K_{eq}$$

$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = e^{-\Delta \bar{G}^0/RT} = e^{-\Delta \bar{H}^0/RT \, + \, \Delta \bar{S}^0/R}$$
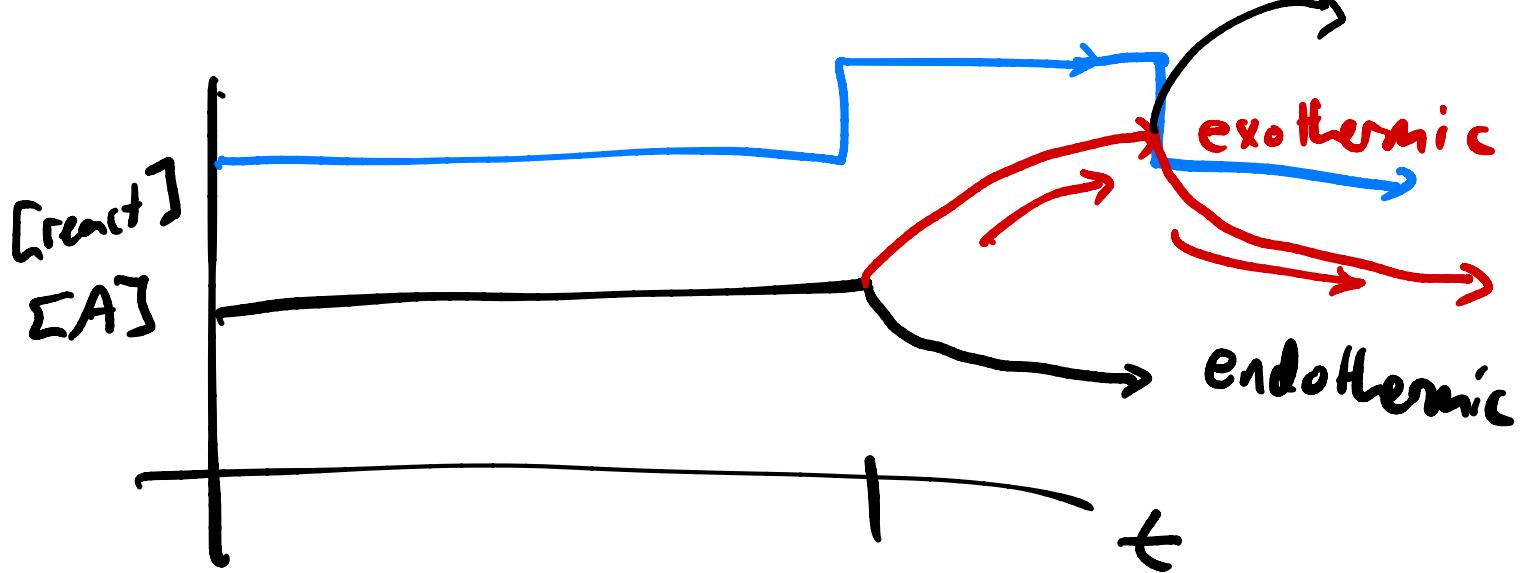
What happens when we change T?

Explicit T dep most important

$$\Delta \bar{H} > 0$$

$$\text{or } \Delta H < 0$$

eg exothermic reaction
$$\Delta H < 0$$

endothermic $\Delta H > 0$

[react]
[A]

exothermic

endothermic

t
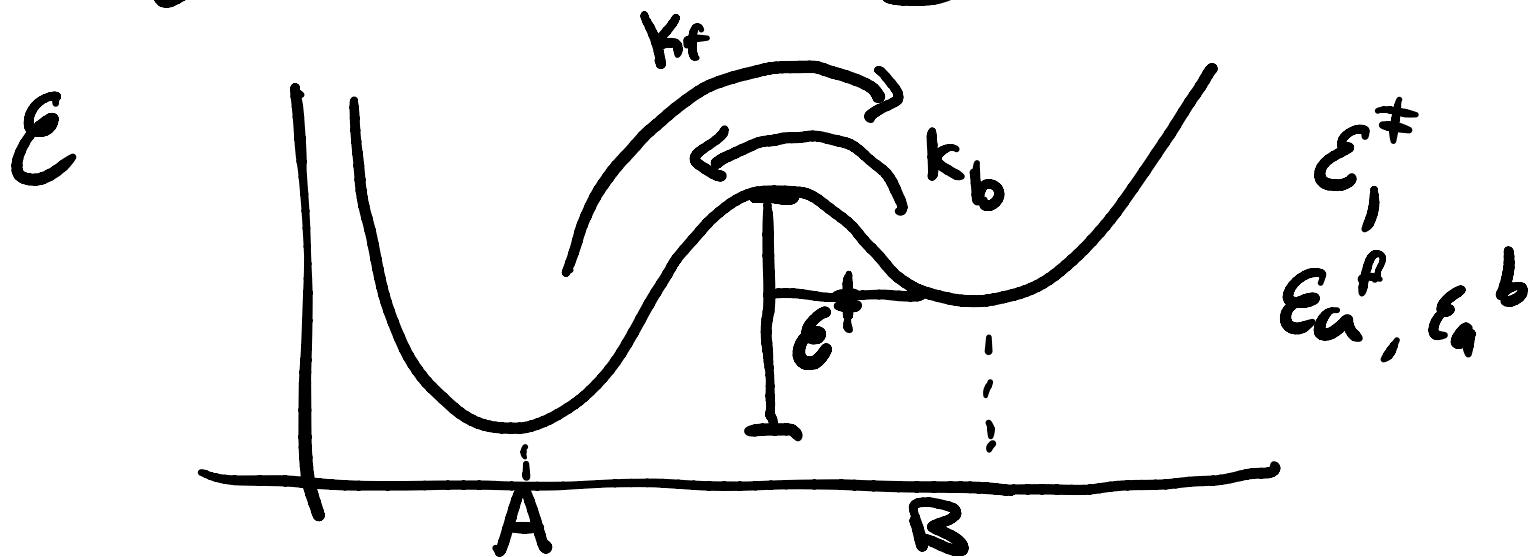
T-jump

How does K_{eq} depend on T
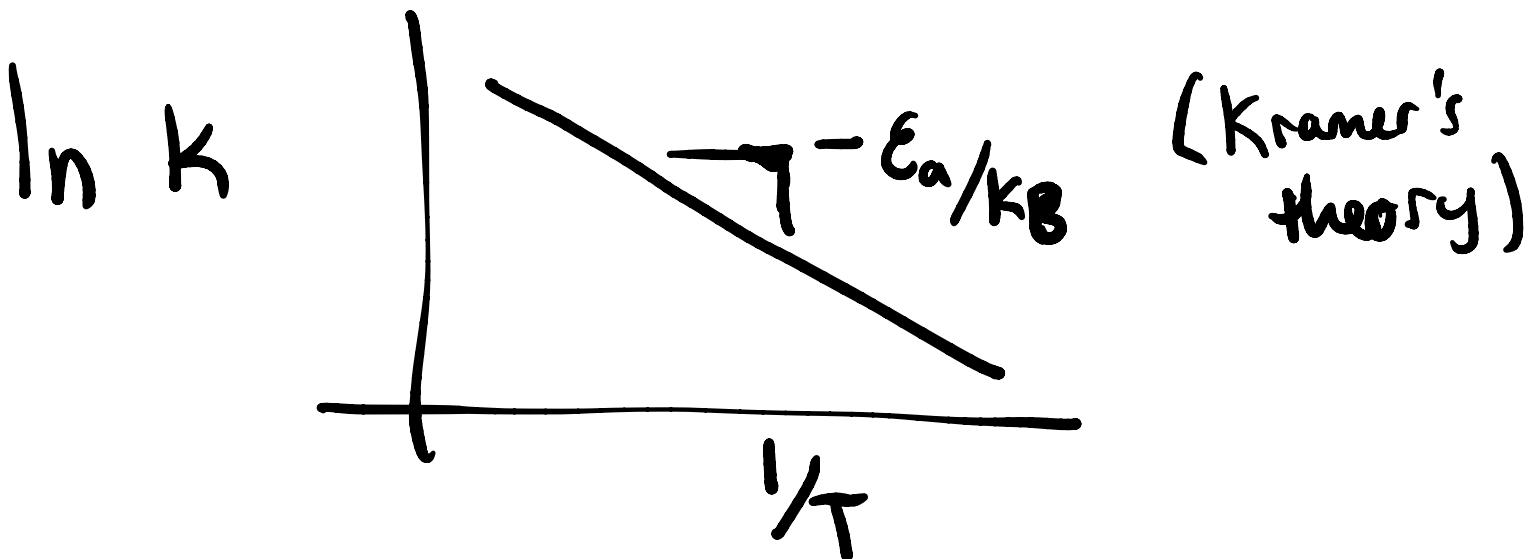
how does a rate constent depend on T

$$\frac{dA}{dt} = -k_f[A] + k_b[B]$$

$\mathcal{E}$

k_f

k_b

$\mathcal{E}^{\ddagger}$

A

B

$\mathcal{E}_1^{\ddagger}$

$\mathcal{E}_a^f, \mathcal{E}_a^b$

Arrhenius's law

$$k = Ae^{-\varepsilon_a / k_B T} = Ae^{-\bar{\varepsilon}_a / RT}$$

$\ln k$

$-q^{-\bar{\varepsilon}_a / k_B}$

(Kramer's theory)
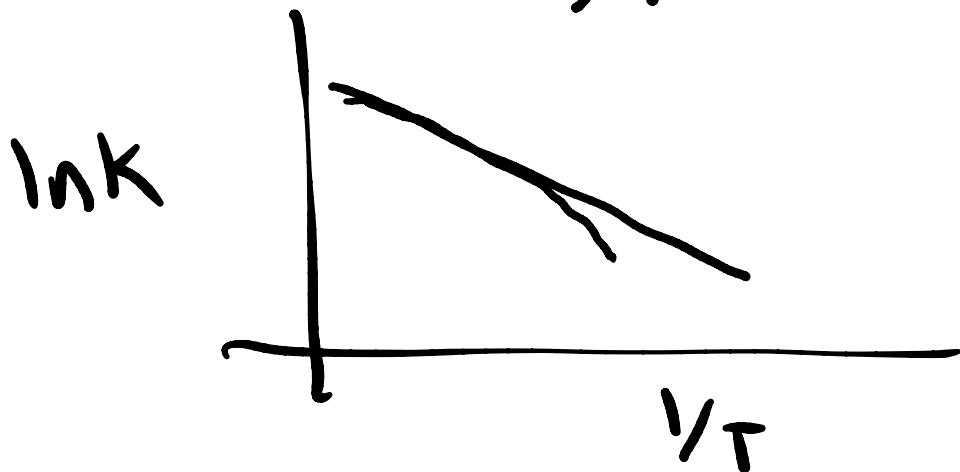
$\frac{1}{T}$

Reality, rxns fit

$$K = \underbrace{a\,T^m}_{A}\, e^{-\bar{\xi}/RT}$$

$\ln K = \text{cont} + m\ln T$
$\qquad\qquad - E_a/RT$

$\ln K$

$1/T$
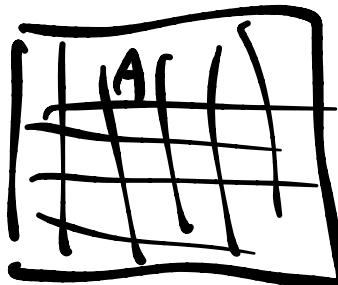
Ch 29 - Reaction mechanisms

Combining elementary reaction
to get overall reaction

$$a A + b B \implies products$$
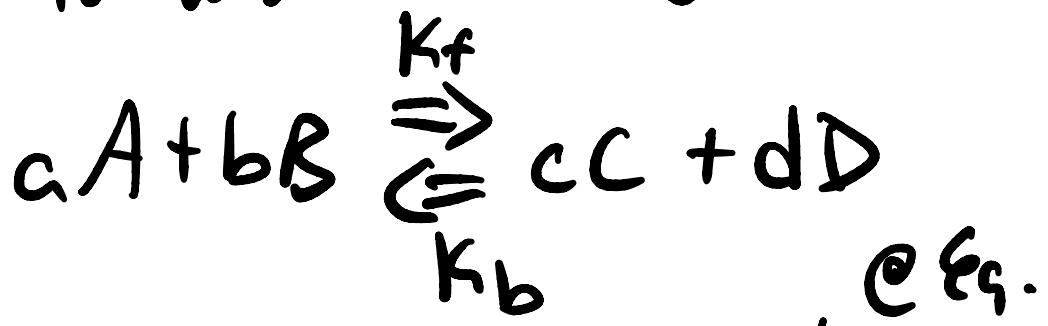
$$r(t) = k [A]^a [B]^b$$

Detailed Balance

At equilibrium rates of all elementary forward and reverse reactions are equal

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

@ Eq.
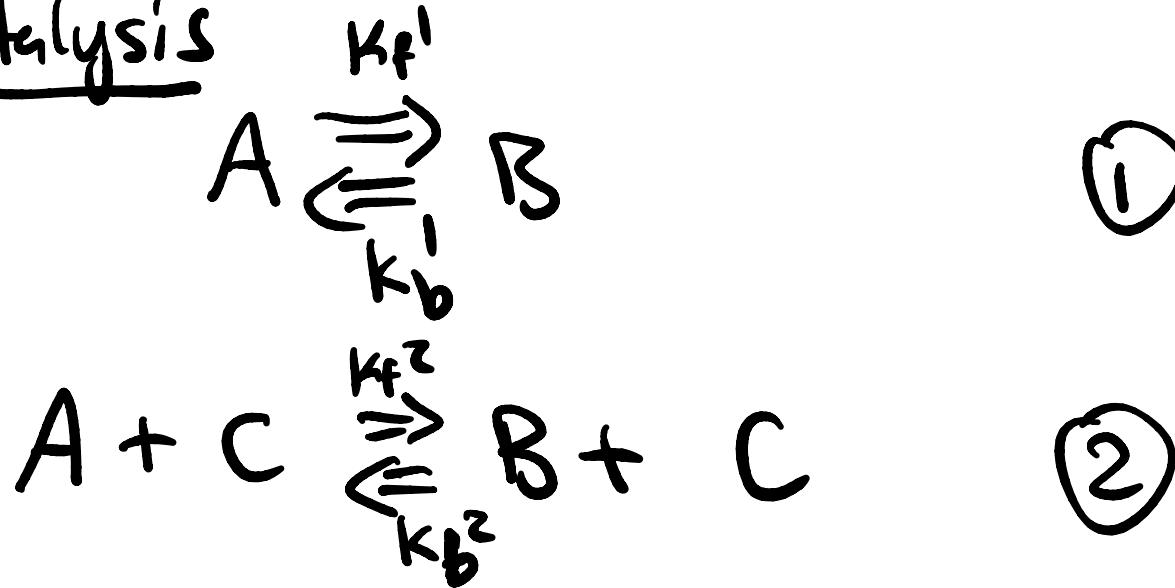
$$r_f = k_f [A]^a [B]^b$$

$$r_b = k_b [C]^c [D]^d$$

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

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

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

for each elementary reaction

Catalysis

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

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

D.B.

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

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

$$k_f^1 [A]_{eq} = k_b^1 [B]_{eq} \quad \nearrow$$
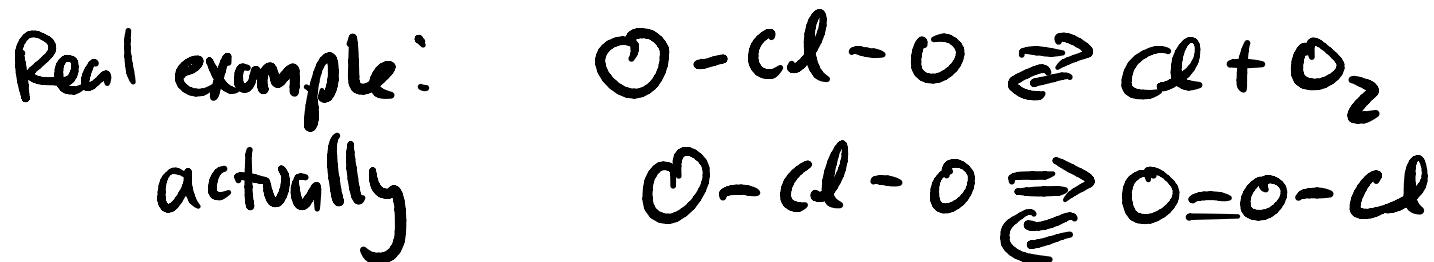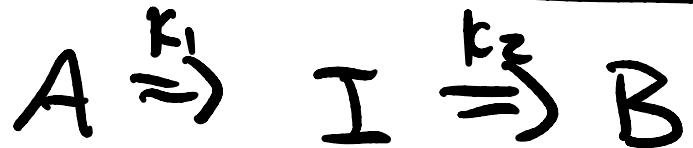
$$k_f^2 [A]_{eq} \cancel{[C]_{eq}} = k_b^2 [B]_{eq} \cancel{[C]_{eq}}$$
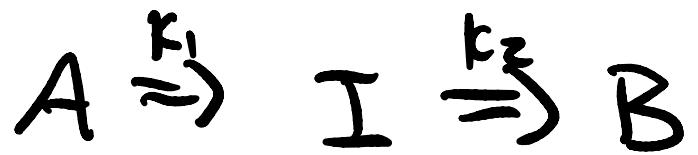
$$k_f^1 / k_f^2 = k_b^1 / k_b^2$$

rate constants are linked

$$r_f^1 + r_f^2 = r_b^1 + r_b^2 \quad @ \; eq$$

How do we know if elementary reaction

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

Real example: $O-Cl-O \rightleftharpoons Cl + O_2$

actually $O-Cl-O \rightleftharpoons O=O-Cl$

$ClOO \rightleftharpoons Cl + O_2$

$OClO \Rightarrow ClOO \Rightarrow Cl + O_2$

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

$$\frac{d[A]}{dt} = -k_1[A] \Rightarrow [A](t) = [A](0) e^{-k_1 t}$$

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

$$\frac{d[B]}{dt} = k_2[I]$$
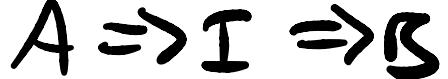
$$\int \frac{d[I]}{dt} = \int k_1[A] - k_2[I] \quad \text{(prob 29-5)}$$

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

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

$$\frac{dB}{dt} = k_2 \cdot I \quad / \quad B = A_0 - I - A$$

$$A \Rightarrow I \Rightarrow B$$

$$[B] = [A_0]\left(1 + \frac{1}{k_1 - t_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right)$$

if there was no I

$$[B] = [A]_0\left(1 - e^{-k_1 t}\right)$$

When different?
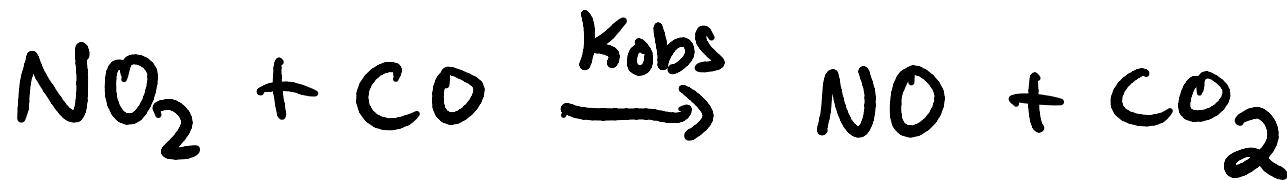
if $k_2 \gg k_1$, can't tell difference

if $k_1 \gg k_2$, measure $-\frac{d[A]}{dt}$, $d[B]/dt$

Rate determining step
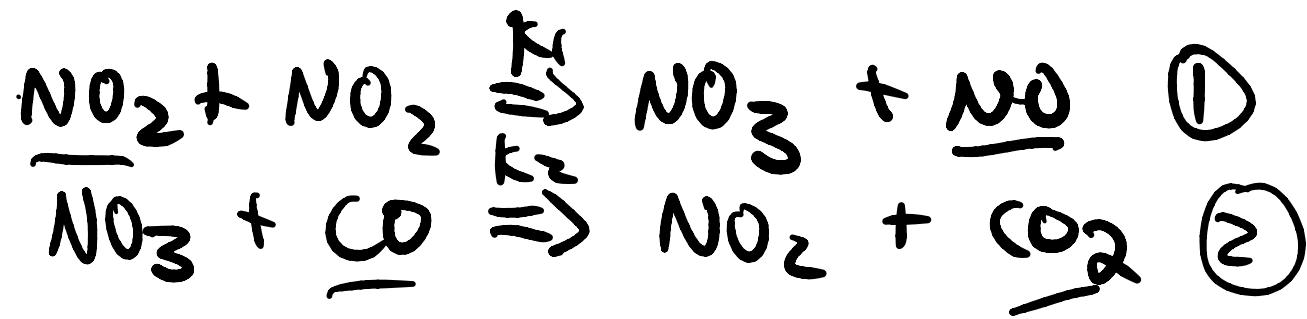
If one step is very slow
this sets the apparent reaction mech.

$$NO_2 + CO \xrightarrow{Kobs} NO + CO_2$$

$\color{red}{\text{xnot}}$ $\color{red}{r(t)= K[NO_2][CO]}$

$$NO_2 + NO_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} NO_3 + NO \quad \text{①}$$

$$NO_3 + CO \xrightarrow{K_2} NO_2 + CO_2$$

$$\underline{NO_2} + NO_2 \overset{k_1}{\underset{}{\Longrightarrow}} NO_3 + \underline{NO} \quad \textcircled{1}$$

$$\underline{NO_3} + \underline{CO} \overset{k_2}{\underset{}{\Longrightarrow}} NO_2 + \underline{CO_2} \quad \textcircled{2}$$

$$r_1 << r_2$$

$$r_{obs} \approx k_1 [NO_2]^2$$

as long as $[CO]$ isn't too small