<u>Previously</u> Saw that we could determine
some rate laws of the form
$$v(t) = k [A]^{M_A} [B]^{M_B} \ldots$$
from initial rates
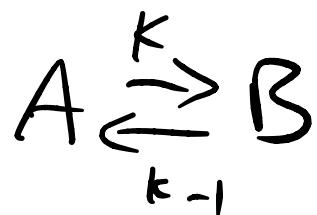
However — does not work well when
reaction is much faster then mixing
so never get equilibrium

Relaxation methods

Start @ Eq & change conditions,
change T or p slightly

Consider
$$A \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} B$$

Last time showed!

$$[A] - [A]_{Eq} = ([A]_o - [A]_{Eq}) e^{-(k+k_{-1})t}$$

What happens in T-Jump

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

$$\uparrow [B]_{eq}/[A]_{eq}$$

suppose $\Delta H < 0$, exothermic

(energy in molecules goes down, released as heat)

Increase T makes exp smaller

so less **B** (product) $A \rightleftharpoons B + q$

pushes left

$\Delta H < 0$ $q + A \rightleftharpoons B$

Increase T makes exp bigger, more product

Suppose $[A]_{eq_1}$, $[B]_{eq_1}$

at $t \to \infty$ and new t,

$[A]_{eq_2}$, $[B_{eq}]_2$
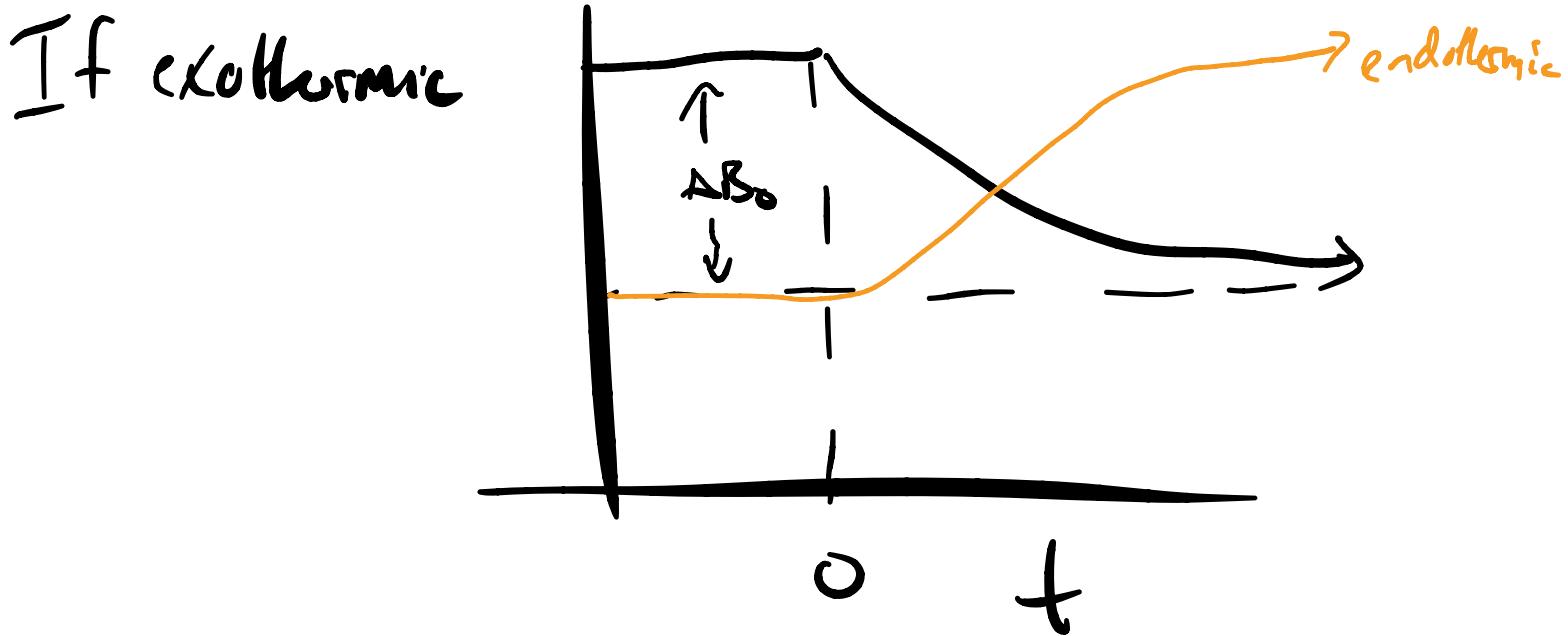
let $\Delta A(t)$ = distance from new eq state

$$\Delta A(t) = [A] - [A]_{eq2}$$

$$\Delta B(t) = [B] - [B]_{eq2}$$

⟶ very similar to prev rate law B⁺ relaxing to eq₂

Can show $\dfrac{d \Delta B}{dt} = -(k + k_{-1}) \Delta B$

or $\Delta B(t) = \Delta B(0) e^{-t/\tau}$, $\tau = \dfrac{1}{k + k_1}$

If exothermic

Can do this kind of analysis to determine rates for diff mechanisms
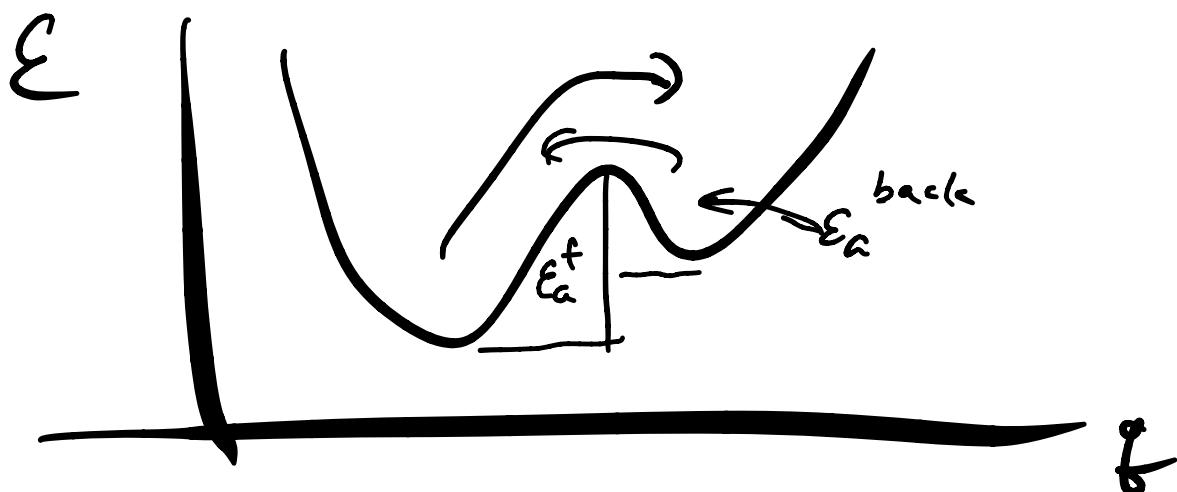
An example of this would be our 2 state protein folding near T_m

Temp dependence of rates/rate constant

often find k gets very slow at low temp

$$k = Ae^{-E_a/RT} \quad \Leftarrow \text{Arrhenius law}$$

E_a is an activation barrier along reaction coordinate

$\mathcal{E}$

E_a^f

E_a^{back}

ξ

Sometimes $\ln k$ vs $1/T$ not linear

Many reactions follow
$$k = aT^m e^{-E/RT}$$

This is because the rate depends on
- how fast moves in basin
- how fast moves over barrier

Derivations in 28-8 are
a bit beyond what we
can cover in this class
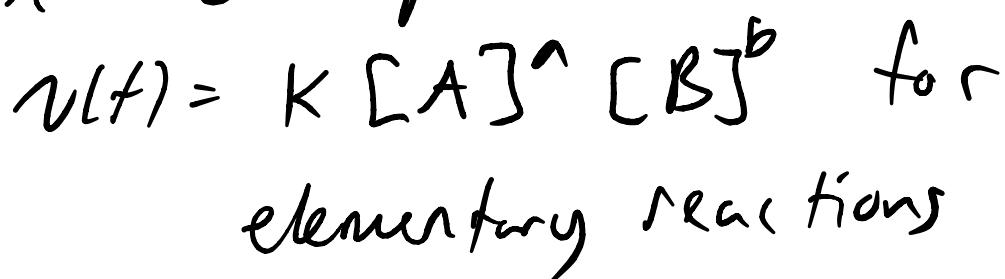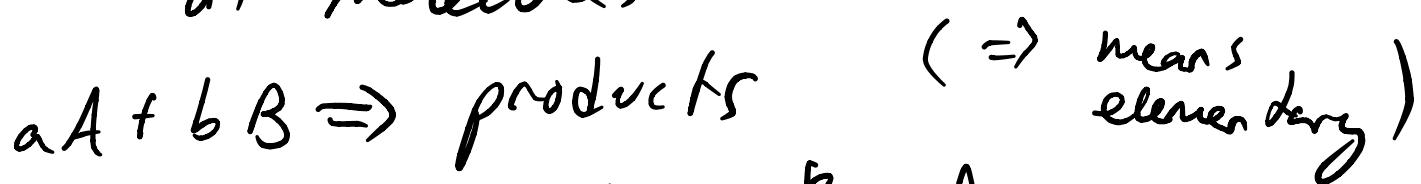
Next: how do these reactions
actually occur

McQuarrie Ch 29 - Reaction Mechanisms

Mechanism: Sequence of single step elementary reactions

Often Reactants → Intermediates → Products

Elementary reactions are those we don't believe to have intermediates, Involve direct colision/interaction of molecules

$$aA + bB \Rightarrow products \qquad (\Rightarrow \text{ means elementary})$$

$$v(t) = K[A]^a[B]^b \text{ for}$$

elementary reactions
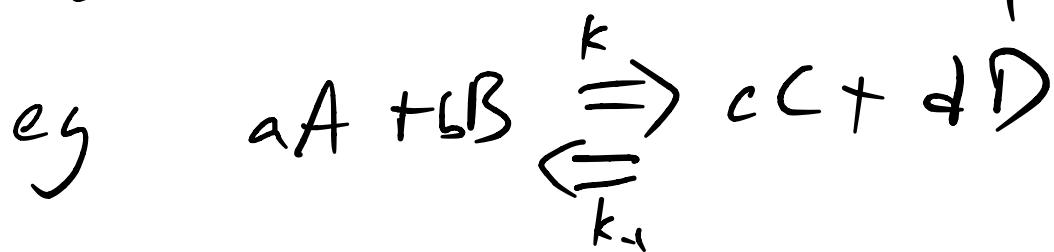
But many reactions involve hidden steps. We will see can even have this same rate law but not be elementary

Principle of Detailed Balance

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

This principle gives us the relation between rate consts & eq const

eg $aA + bB \overset{k}{\underset{k_{-1}}{\rightleftharpoons}} cC + dD$

$$V_f = k[A]^a [B]^b \qquad V_b = k_{-1}[C]^c [D]^d$$

if $V_f = V_b$ then

$$k[A]^a_{eq}[B]^b_{eq} = k_{-1}[C]^c_{eq}[D]^d_{eq}$$

or $k/k_{-1} = \dfrac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}} = K_{eq}$
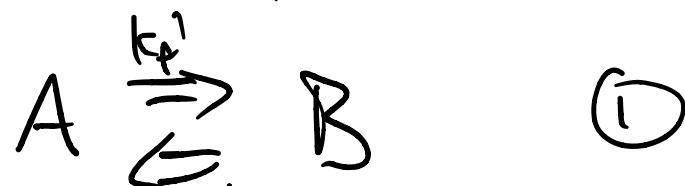
$$K^i_{Eq} = k^i_f / k^i_b \quad \text{for each elementary reaction}$$
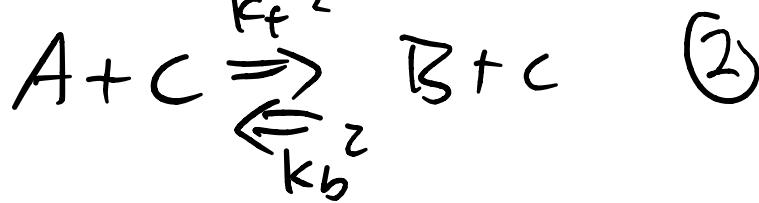
* Detailed balance links steps in reaction mechanism

Consider 2 pathways

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

(catalysis)

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

$$v_f^1 = v_b^1 \qquad \& \qquad v_f^2 = v_b^2$$

so from ① $\qquad k_f^1 [A]_{eq} = k_b^1 [B]_{eq}$

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

combining $\qquad k_f^1 / k_b^1 = k_f^2 / k_b^2$

Rate constants not independent!

Also, total mechanism is a sum of ① & ②

so $\qquad v_f^1 + v_f^2 = v_b^1 + v_b^2$

Results in same condition for rates

How can we distinguish multistep
from single step?
good example comes from
$$A \overset{k_1}{\Longrightarrow} \underline{I} \overset{k_2}{\Longrightarrow} P$$