Previously saw that we could determine some rate laws of the form

\[ v(t) = K [A]^m \cdot [B]^n \]

from initial rates.

However, does not work well when reaction is much faster than mixing, so never get equilibrium.

**Relaxation methods**

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

Consider

\[ A \xrightleftharpoons[k^-1]{k^+} B \]

Last time showed:

\[ [A]_0 - [A]_t = ([A]_0 - [A]_t_0) e^{-(k+k^-)} t \]
What happens in \( T \)-Jump

\[
K_{eq} = e^{-\Delta G^0 / RT} = e^{\Delta H^0 / RT + \Delta S^0 / R}
\]

\[
T \left[ \frac{[B]_{eq}}{[A]_{eq}} \right]
\]

Suppose \( \Delta H < 0 \), exothermic

(energy in molecules goes down, released as heat)

Increase \( T \) makes exp smaller
so less \( B \) (product) \( A \rightarrow B + g \)

pushes left

\( \Delta H < 0 \) \( g + A \rightarrow B \)

Increase \( T \) makes exp bigger, more product

Suppose \([A]_{eq1}, [B]_{eq1}\)

\( a + t \to \infty \) and new \( t \)

\([A]_{eq2}, [B]_{eq2}\)
let $\Delta A(t) = \text{distance from new eq. state}$

$\Delta A(t) = [A] - [A]_{eq-2}$

$\Delta B(t) = [B] - [B]_{eq-2}$

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

or $\Delta B(t) = \Delta B(0)e^{-t/z}, \quad z = \frac{1}{k + k_{-1}}$

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 $Tm$
Temp dependence of rates/rate constant

Often find $k$ gets very slow at low temp

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

$Ea$ is an activation barrier along reaction coordinate

Sometimes $\ln k$ vs $1/T$ not linear
Many reactions follow

\[ k = aT \exp(-E/kT) \]

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

Derivations in 28-8 are a bit beyond what we can cover in this class.

Next: how do these reactions actually occur?
Mechanism: Sequence of single step elementary reactions

Often Reactants $\rightarrow$ Intermediates $\rightarrow$ Products

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

$aA + bB \rightarrow \text{products}$ ( Elementary)

$\nu(t) = k [A]^a [B]^b$ 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

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

This principle gives us the relation between rate constants & eq const.

\[ k_f = k_b \]

\[ \frac{V_f}{V_b} = k_c \]

\[ k_f = k_b \]

If \( V_f = V_b \) then

\[ k_c = \frac{k_f}{k_b} \]

\[ K_eq = \frac{k_f}{k_b} \]

For each elementary reaction.
Detailed balance links steps in reaction mechanism.

Consider

\[ A \xrightarrow{k_r^1} B \quad (\text{catalysis}) \]

and

\[ A + C \xrightarrow{k_r^2} B + C \quad (\text{catalysts}) \]

2 pathways

\[ k_i^1 \]

\[ k_i^2 \]

\[ k_b \]

\[ k_f \]

\[ U_f' = U_b' \quad \text{and} \quad U_f'' = U_b'' \]

so from (1)

\[ k_i^1 [A]_{eq} = k_b [B]_{eq} \]

(2)

\[ k_i^2 [A]_{eq} [C]_{eq} = k_b^2 [B]_{eq} [C]_{eq} \]

Combining

\[ \frac{k_i^1}{k_b} = \frac{k_i^2}{k_b^2} \]

Rate constants not independent!

Also, total mechanism is a sum of (1) & (2)

\[ U_f' + U_f'' = U_b' + U_b'' \]

Results in same condition for rates.
How can we distinguish multistep from single step?

A good example comes from

\[ A \Rightarrow I \Rightarrow P \]