Can determine rate laws for chemical reactions

\[ aA + bB \xleftrightarrow{\text{rate}} ^{\text{forward}} \underset{\text{reverse}}{\text{rate}} cC + dD \]

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

Does not work (initial rate method) when reaction is faster than mixing.
Relaxation Method

- Start @ Equilibrium
- Change conditions
- Watch system "relax" to a new equilibrium

\[ A \rightleftharpoons B \]

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

Last time, we showed

\[ [A] - [A]_{eq} = ([A]_0 - [A]_{eq}) e^{-\left(\frac{k_f + k_b}{k_b}\right)t} \]
\[ t=0 \]

Increase temp

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

\[ K_{eq} = e^{\frac{-\Delta G^0}{RT}} \]

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]
\begin{align*}
K_{eq} &= e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{\Delta H^\circ}{RT} \frac{\Delta S^\circ}{R}} \\
\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ
\end{align*}

Is the reaction \underline{exothermic} \ [\text{releases heat}] \ \text{or} \ \underline{endothermic} \ [\text{absorbs heat}] \\

- \Delta H^\circ < 0 \quad \text{energy in the molecules goes down in the reaction} \\
\text{heat released, exothermic case}
Increasing $T$ or adding heat, reaction shift to the left

$$K_{eq}(T) = e^{-\frac{\Delta H^0}{RT}} (1) = \frac{[B]_{eq}}{[A]_{eq}}$$

$\Delta H^0 < 0$

$e^{a/T}, a > 0$

$T \uparrow \rightarrow e^{a/T} \downarrow \rightarrow B_{eq}, A \uparrow_{eq}$
q + A \rightleftharpoons B

\Delta H > 0

\frac{[B]_{eq}}{[A]_{eq}} = e

\Delta H / RT = \Delta S^o / R

heat drives reaction to the right

\text{endothermic}

\text{exothermic}

all negative
Consider exothermic

\[ \Delta A(t) = [A]_{t=0} - [A]_{eq2} \]

\[ \Delta B(t) = [B]_{t=0} - [B]_{eq2} \]

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

\[ t = 0 \quad \Delta B(t) = \Delta B(0)e^{-kt} \]

\[ z = (k_f + k_b)^{-1} \]
Temperature dependence of rate constants

Rate of a reaction slows down at low temperature

- How often collide & how much energy

\[ k = A e^{-\frac{E_a}{RT}} \]

"high barrier" relative to RT or kBT
\[ k = A e^{-\frac{E_a}{RT}} \]

\[ \ln(k) = \ln(A) - \frac{E_a}{RT} \]

Sometimes - is not linear

\[ \Rightarrow A(T) \text{ and/or } E_a(T) \]

Many reactions follow

\[ k = a T^m e^{-\frac{E'}{RT}} \]

(28.8) McQuarrie
1. how long in basin
2. how fast does it cross

diffusion in reactant basin

"Kramers' theory"
McQuarrie Ch29 - Reaction Mechanism

Mechanism: Sequence of single step elementary reactions

Reactants $\rightarrow$ Intermediates $\rightarrow$ Products

Elementary Reactions

- we don't think has intermediates
- involves direct collision/interaction

$aA + bB \Rightarrow \text{products}$
\[ aA + bB \Rightarrow \text{products} \]
rate law: \( \nu(t) = k \left[ AJ^a [BJ]^b \right] \)

Principle of Detailed Balance

At equilibrium, forward rate & backward rate of every elementary reaction are equal.

\[ K_{eq} = \frac{[R]}{[L]} \]

flux: \( L \rightarrow R = R \rightarrow 2 \)
\[ aA + bB \Rightarrow cC + dD \]

\[ V_f = k_f [A]^a [B]^b \quad V_b = k_b [C]^c [D]^d \]

Detailed balance means \[ V_f = V_b \quad \text{eq} \]

\[ k_f [A]^a [B]^b = k_b [C]^c [D]^d \]

\[ \frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq} \]
for each elementary reaction
\[ k_{eq} = \frac{k_i^r}{k_i} \]

**Detailed Balance links steps in a reaction mechanism**

\[ A \rightleftharpoons \frac{k_f}{k_b} \]

\[ A \rightleftharpoons B \quad (1) \]

\[ A + C \rightleftharpoons B + C \quad (2) \]
At equilibrium:

\[ k_f' [A]_{eq} = k_b' [B]_{eq} \]

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

\[ \frac{k_f'}{k_b'} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f^2}{k_b^2} \]
Aside

Sum up reactions

\[ V_f^1 = V_b^1 \]

\[ + \quad V_f^2 = V_b^2 \]

\[ V_f^1 + V_f^2 = V_b^1 + V_b^2 \]

Next: How do we know if a reaction is elementary

\[ \frac{K_f^n}{K_f^2} \]

\[ A \rightarrow I \rightarrow P \]