Chemical reactions

\[ \sum_{i=1}^{n} x_i \cdot r_i + \sum_{k=1}^{m} v_k \cdot x_k \rightleftharpoons \sum_{i=1}^{n} v_{i1} \cdot x_{i1} + \cdots + \sum_{k=1}^{m} v_{k1} \cdot x_{k1} \]

\[ V_k = \text{stoichiometric coefficients (order)} \]

Chemical potential

\[ \mu_i = -T \frac{\partial S_i}{\partial n_i} + E_i, \mu_{ix} = -k_B T \ln \frac{c_i}{c_0} + \mu^0(E) \]

\[ \Delta G_i = -\sum_{k=1}^{m} V_k \mu_k - \sum_{i=1}^{n} V_i \mu_{ik} + \sum_{k=1}^{m} v_{ki} \mu_{xik} + \cdots + \sum_{k=1}^{m} v_{km} \mu_{xkm} \]

\[ -\Delta G \text{ free energy change for forward step} \]

\[ \Delta G < 0 \Rightarrow \text{forward reaction} \quad \Delta G_i < 0 \]

\[ \Delta G > 0 \Rightarrow \text{backward reaction} \quad \text{isolated} \]

\[ \Delta G = 0 \Rightarrow \text{equilibrium} \quad \text{open} \]

Standard free energy change \( \Delta G^0 \)

\[ \Delta G^0 = -\sum_{k=1}^{m} V_k \mu^0_k - \sum_{i=1}^{n} V_i \mu^0_{ik} \]

at equilibrium

\[ (\Delta G = 0) \]

\[ \left[ \frac{[K_{11}]^{V_{11}} \cdots [K_{1m}]^{V_{1m}}}{[X_1]^{V_1} \cdots [X_m]^{V_m}} \right] = K^0 = e^{-\Delta G^0/k_B T} \]

Mass action rule

\[ M_i^0 \Delta G^0 \text{ bond in table} \]

\[ \Delta G_i^{10} \text{ at room temperature} \]

\[ \sum x_j = c_j/c_0 \quad \text{where} \quad c_0 = 1 \text{ M} \]

Units (exercise)

\[ \frac{\Delta G_i^{10}}{RT} \iff \frac{\Delta G^0}{RT} \quad \text{Vmode} \]

\[ k_B = 1.38 \times 10^{-23} \text{ J/K} \]

\[ N_A = 6 \times 10^{23} \]

\[ R = 8.32 \text{ J/mole.K} \]
Multiple reactions
\[ \begin{align*}
A & \overset{k_{1+}}{\rightarrow} \overset{k_{1-}}{\rightarrow} B \\
B & \overset{k_{2+}}{\rightarrow} \overset{k_{2-}}{\rightarrow} C
\end{align*} \]

\[ \text{Equilibrium: } \frac{C_A}{C_B} = K_{eq_1} = e^{\frac{-\Delta G_1}{RT}} \]

\[ \frac{C_C}{C_B} = K_{eq_2} = e^{\frac{-\Delta G_2}{RT}} \]

\[ \frac{C_C}{C_A} = \frac{C_B}{C_A} K_{eq_2} \]

\[ K_{eq} = K_{eq_1} K_{eq_2} = K_{eq} = e^{\frac{-\Delta G_{net}}{RT}} \]

Note: Details of the intermediate steps are immaterial for overall equilibrium.

Equations in equilibrium?

Example 1: \( 2H_2 + O_2 \rightarrow 2H_2O \) at room temp (must be heated)

Example 2: \( \text{our bodies} \rightarrow \text{energy from sun} \)

(To fuel cars, road for our work)

Reaction rates: \( 3.2.4, 6.6.7, 10.3.2 \)

Reaction coordinate:
- Chemical reactions reflect random walk on a true energy landscape of molecular configurations.
- Assume a valley in the landscape \( \Rightarrow \) reaction coordinate.
- Transition state = highest point along reaction path.

Example:
\[ \begin{align*}
H_2 + H^+ & \rightarrow H^+ + H_2 \\
O + O & \rightarrow O = O \quad \Delta_{\text{el}} \rightarrow \text{trans state}
\end{align*} \]

\[ \text{Diagram:} \]
- Reaction coordinate: \( \Delta G^* \)
- Local minima: \( \Delta G^* \)
- Reaction coordinate: \( \Delta G \)
Collision Theory

For a reaction $A + B \rightarrow C$ to occur:

- an $A$ and a $B$ molecule must meet (collide)
- the kinetic energy of the molecules must exceed an energy barrier $\Delta E^*$

- probability that $A$ and $B$ meet per time $P_{AB} \propto c_A c_B$
- fraction of colliding particles with $E > \Delta E^*$

- other "constant" factors, e.g. steric factor

reaction rate $\nu = k A \cdot B$

$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[C]}{dt} = -k[A][B]$  

$k' = A \cdot e^{-\Delta E^*/kT}$  

Arrhenius rate law

often seen in experiments (not only for simplistic reactions)
Transition state theory

A + B \rightarrow C

\[ A + B \rightleftharpoons AB^+ \rightarrow C \]

in equilibrium

rate

\[ r = \frac{K_{eq}^+}{k_{eq}^+} = \frac{C_{AB}^+}{C_A C_B} \]

\[ k_{obs} = \frac{k_{eq}^+}{k_{eq}^+} \exp\left(-\frac{\Delta G^0}{kT}\right) \]

Eyring equation

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S \]

\( \Delta H^\circ = \Delta E^r + kT \)

Consistent example

\[ X_2 + Y_2 \rightleftharpoons ZXY \]

1st order in \( X_2 \) \& \( Y_2 \)

theory

\[ \text{forward rate} \hspace{1cm} v^+ = k_+ C_{X_2} C_{Y_2} \]

\[ \text{backward rate} \hspace{1cm} v^- = k_- C_{XY} \]

experiments

\[ C_{X_2} \rightarrow Z \rightarrow C_{XY} \rightarrow v^+ \rightarrow Y_2 \]

\[ C_{Y_2} \rightarrow Z \rightarrow C_{XY} \rightarrow v^+ \rightarrow v^+ \]

(2nd order)

(1st order)

Intermediate steps:

1. \( X_2 + X_2 \rightarrow Z \rightarrow X_1 \)
2. \( X + Y_2 \rightarrow X_2 Y_1 \)
3. \( X + X_2 Y_2 \rightarrow Z \rightarrow X_2 \)
4. \( \Delta E^r + kT \rightarrow ZXY \rightarrow RC \)
Enzymes (10.3.3, 10.4.1)

- Molecules created by cells (proteins) that catalyze a reaction, i.e., increase the rate
- Is not used up in the reaction (cyclic machine)
- Effect from lowering activation barrier

**Example**

\[ \Delta G^+ \text{ decreased while } \Delta G \text{ unchanged} \]

**Michaelis-Menten rule**

- Describes kinetics of simple enzymatic reactions

\[ S + E \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} SE \rightarrow \overset{k_2}{\underset{k_3}{\rightleftharpoons}} P + E \]

Assume:

- Second reaction rate limiting

  \( SE \) in quasi-equilibrium

- Fixed amount of enzyme \( E_0 = E + SE \)

Goal: describe production of \( P \) by \( E \)

\[
\frac{dC_E}{dt} = -k_1 C_E C_S + (k_2 + k_3) C_{SE} \\
\frac{dC_S}{dt} = k_1 C_S C_E - (k_2 + k_3) C_{SE} = 0 \implies C_S = \frac{C_E - C_{SE}}{k_2}
\]

\[
\frac{dC_{ES}}{dt} = k_1 C_S C_E - (k_2 + k_3) C_{SE} = 0 = k_1 C_S (C_{E_0} - C_{SE}) - (k_2 + k_3) C_{ES}
\]

\[
\frac{dP}{dt} = k_2 C_S C_E
\]

\[
k_1 C_S C_{E_0} = C_{ES} (k_2 C_S + k_3 + k_4) \\
C_{ES} = \frac{k_2 C_S C_{E_0}}{k_1 + k_2 + k_4 C_S}
\]
\[ \frac{dC_p}{dt} = \frac{k_2 C_s C_{G_0}}{k_{-2} + \frac{k_2}{C_s} + C_s} \]

\[ \begin{cases} 
V_{\text{max}} = \frac{k_2 C_{G_0}}{k_{-2} + \frac{k_2}{C_s}} \\
K_m = \frac{k_{-2}}{C_s} 
\end{cases} \]

Michaelis-Menten equation

\[ \frac{dC_p}{dt} = \frac{V_{\text{max}} C_s}{K_m + C_s} \]

Saturation at high \( C_s \)

e.g. gene transcription

\[ 2T_F + DNA \rightleftharpoons DNA^T \rightarrow mRNA \]

mediated by transport