

Physical Principles in Biology
Biology 3550
Fall 2017

Lecture 28

Thermodynamics: Gibbs Free Energy, Equilibrium Constants and the Entropy Change for a Bimolecular Reaction

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Enthalpy (H)

Two consistent definitions for ΔH at constant pressure:

- ΔE minus work due to volume change

$$\begin{aligned}\Delta H &= \Delta E + P\Delta V \\ &= \Delta E - w_p\end{aligned}$$

If there is no volume change, then $w_p = 0$, and $\Delta H = \Delta E$.

- The heat absorbed during the constant pressure process:

$$\Delta H = q_p$$

Chemical and biochemical reactions are usually studied under conditions of constant (or nearly constant) pressure, and ΔV is usually very small.

ΔH can be experimentally measured.

The Gibbs Free Energy (G)

■ $G = H - TS_{\text{sys}}$

- For a process at constant temperature:

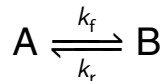
$$\Delta G = \Delta H - T\Delta S_{\text{sys}}$$

- For a process at constant temperature and constant pressure:

$$\Delta G = -T\Delta S_{\text{univ}}$$

- The Gibbs free energy is used to apply the second law.
- If $\Delta G < 0$, the process will be spontaneous.
 - If $\Delta G > 0$, the reverse process will be spontaneous.
 - If $\Delta G = 0$, the system and the surroundings are at equilibrium.

The Equilibrium Constant for a Chemical Reaction



- Rate expression:

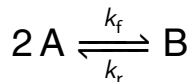
$$\frac{d[A]}{dt} = -k_f[A] + k_r[B]$$

- At equilibrium:

$$\frac{d[A]}{dt} = -k_f[A] + k_r[B] = 0$$

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_f}{k_r} = K_{\text{eq}}$$

A Slightly More Complicated Reaction



- Rate expression:

$$\frac{d[A]}{dt} = -k_f[A]^2 + k_r[B]$$

- At equilibrium:

$$\frac{d[A]}{dt} = -k_f[A]^2 + k_r[B] = 0$$

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}^2} = \frac{k_f}{k_r} = K_{\text{eq}}$$

The Equilibrium Constant and Free Energy Change for a Chemical Reaction



- At equilibrium, a little bit of work can push the reaction in either direction.

This defines the condition where $\Delta G = 0$

- Definition of ΔG for a chemical reaction:

The free energy change for converting one mole of reactants to one mole of products, at specified concentrations, without significantly changing concentrations(!).

Implies a very, very large volume!

Or, a mechanism that restores concentrations continuously.

The Relationship Between Free Energy and the Equilibrium Constant



- ΔG depends on concentrations of A and B.
 - If $\frac{[B]}{[A]} < K_{\text{eq}}$, the reaction will try to shift towards B, $\Delta G < 0$
 - If $\frac{[B]}{[A]} > K_{\text{eq}}$, the reaction will try to shift back to A, $\Delta G > 0$
- Define standard concentrations to specify ΔG :
 - Concentrations of all species are 1 M for solutions or 1 atm for gasses.
 - Free energy change at these concentrations is called ΔG° .

The Relationship Between Free Energy and the Equilibrium Constant

- If reactants and products are at equilibrium concentrations:

$$\Delta G = 0$$

- If reactants and products are at standard state concentrations (1 M):

$$\Delta G \equiv \Delta G^\circ$$

$$\Delta G^\circ = -RT \ln \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = -RT \ln K_{\text{eq}}$$

ΔG° and K_{eq} convey essentially the same information.

- For other concentrations:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[B]}{[A]}$$

The Relationship Between Free Energy and the Equilibrium Constant

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad A \rightleftharpoons B \quad K_{\text{eq}} = \frac{[\text{B}]_{\text{eq}}}{[\text{A}]_{\text{eq}}}$$

- If $K_{\text{eq}} > 1$:
 - Reaction favors B over A.
 - $\Delta G^\circ < 0$
- If $K_{\text{eq}} < 1$:
 - Reaction favors A over B.
 - $\Delta G^\circ > 0$
- If $K_{\text{eq}} = 1$:
 - A and B have equal free energies.
 - $\Delta G^\circ = 0$

Reactions with More than One Reactant or Product

- A reaction with two reactants and two products: $aA + bB \rightleftharpoons cC + dD$
a, b, c and d represent stoichiometry

- The equilibrium constant:

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

Products over reactants! (Mrs. Freeman)

- The reaction quotient:

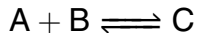
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

When concentrations are not necessarily at equilibrium.

- $\Delta G = \Delta G^\circ + RT \ln Q$

Clicker Question #1

For the reaction:



What are the units of the equilibrium constant?

1 M

2 No units

3 M^{-1}

From Two Molecules to One

- A reaction with two reactants and one products: $A + B \rightleftharpoons C$
- The equilibrium constant:

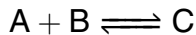
$$K_{\text{eq}} = \frac{[C]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}}$$

- Some problems:
 - The equilibrium constant has units of inverse concentration.
 - The numerical value of K_{eq} will depend on the units that we use for concentration
 - What happens when we try to calculate ΔG° ?

$$\Delta G^\circ = RT \ln K_{\text{eq}}$$

Logarithms are functions of pure numbers. How do we take a logarithm of a value with units?

From Two Molecules to One



■ Defining standard states is important!

- Standard state concentration is usually defined as 1 M
- For thermodynamic purposes, refine the definition of the equilibrium constant:

$$K_{\text{eq}} = \frac{([C]_{\text{eq}}/1 \text{ M})}{([A]_{\text{eq}}/1 \text{ M})([B]_{\text{eq}}/1 \text{ M})}$$

- Now, K_{eq} is dimensionless, and we don't have to feel guilty about taking the logarithm.
- But, value of ΔG depends on choice of standard state concentrations. Why?

The Entropy Change for a Bimolecular Reaction



■ Assume a volume made up of N_c little cubes:

- The number of ways to place a molecule of A and a molecule of B in the volume:

$$\Omega_{A,B} = N_c^2$$

- The number of ways to place a molecule of C in the volume:

$$\Omega_C = N_c$$

■ The entropy change

$$\Delta S = k \ln(\Omega_C) - k \ln(\Omega_{A,B}) = k \ln(N_c) - k \ln(N_c^2)$$

$$= k \ln\left(\frac{N_c}{N_c^2}\right) = -k \ln(N_c)$$

■ The entropy decreases!

The Entropy Change for a Bimolecular Reaction

- From previous slide:

$$\Delta S = -k \ln(N_c)$$

- In this case, the number of little cubes doesn't cancel out, and the size of the cubes matters.
- A plausible estimate:
 - Make the cubes about the right size to hold one or two small molecules,

$$V_c = (1 \text{ nm})^3 = 1 \text{ nm}^3$$

- Specify the reaction volume, V in liters.

$$N_c = \frac{V(\text{L})}{1 \text{ nm}^3} \times \frac{10^{-3} \text{ m}^3}{\text{L}} \times \left(\frac{10^9 \text{ nm}}{\text{m}} \right)^3 \approx V(\text{L}) \times 10^{24}$$

The Entropy Change for a Bimolecular Reaction

- From previous slide:

$$\Delta S = -k \ln(N_c) = -k \ln(V(L) \times 10^{24})$$

- For one mole each of A and B converted to C:

$$\Delta S = -N_A k \ln(V(L) \times 10^{24})$$

$$= -R \ln(V(L) \times 10^{24})$$

- For $V = 1$ L:

$$\Delta S = -R \ln(10^{24}) = -8.31 \text{ J/K} \times 53 = -460 \text{ J/K}$$

Clicker Question #2

If the reaction volume is doubled for the reaction $A + B \rightleftharpoons C$, How will the entropy change be affected?

- 1 ΔS will be unaffected.
- 2 ΔS will become more negative.
- 3 ΔS will become less negative.

$$\Delta S = -k \ln(N_c) = -k \ln(V(L) \times 10^{24})$$

A Bimolecular Reaction



- $\Delta S = -460 \text{ J/K}$

- Total free energy change for the reaction:

$$\Delta G = \Delta H - T\Delta S$$

- Contribution of entropy change to the free energy change at 298 K:

$$\begin{aligned} -T\Delta S &= 298 \text{ K} \times 460 \text{ J/K} \\ &= 140 \text{ kJ/mol} \end{aligned}$$

- This is a large, unfavorable contribution to ΔG .
- For the reaction to be favorable, there must be other factors that make the total free energy change negative.
- What factors might do that?