Physical Principles in Biology
Biology 3550
Fall 2018

Lecture 29

Thermodynamics:

Gibbs Free Energy and Equilibrium Constants

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Enthalpy (H)

Two consistent definitions for ΔH at constant pressure:

- ΔE minus work due to volume change

    $$\Delta H = \Delta E + P\Delta V$$

    $$= \Delta E - w_p$$

    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 <u>reverse</u> process will be spontaneous.
  - If $\Delta G = 0$, the system and the surroundings are at equilibrium.

The Equilibrium Constant for a Chemical Reaction

$$A \rightleftharpoons B$$

- The reaction can occur in either direction. (at least in principle)
- The probability that any molecule of A will be converted to a molecule of B is the same as for any other molecule of A.
  - The total rate of conversion of A to B is proportional to the concentration of A.
  - Similarly, the total rate of conversion of B to A is proportional to the concentration of B.
- A differential equation:

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

The constants k_f and k_r are called rate constants.

The Equilibrium Constant for a Chemical Reaction

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$
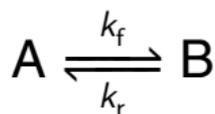
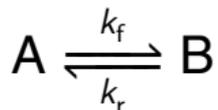■ From the previous slide: $\dfrac{d[A]}{dt} = -k_f[A] + k_r[B]$

■ Whatever the starting concentrations, [A] and [B] will eventually adjust so that they no longer change.

■ At equilibrium:

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

$$-k_f[A] + k_r[B] = 0$$

The Equilibrium Constant for a Chemical Reaction

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

- At equilibrium:

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

$[A]_{eq}$ and $[B]_{eq}$ are the concentrations of A and B at equilibrium.

- Rearranging:

$$k_r[B]_{eq} = k_f[A]_{eq}$$

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

K_{eq} is defined as the equilibrium constant.

The Equilibrium Constant and Free Energy Change for a Chemical Reaction

$$A \rightleftharpoons B \qquad\qquad K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$$

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

  This defines the condition where $\Delta G = 0$
  No work can be done!

- 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

$$A \rightleftharpoons B \qquad\qquad K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$$

- ΔG depends on concentrations of A and B.

  - If $\quad \dfrac{[B]}{[A]} < K_{eq}$, the reaction will try to shift towards B, $\quad \Delta G < 0$

  - If $\quad \dfrac{[B]}{[A]} > K_{eq}$, the reaction will try to shift back to A, $\quad \Delta G > 0$

- 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 $\Delta G°$.

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):

$$\Delta G \equiv \Delta G°$$

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

$\Delta G°$ and K_{eq} convey essentially the same information.

- For other concentrations:

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

The Relationship Between the Standard Free Energy Change and the Equilibrium Constant

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

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

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

  Products over reactants! (Mrs. Freeman)

- The reaction quotient:

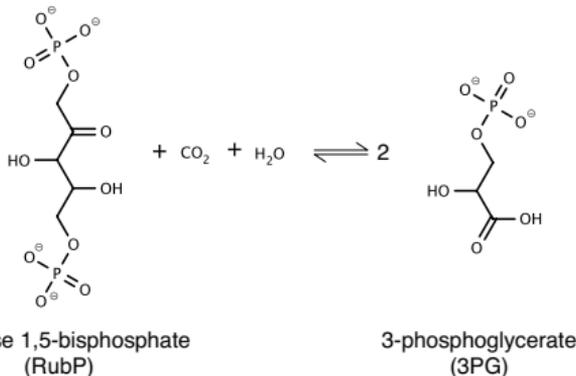$$Q = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

  When concentrations are not necessarily at equilibrium.

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

- The key reaction in CO_2 fixation:

Ribulose 1,5-bisphosphate
(RubP)

3-phosphoglycerate
(3PG)

- Catalyzed by the enzyme ribulose bisphosphate carboxylase, Rubisco.

- The most abundant enzyme on earth.

- The equilibrium constant at 25°C:

$$K_{eq} = \frac{[3PG]_{eq}^{2}}{[CO_2]_{eq}[RubP]_{eq}} = 1.3 \times 10^9$$

(Water is ignored)

- Calculate $\Delta G°$ for this reaction at 25°C.

The Standard Free Energy Change for the Rubisco Reaction

- $\Delta G° = -RT \ln K_{eq}$

- $R = 8.314\,\text{J} \cdot \text{K}^{-1}\text{mol}^-1$

- $T = 298\,\text{K}$

- $K_{eq} = 1.3 \times 10^9$

  $$\Delta G° = -RT \ln K_{eq}$$
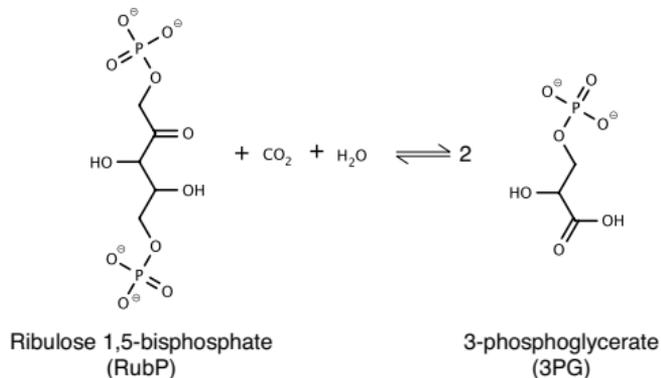 $$= -8.314\,\text{J} \cdot \text{K}^{-1}\text{mol}^{-1} \times 298\,\text{K} \times \ln(1.3 \times 10^9)$$
  $$= -5.2 \times 10^4\,\text{J/mol} = -52\,\text{kJ/mol}$$

- $1\,\text{J} = 1\,\text{watt} \cdot \text{s}$

- $1\,\text{W} \cdot \text{h} = 3600\,\text{J}$

- $-52\,\text{kJ/mol} = 14\,\text{W} \cdot \text{h}$

Ribulose 1,5-bisphosphate
(RubP)

3-phosphoglycerate
(3PG)

- The enthalpy change at standard concentrations:
  $\Delta H° = -21\,\text{kJ/mol}$

- Calculate ΔS_{sys} for this reaction at 25°C and standard-state conditions ($\Delta S°$).

The Standard Entropy Change for the Rubisco Reaction

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

- $\Delta G° = -52\,\text{kJ/mol}$

- $\Delta H° = -21\,\text{kJ/mol}$

- $T = 298\,\text{K}$

$$\Delta G° = \Delta H° - T\Delta S°$$
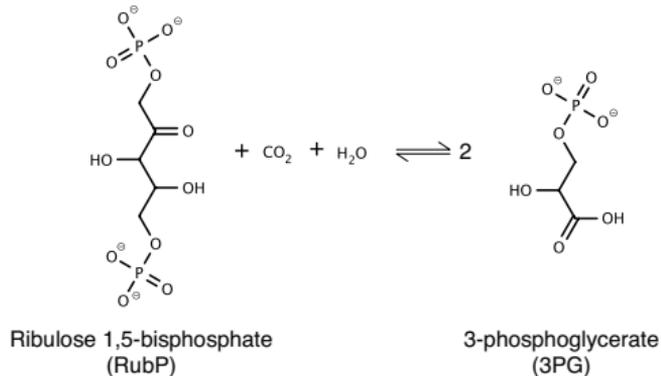
$$\Delta S° = \frac{\Delta H° - \Delta G°}{T}$$

$$\Delta S° = \frac{-21\,\text{kJ/mol} - (-52\,\text{kJ/mol})}{298\,\text{K}}$$
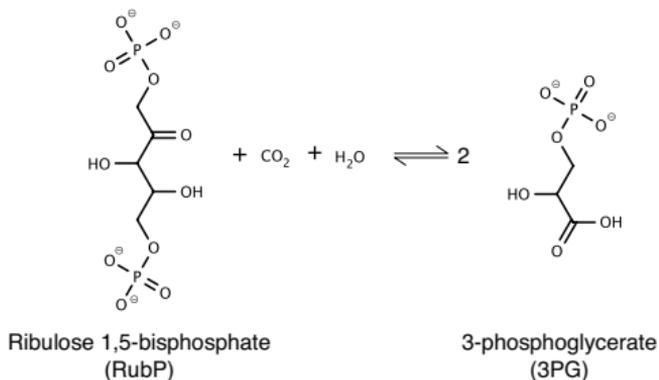
$$\Delta S° = 100\,\text{J/(K}\cdot\text{mol)}$$

- Entropy of the system increases.

Ribulose 1,5-bisphosphate
(RubP)

3-phosphoglycerate
(3PG)

- $\Delta G° = -52\,\text{kJ/mol}$
  The reaction is very favorable and can, in principle produce work.

- $\Delta H° = -21\,\text{kJ/mol}$
  Heat is *released* by the system. What can we infer from this?

- $\Delta S° = 100\,\text{J/(K} \cdot \text{mol)}$
  What can we infer from this?

Group Problem #3

Ribulose 1,5-bisphosphate
(RubP)

3-phosphoglycerate
(3PG)

- In the plant chloroplasts, typical concentrations are:

  [3PG] = 1 mM
  [RubP] = 1 mM
  [CO$_2$] = 1 μM

- Calculate the free energy change (ΔG) at these concentrations and 298 K.

  Be careful with the concentration units!

(We didn't get to this problem in class)