

Physical Principles in Biology
Biology 3550
Fall 2016

Lecture 28

Thermodynamics V: Chemical Thermodynamics

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The Gibbs Free Energy

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

- Gibbs free energy provides a means of applying the second law using parameters that depend only on the system state.
- ΔH is the heat absorbed by the system in a constant-pressure process, and reflects the entropy change of the surroundings.
- If $\Delta G < 0$
 - $\Delta S_{\text{univ}} > 0$, and the process will be spontaneous.
- If $\Delta G > 0$
 - $\Delta S_{\text{univ}} < 0$, and the reverse process will be spontaneous.
- If $\Delta G = 0$
 - $\Delta S_{\text{univ}} = 0$, and the process is reversible.
 - $\Delta G = 0$ defines a system at equilibrium.

The Equilibrium Constant for a Chemical Reaction



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

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

- 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, $\Delta G > 0$

The Relationship Between Free Energy and the Equilibrium Constant

- ΔG depends on concentrations of A and B.
- Have to define standard state concentrations:
 - Starting concentrations of all species are 1 M for solutions or 1 atm for gasses.
 - Free energy change for conversion of these concentrations to equilibrium concentrations is defined as ΔG° .
- At any other concentration, the free energy change can be calculated as:

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

[A] and [B] are not *necessarily* the equilibrium concentrations.

- Equation is derived by considering the entropy change associated with the changes in concentration.

The Relationship Between Free Energy and the Equilibrium Constant

- From the previous slide:

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

- ΔG is the free energy change for converting 1 mole of A to B, when:
 - The starting concentrations are [A] and [B]
 - The ending state is at equilibrium.
- If $[A] = [B] = 1 \text{ M}$

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln \left(\frac{1 \text{ M}}{1 \text{ M}} \right) \\ &= \Delta G^\circ + RT \ln 1 = \Delta G^\circ\end{aligned}$$

This was the definition of ΔG° ,

but it shows that the equation makes some sense!

The Relationship Between Free Energy and the Equilibrium Constant

- From the previous slide:

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

- If the concentrations are already at equilibrium, $\Delta G = 0$

$$0 = \Delta G^\circ + RT \ln \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}}$$

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

$$= -RT \ln K_{\text{eq}}$$

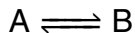
- ΔG° and K_{eq} convey essentially the same information.

The Relationship Between Free Energy and the Equilibrium Constant

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

- 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.
 - $\Delta G^\circ = 0$

Thermodynamic Characterization of a Chemical Reaction



1 Measure K_{eq}

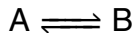
- Mix A and B under conditions where they will interconvert.
- Allow A and B to equilibrate.
- Measure concentrations at equilibrium.
- Calculate equilibrium constant:

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

2 Calculate ΔG° :

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

Thermodynamic Characterization of a Chemical Reaction



- 3 Measure ΔH , using a calorimeter.
(or by measuring change in K_{eq} with temperature)

- 4 Calculate ΔS :

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

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

- 5 Additional insights can be gained by measuring ΔH as a function of temperature.