

Physical Principles in Biology
Biology 3550
Fall 2018

Lecture 30

Chemical Thermodynamics

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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 $\Delta G = 0$
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



- 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 the Standard Free Energy Change 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!

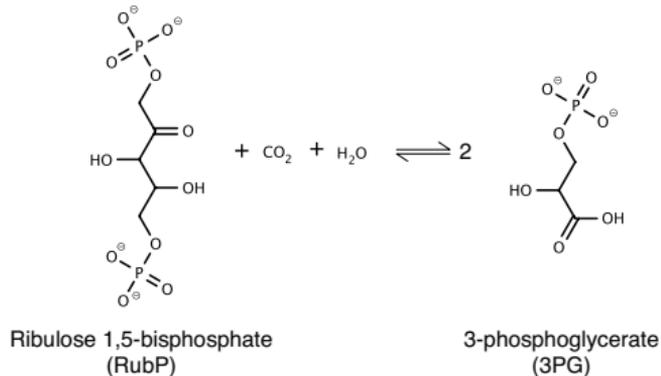
- The reaction quotient:

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

When concentrations are not necessarily at equilibrium.

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

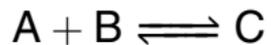
Thermodynamics of the Rubisco Reaction



- $\Delta G^\circ = -52 \text{ kJ/mol}$
The reaction is very favorable and can, in principle produce work.
- $\Delta H^\circ = -21 \text{ kJ/mol}$
Heat is *released* by the system.
What can we infer from this?
- $\Delta S^\circ = 100 \text{ J/(K} \cdot \text{mol)}$
What can we infer from this?

Clicker Question #1

For the reaction:



What are the units of the equilibrium constant?

- A) M
- B) No units
- C) M^{-1}

From Two Molecules to One

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

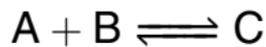
$$K_{\text{eq}} = \frac{[C]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}}$$

- 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?

- A) ΔS will be unaffected.
- B) ΔS will become more negative.
- C) 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?

A Bimolecular Reaction

- $A + B \rightleftharpoons C$
- $\Delta S = -460 \text{ J/K}$
- $-T\Delta S = 140 \text{ kJ/mol}$
- Some caveats:
 - This is a highly simplified treatment.
 - Choice of V_c is not very well justified.
 - Ignores rotational freedom of molecules.
 - Ignores internal motions of molecules.
 - This is a controversial subject, but this estimate is within the bounds of the controversy! (at the lower end)
- ΔG° , defined with specific concentration units, contains within it the entropy loss at the standard state concentration.