

Physical Principles in Biology  
Biology 3550  
Fall 2017

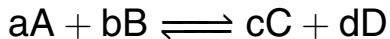
## Lecture 29

# Chemical Thermodynamics and Metabolism

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# The Equilibrium Constant for a Chemical Reaction



- The equilibrium constant:

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

- The reaction quotient:

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

# 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):

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

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

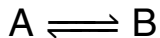
$\Delta G^\circ$  and  $K_{\text{eq}}$  convey essentially the same information.

$\Delta G^\circ$  represents the drive of the reaction to shift from the standard state concentrations towards equilibrium.

- For other concentrations:

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

# Clicker Question #1



If  $\Delta G^\circ = 0$ , which of the following is true (for sure)?

Choose up to two.

1  $K_{\text{eq}} < 1$

2  $K_{\text{eq}} = 1$

3  $K_{\text{eq}} > 1$

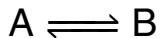
4  $\Delta H^\circ = 0$

5  $\Delta S^\circ = 0$

6  $\Delta H^\circ = T\Delta S^\circ$

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

## Clicker Question #2



If  $\Delta G^\circ > 0$ , which of the following is true (for sure)?

Choose up to two.

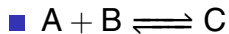
- 1 At equilibrium,  $[A] > [B]$ .
- 2 At equilibrium,  $[A] = [B]$ .
- 3 At equilibrium,  $[A] < [B]$ .
- 4  $\Delta H^\circ > 0$  and  $\Delta S^\circ < 0$
- 5  $\Delta H^\circ > 0$  or  $\Delta S^\circ < 0$
- 6  $\Delta H^\circ < 0$  or  $\Delta S^\circ < 0$

Note: “or” is inclusive of “and”.

# Some Fancy Words to Describe Reaction Thermodynamics

- Exothermic: Releases heat to the surroundings,  $\Delta H < 0$ 
  - Exothermic reactions are often favorable, but not always.
  - More generally, energy is released to the environment (such as light).
- Endothermic: Absorbs heat from the surroundings,  $\Delta H > 0$ 
  - Endothermic reactions are often unfavorable, but not always.
  - More generally, energy is absorbed from the environment.
- Exergonic:  $\Delta G < 0$ 
  - Reaction is always favorable, by definition!
- Endergonic:  $\Delta G > 0$ 
  - Reaction is always unfavorable, by definition!

# A Bimolecular Reaction



- $\Delta S = -460 \text{ J/K}$  (From counting little cubes.)

- 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  $\Delta G$ .

- For the reaction to be favorable, there must be other factors that make the total free energy change negative.

# 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)
- $\Delta G^\circ$ , defined with specific concentration units, contains within it the entropy loss at the standard state concentration.



# Chemical Energy



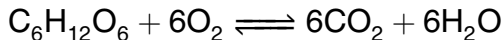
- What does “chemical energy” mean?

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<http://www.caffeineinformer.com>

<http://www.philosophersguild.com>

## An Energetic Chemical Reaction, Under Some Conditions



- Oxidation of glucose (or other hexose) by molecular oxygen.
- Free energy change depends on concentrations.
- Standard state conditions: 1 M glucose, 1 atm  $\text{O}_2$  and  $\text{CO}_2$

- $\Delta G^\circ = -2.7 \times 10^6 \text{ J/mol} = -2,700 \text{ kJ/mol}$
- Equilibrium constant:

$$K_{\text{eq}} = \frac{[\text{CO}_2]_{\text{eq}}^6}{[\text{C}_6\text{H}_{12}\text{O}_6]_{\text{eq}}[\text{O}_2]_{\text{eq}}^6} = e^{-\Delta G^\circ/(RT)} \approx 10^{473} \text{ M}^{-1}$$

(Water is ignored in free energy change calculation)

- Extremely favorable!
- But, this assumes 1 atm  $\text{O}_2$  and  $\text{CO}_2$ .
- Reaction only became favorable about 2.5 billion year ago, when oxygen became abundant on earth.

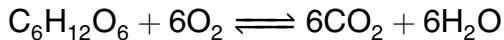
# Nutritional Calories

- Measured as the heat for complete combustion with excess  $O_2$  at constant volume (no work).

“bomb calorimeter”

- Since,  $w = 0$ ,  $q = \Delta E$
- For glucose, value is  $-4 \text{ kcal/g} = -175 \text{ kJ/mol}$ , vs  $\Delta G^\circ = -2,700 \text{ kJ/mol}$ .
- Why are these numbers so different?

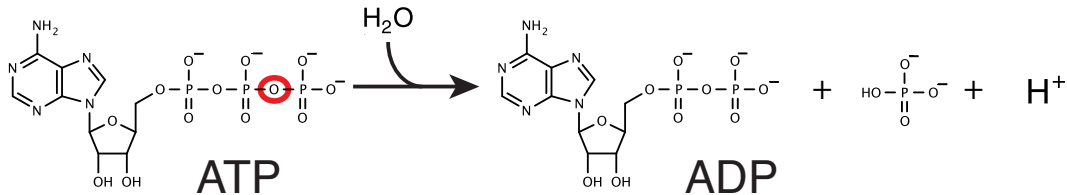
$$\Delta G = \Delta H - T\Delta S$$



There is a large increase in entropy, 7 molecules are converted to 12.

- Nutritionists estimate the amount of work required to offset the metabolism of a given number of nutritional calories.

# Another “High-energy” Reaction



- $\Delta G^\circ = -30 \text{ kJ/mol}$
- ATP serves as an “energy currency” in metabolism.
- Is there a “high-energy bond”?

## Clicker Question #3

What is the equilibrium constant for the reaction?



1  $\approx 10^{-5} \text{ M}$

2  $\approx 10^{-3} \text{ M}$

3  $\approx 10 \text{ M}$

4  $\approx 10^3 \text{ M}$

5  $\approx 10^5 \text{ M}$

$$R = 8.314 \text{ J}/(\text{K} \cdot \text{mol})$$

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

# Calculation of Equilibrium Constant from $\Delta G^\circ$

$$\Delta G^\circ = -30 \text{ kJ/mol} \quad R = 8.314 \text{ J/(K} \cdot \text{mol)} \quad T = 298 \text{ K}$$

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

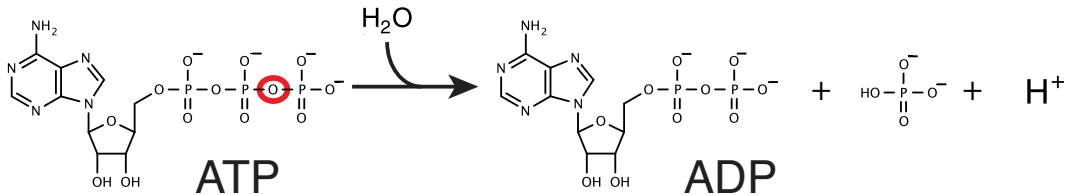
$$\ln K_{\text{eq}} = -\Delta G^\circ / (RT)$$

$$K_{\text{eq}} = e^{-\Delta G^\circ / (RT)}$$

$$\begin{aligned} -\Delta G^\circ / (RT) &= 30 \text{ kJ/mol} / (8.314 \text{ J/(K} \cdot \text{mol)} \cdot 298 \text{ K}) \\ &= 30 \times 10^3 \text{ J/mol} / 2.48 \times 10^3 \text{ J/mol} = 12 \end{aligned}$$

$$K_{\text{eq}} = e^{12} = 1.8 \times 10^5$$

# ATP Hydrolysis



- $\Delta G^\circ = -30 \text{ kJ/mol}$
- Why is the reaction so favorable?
  - High density of negative phosphate charges is reduced.
  - More resonance stabilization in ADP and  $\text{P}_i$ .
  - More favorable interaction with water by ADP and  $\text{P}_i$ .