5.111 Lecture Summary #17

Friday, October 17, 2014

Reading for today: Sections 8.8, 8.12, 8.13, 8.15, and 8.16 (same sections but in Chapter 7 in 4th ed): Entropy and Gibbs Free Energy, and Free-Energy Changes in Biology.

Reading for Lecture #18: Sections 10.1-10.9 (same sections but in Chapter 9 in 4th ed): Chemical Equilibrium

Topics: Thermodynamics

I. Effect of temperature on spontaneity
II. Thermodynamics in biological systems
   A. Hydrogen-bonding
   B. ATP-coupled reactions

I. EFFECT OF TEMPERATURE ON SPONTANEITY

Consider the decomposition of sodium bicarbonate at 298 versus 450. K.

\[ 2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g) \]

\[ \Delta H^\circ = 135.6 \text{ kJ/mol} \]

\[ \Delta S^\circ = \underline{\text{kJ/(K\text{ mol})}} \]

\[ \Delta G^\circ_r = \Delta H^\circ_r - T(\Delta S^\circ_r) \]

At \( T = 298\text{K} \)

\[ \Delta G^\circ = 135.6 \text{ kJ/mol} - 298 \text{K}(\underline{\text{kJ/(K\text{ mol})}}) = \underline{\text{kJ/mol}} \]

The reaction is \underline{[blank]} at room temperature.

But at baking temperatures of 350°F or 450.K

\[ \Delta G^\circ = 135.6 - (450.)(0.334) = \underline{\text{kJ/mol}} \]

The reaction is \underline{[blank]} at baking temperature.

When \( \Delta H^\circ \) and \( \Delta S^\circ \) have the \underline{[blank]} sign, it is possible to control spontaneity with \( T \).

Assuming that \( \Delta H^\circ \) and \( \Delta S^\circ \) are independent of \( T \), a reasonable first-order assumption, then \( \Delta G^\circ \) is a \underline{[blank]} function of \( T \).
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \text{ or } \Delta G^\circ = -\Delta S^\circ(T) + \Delta H^\circ \]

Calculate \( T^* \) (at which \( \Delta G^\circ = 0 \)) for the decomposition of sodium bicarbonate.

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

\[
0 = \Delta H^\circ - T^* \Delta S^\circ
\]

\[
T^* = \frac{\Delta H^\circ}{\Delta S^\circ} \text{ kJ/mol} = \frac{\text{kJ}}{\text{(K}\cdot\text{mol)}}
\]

Consider the plot of temperature dependence when both \( \Delta H^\circ \) and \( \Delta S^\circ \) are negative.

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

spontaneous

\( \Delta G^\circ \) kJ/mol

0

non-spontaneous

\( T^* \quad T[\text{K}] \)
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

<table>
<thead>
<tr>
<th>( \Delta H^\circ )</th>
<th>( \Delta S^\circ )</th>
<th>Spontaneous</th>
<th>( \Delta G^\circ ) at T*</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0</td>
<td>&gt; 0</td>
<td>Spontaneous</td>
<td>&lt; at any T*</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>&lt; 0</td>
<td>Spontaneous</td>
<td>&gt; 0 when T &gt; T*</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>&gt; 0</td>
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</tr>
<tr>
<td>&lt; 0</td>
<td>&lt; 0</td>
<td>Spontaneous</td>
<td>&gt; T*</td>
</tr>
</tbody>
</table>

Temperature is important! It can influence both spontaneity and rate of reaction.

II. THERMODYNAMICS IN BIOLOGICAL SYSTEMS

A) HYDROGEN BONDING

A hydrogen bond is an interaction between a hydrogen bond donor (a hydrogen atom in a polar bond, typically a H-F, H-O or H-N bond), and a hydrogen-bond acceptor (an electronegative atom with a \( \delta^- \) of electrons available for bonding).

\[ \text{X---H} \cdots \cdots \text{Y} \]

where X = O, N, F

And Y is the hydrogen bond acceptor such as: _____, _____, _____

For example, hydrogen bonds form between water molecules:

Mean bond enthalpies of hydrogen-bonds (H-bonds):
H-bonds are the strongest type of intermolecular interaction. However, H-bonds are weaker than covalent or ionic bonds.

<table>
<thead>
<tr>
<th>Bond</th>
<th>mean bond enthalpy (in kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH---O</td>
<td>H-bond</td>
</tr>
<tr>
<td>H-O</td>
<td>covalent bond</td>
</tr>
<tr>
<td>OH---N</td>
<td>H-bond</td>
</tr>
<tr>
<td>NH---N</td>
<td>H-bond</td>
</tr>
<tr>
<td>H-N</td>
<td>covalent bond</td>
</tr>
</tbody>
</table>

H-bonding can be intermolecular (as in the water molecules above) or intramolecular. Intramolecular H-bonds in proteins are required for a protein’s 3-dimensional shape.
Hydrogen Bonding in DNA

Hydrogen bonding binds together complementary strands of DNA to form a double helix.

The lower bond enthalpies of hydrogen bonds compared to covalent bonds facilitate the separation of DNA strands during DNA replication.

**IN THEIR OWN WORDS: WHY HYDROGEN BONDS ARE IMPORTANT**

RNA interference (RNAi) is a process in which small pieces of “silencing” RNA (siRNA), typically 19 to 25 base pairs in length, inhibit gene expression.

Dr. Lourdes Aleman discusses how understanding hydrogen bonding is essential to her research on RNAi in the lab of Prof. Phil Sharp, and how scientists hope to use their understanding of RNAi to design treatments for genetic and viral diseases.

**B) ATP-COUPLED REACTIONS**

Many biological reactions are non-spontaneous, meaning they require energy to proceed in the forward direction.

The hydrolysis of ATP (ATP → ADP), a spontaneous process, can be ________________ to a non-spontaneous reaction to drive the reaction forward.

\[ \Delta G^\circ \]

The resulting $\Delta G^\circ$ of the coupled reaction is the sum of the individual $\Delta G^\circ$ values.
First, let’s calculate the $\Delta G^\circ$ for ATP hydrolysis at 310 K (body temperature).

$\Delta H^\circ = -24 \text{ kJ/mol}$ (from Lecture #16)  

$\Delta S^\circ = +22 \text{ J/K.mol}$

\[
\begin{align*}
\text{C} & \quad \text{NH}_2 & \quad \text{C} & \quad \text{NH}_2 \\
\text{N} & \quad \text{C} & \quad \text{N} & \quad \text{C} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{OH} \\
\text{HC} & \quad \text{CH}_2 & \quad \text{N} & \quad \text{C} \quad \text{CH} \\
\text{N} & \quad \text{O} & \quad \text{P} & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{P} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{NH}_2 & \quad \text{C} & \quad \text{NH}_2 \\
\text{N} & \quad \text{C} & \quad \text{N} & \quad \text{C} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{OH} \\
\text{HC} & \quad \text{CH}_2 & \quad \text{N} & \quad \text{C} \quad \text{CH} \\
\text{N} & \quad \text{O} & \quad \text{P} & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{P} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

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\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{OH} \\
\text{HC} & \quad \text{CH}_2 & \quad \text{N} & \quad \text{C} \quad \text{CH} \\
\text{N} & \quad \text{O} & \quad \text{P} & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{P} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
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\text{N} & \quad \text{O} & \quad \text{P} & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{P} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
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\text{N} & \quad \text{O} & \quad \text{P} & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{P} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

$\Delta G^\circ = -24 \text{ kJ/mol} - (310 \text{ K})(0.022 \text{ kJ/(K.mol)}) = \text{_____________ kJ/mol}$

Note: the calculated free energies are under standard conditions. This is an approximation since these molecules are NOT under standard conditions in cells.

Example of an ATP-coupled reaction: the conversion of glucose to glucose-6-P.

Adding a phosphate (P) group to glucose gives the glucose a negative charge, which prevents the glucose molecule from diffusing back out of the cell through the “greasy” cell membrane.

\[
\Delta G^\circ = +17 \text{ kJ/mol for glucose to glucose-6-P}
\]

$\Delta G^\circ = \text{_______ kJ/mol for ATP hydrolysis}$

An enzyme couples the glucose-to-glucose-6-P reaction to ATP hydrolysis.

The net change in free energy $\Delta G_{\text{total}}^\circ = \text{_______} - \text{_______} = \text{_______ kJ/mol}$

If ATP hydrolysis is spontaneous, why is it not occurring unregulated in the cell?

Kinetics. A reaction can be thermodynamically spontaneous, but kinetically very very slow.