5.111 Lecture Summary #18

Reading for today: Section 7.16 – Free-Energy Changes in Biological Systems.

Exam #2 coming up

Topics: **Thermodynamics**
- **I.** Free energy of formation
- **II.** Effect of temperature on spontaneity
- **III.** Thermodynamics in biological systems
  - **A.** ATP-coupled reactions
  - **B.** Hydrogen bonding

I. FREEE ENERGY OF FORMATION, ΔG_f (continued from Lecture #17)

ΔG_f^o is a measure of a compound's stability relative to its elements.

If $\Delta G_f^o < 0$, a compound is thermodynamically ________________ relative to its elements.

If $\Delta G_f^o > 0$, a compound is thermodynamically ________________ relative to its elements.

$6C(gr) + 3H_2(g) \rightarrow C_6H_6(l)$ $\quad \Delta G_f^o = 124$ kJ/mol

$C_6H_6(l) \rightarrow 6C(gr) + 3H_2(g)$ $\quad \Delta G^o = -124$ kJ/mol

The reverse reaction spontaneous, but very, very slow!

Free energy tells whether or not a reaction will happen spontaneously, but tells us ______________ about the rate of the reaction (for rate information we need kinetics).

To calculate $\Delta G°$ for a reaction…

$$\Delta G_r° = \Sigma\Delta G_f°(\text{products}) - \Sigma\Delta G_f°(\text{reactants})$$

$$\text{OR} \quad \Delta G_r° = \Delta H_r° - T\Delta S_r°$$

II. EFFECT OF TEMPERATURE ON SPONTANEITY

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

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

$\Delta H^o = 135.6$ kJ/mol $\quad \Delta S^o =$ ________ kJ/(K•mol)

$$\mathbf{\Delta G_r° = \Delta H_r° - T(\Delta S_r°)}$$

At T = 298K ΔG^o = ________-298(________) = ________ kJ/mol

The reaction is ______________________ at room temperature.

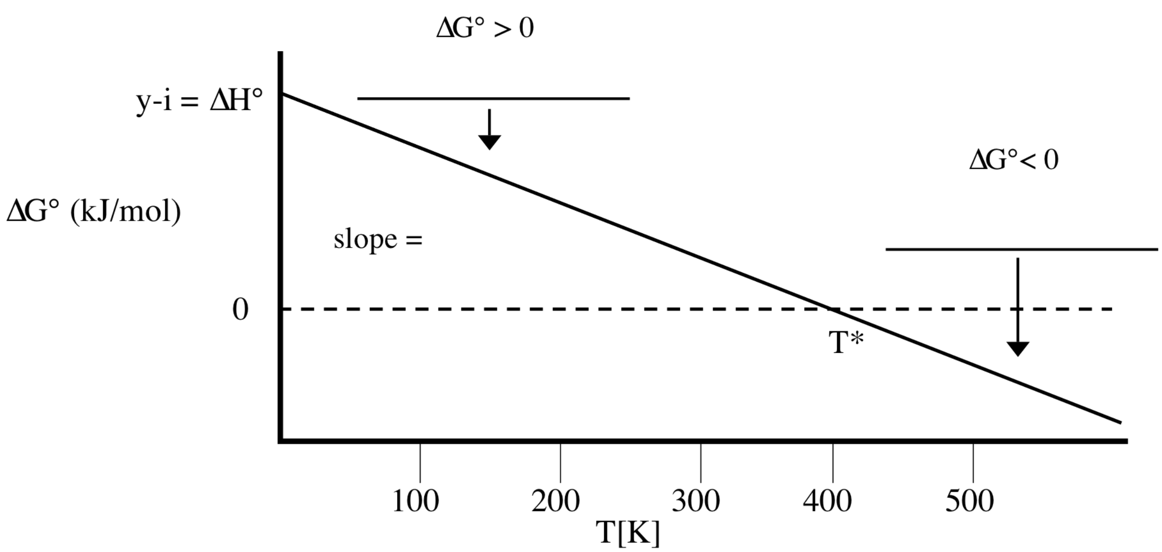
But at baking temperatures of 350°F or 450.K

ΔG^o = 135.6 – ________ (0.334) = ________ kJ/mol

The reaction is ______________________ at baking temperature.

- When ΔH^o and ΔS^o have same sign, it is possible to control spontaneity with T.
- Assuming that ΔH^o and ΔS^o are independent of T, a reasonable first-order assumption, then ΔG^o is a _____________ function of T.

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



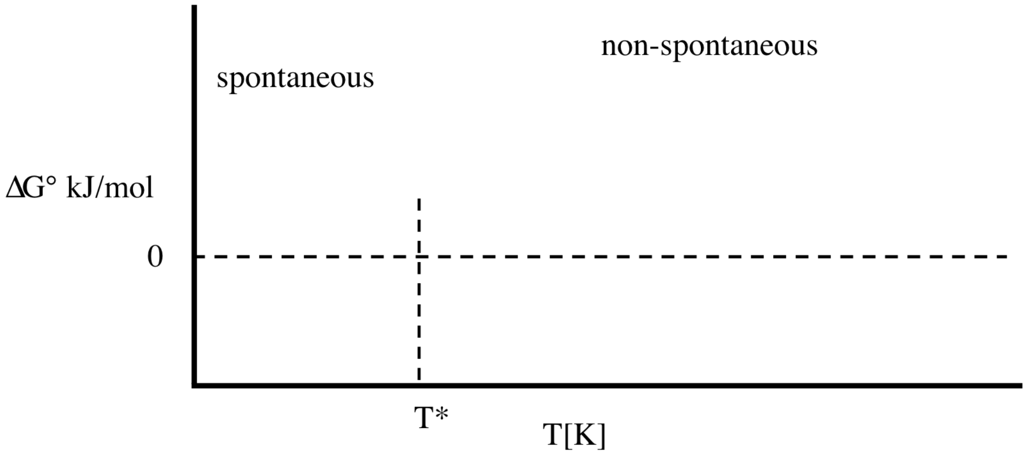
Calculate T* (at which ΔG^o = ____) for the decomposition of sodium bicarbonate.

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

$0 = \Delta H^o - T^*\Delta S^o$ T* = _____________

T* = ____________________ = __________

Consider the plot of temperature dependence when both ΔH^o and ΔS^o are negative,



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

$\Delta H^\circ < 0$ $\Delta S^\circ > 0$ ________________ spontaneous $\Delta G^\circ < 0$ at _________

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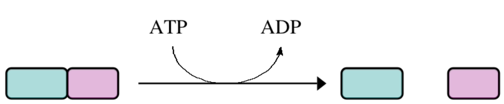
$\Delta H^\circ < 0$ $\Delta S^\circ < 0$ ________________ spontaneous $\Delta G^\circ < 0$ when T ____ T*

III. THERMODYNAMICS IN BIOLOGICAL SYSTEMS

A) ATP-COUPLED REACTIONS

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

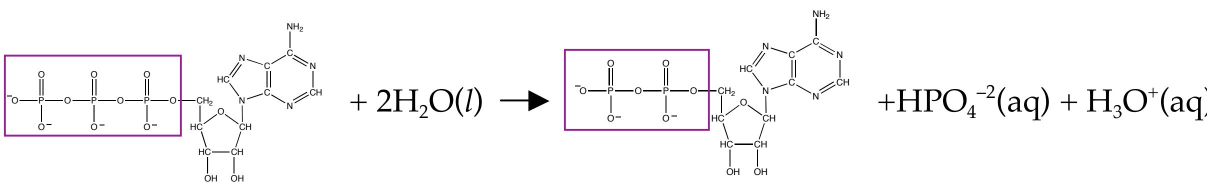
The hydrolysis of ATP (ATP → ADP), a spontaneous process, can be _______________ to a non-spontaneous reaction to drive the reaction forward.



The resulting ΔG° of the coupled reaction is the sum of the individual ΔG° values.

First, let's calculate the ΔG° for ATP hydrolysis at 310 K (body temperature).

ΔH° = -24 kJ/mol (from Lecture #17) **ΔS°** = +22 J/K•mol

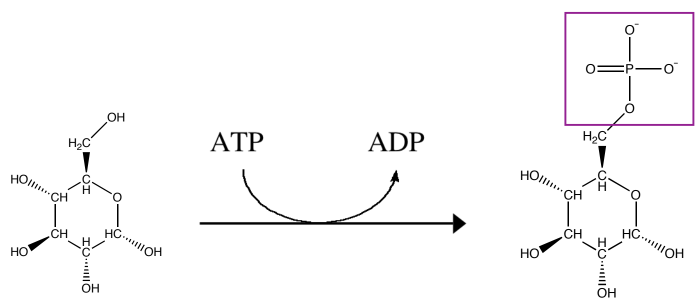


ΔG° =

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.



ΔG^{o} = +17 kJ/mol for glucose to glucose-6-P

ΔG^{o} = ________ kJ/mol for ATP hydrolysis

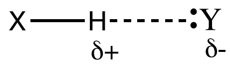
An enzyme **couples** the glucose-to-glucose-6-P reaction to ATP hydrolysis.
The net change in free energy =

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.

B) HYDROGEN BONDING

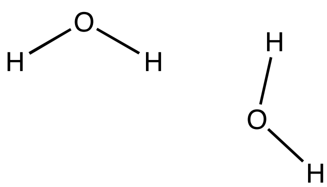
A **hydrogen bond** is an electrostatic interaction between a hydrogen atom in a polar bond (typically a H-F, H-O or H-N bond) and a "hydrogen-bond donor", a strongly electronegative atom.



where X = O, N, F
And Y is the hydrogen bond donor: _____, _____, _____

The H-bond donor (Y) atom must be small, highly electronegative atom with a ___________________ of electrons available for bonding.

For example, hydrogen bonds form between water molecules:



Mean bond enthalpies of hydrogen-bonds (H-bonds):

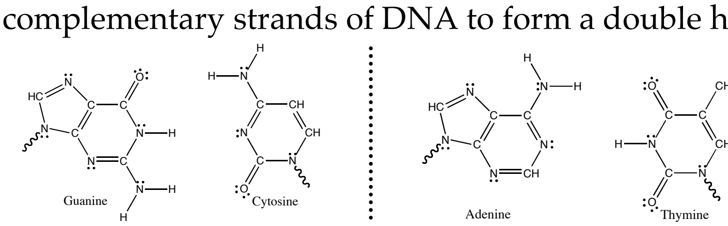
H-bonds are the strongest type of intermolecular interaction. However, H-bonds are weaker than covalent or ionic bonds.

		mean bond enthalpy (in kJ/mol)
OH---O	H-bond	_______
H-O	covalent bond	463
OH---N	H-bond	29
NH---N	H-bond	14
H-N	covalent bond	_______

H-bonding can be *inter*molecular (as in the water molecules above) or *intra*molecular. 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.