

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.

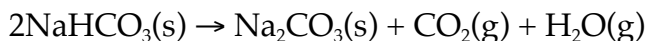
Reading for Lecture #18: Sections 10.1-10.9 (same sections but in Chapter 9 in 4th ed): Chemical Equilibrium

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.



$$\Delta H^\circ = 135.6 \text{ kJ/mol} \quad \Delta S^\circ = \text{_____ kJ/(K}\cdot\text{mol)}$$

$$\Delta G_r^\circ = \Delta H_r^\circ - T(\Delta S_r^\circ)$$

$$\text{At } T = 298\text{K} \quad \Delta G^\circ = 135.6 \text{ kJ/mol} - 298 \text{ K}(\text{_____ kJ/(K}\cdot\text{mol)}) = \text{_____ kJ/mol}$$

The reaction is _____ at room temperature.

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

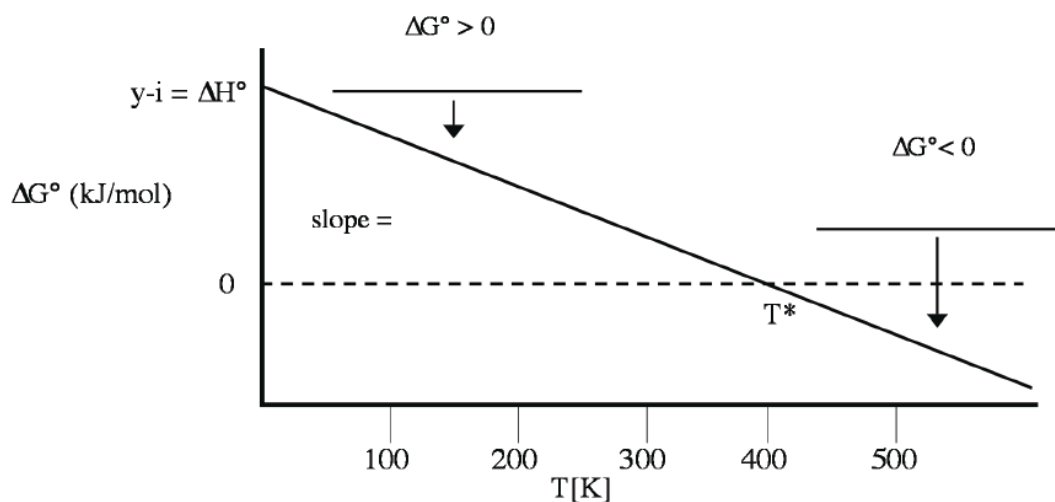
$$\Delta G^\circ = 135.6 - (450.)(0.334) = \text{_____ kJ/mol}$$

The reaction is _____ at baking temperature.

When ΔH° and ΔS° have the _____ sign, it is possible to control spontaneity with T.

Assuming that ΔH° and ΔS° are independent of T, a reasonable first-order assumption, then ΔG° is a _____ 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.

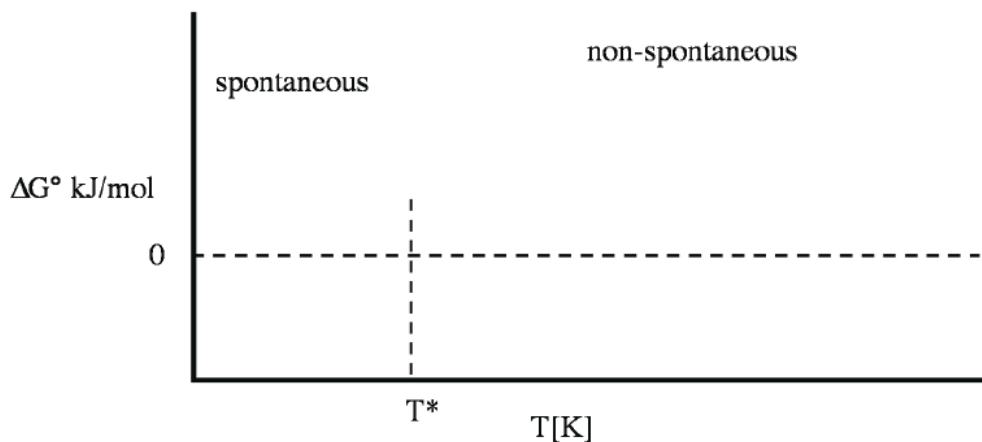
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$0 = \Delta H^\circ - T^*\Delta S^\circ \quad T^* = \underline{\hspace{2cm}}$$

$$T^* = \frac{\underline{\hspace{2cm}} \text{ kJ/mol}}{\text{kJ/(K}\cdot\text{mol)}} = \underline{\hspace{2cm}} \text{ K}$$

Consider the plot of temperature dependence when both ΔH° and ΔS° are **negative**

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



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

$$\Delta H^\circ < 0 \quad \Delta S^\circ > 0 \quad \text{spontaneous} \quad \Delta G^\circ < 0$$

$$\Delta H^\circ > 0 \quad \Delta S^\circ < 0 \quad \text{non-spontaneous} \quad \Delta G^\circ > 0$$

$$\Delta H^\circ > 0 \quad \Delta S^\circ > 0 \quad \text{spontaneous at high } T \quad \Delta G^\circ < 0 \text{ at high } T$$

$$\Delta H^\circ < 0 \quad \Delta S^\circ < 0 \quad \text{spontaneous at low } T \quad \Delta G^\circ < 0 \text{ at low } T$$

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

II. THERMODYNAMICS IN BIOLOGICAL SYSTEMS

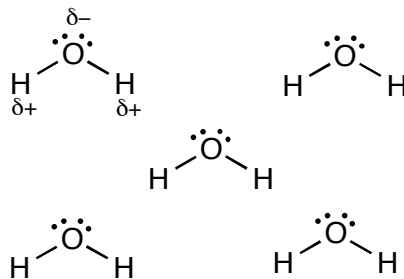
A) HYDROGEN BONDING

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 lone pair of electrons).



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

For example, hydrogen bonds form between water molecules:



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

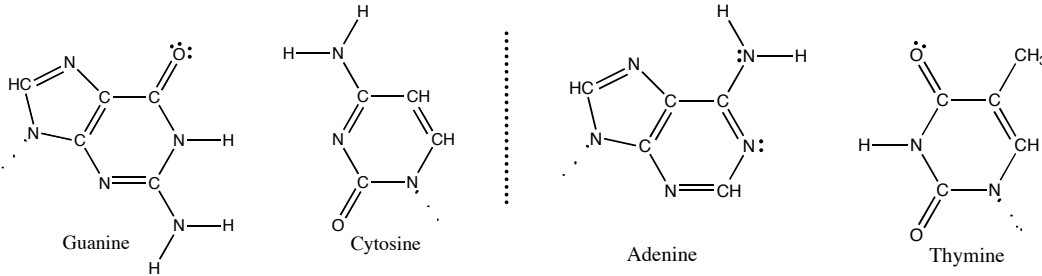
H-bonds are the strongest type of intermolecular interaction. However, H-bonds are weaker than covalent or ionic bonds.

	<i>mean bond enthalpy (in kJ/mol)</i>
OH---O H-bond	21
H-O covalent bond	463
OH---N H-bond	29
NH---N H-bond	14
H-N covalent bond	431

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.

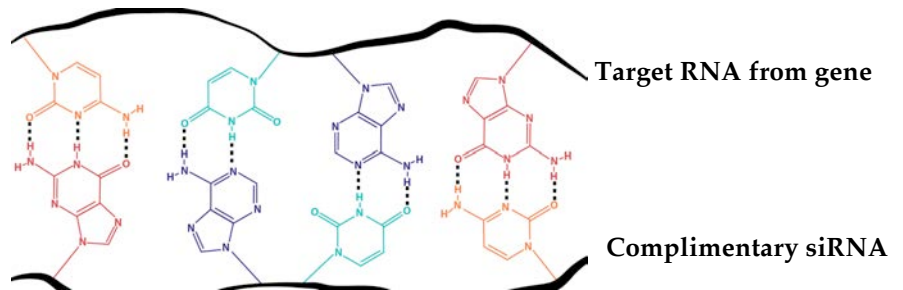


Image from "Behind the Scenes at MIT". The Drennan Education Laboratory.

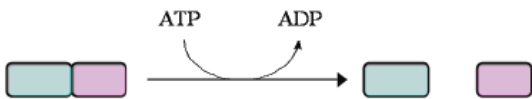
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Dr. Lourdes Aleman discusses how understanding hydrogen bonding is essential to her research on RNAi in the lab of Prof. Phil Sharp, and how scientists hope to use their understanding of RNAi to design treatments for genetic and viral diseases.

B) ATP-COUPLED REACTIONS

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

The hydrolysis of ATP ($\text{ATP} \rightarrow \text{ADP}$), a spontaneous process, can be _____ to a non-spontaneous reaction to drive the reaction forward.

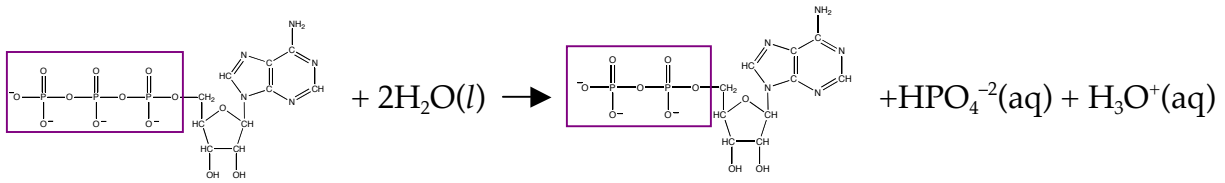


The resulting ΔG° of the coupled reaction is the sum of the individual ΔG° values.

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

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

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

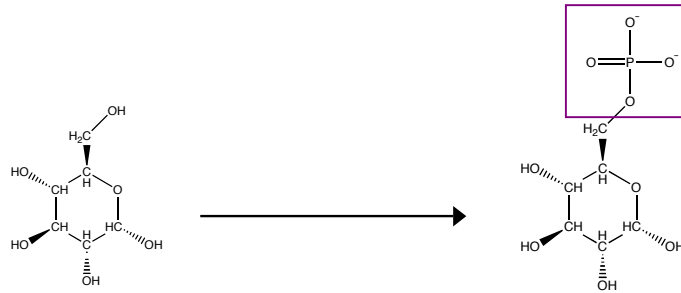


$$\Delta G^\circ = -24 \text{ kJ/mol} - (310 \text{ K})(0.022 \text{ kJ/(K}\cdot\text{mol)}) = \underline{\hspace{2cm}} \text{ kJ/mol}$$

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.



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

$$\Delta G^\circ = \underline{\hspace{2cm}} \text{ kJ/mol for ATP hydrolysis}$$

An enzyme **couple**s the glucose-to-glucose-6-P reaction to ATP hydrolysis.

$$\text{The net change in free energy} = \Delta G_{\text{total}}^\circ = \underline{\hspace{2cm}} - \underline{\hspace{2cm}} = \underline{\hspace{2cm}} \text{ kJ/mol}$$

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.

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5.111 Principles of Chemical Science
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