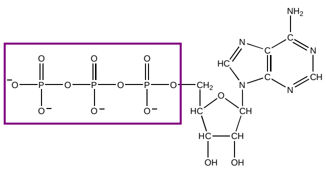
5.111 Principles of Chemical Science
Fall 2008

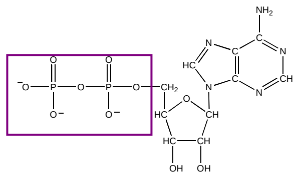
Thermochemistry: Biology-Related Examples

See Lectures 16-18 for thermodynamics. See Lecture 18 notes for ATP coupled reactions and enthalpies of hydrogen bonds.

Recall from Lecture 17 that the $\Delta H°$ of ATP hydrolysis is -24 kJ/mol of ATP**.**



+ $2H_2O$ (*l*) (aq) $\longrightarrow$



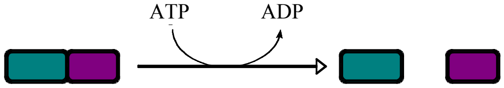
+HPO_4^{-2} (aq) + H_3O^+

ATP (aq) ADP (aq) **$\Delta H°$ = -24 kJ/mol ATP**

Example 1) from page 3 of Lecture 18 notes: ATP-coupled reactions in the body

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

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



The resulting $\Delta G°$ of the coupled reaction is the sum of the individual $\Delta G°$ values.

First, let's calculate the $\Delta G°$ for ATP hydrolysis at 310 K (body temperature) given that $\mathbf{\Delta H°}$ = -24 kJ/mol (from Lecture #17) and $\mathbf{\Delta S°}$ = +22 J/K•mol.

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

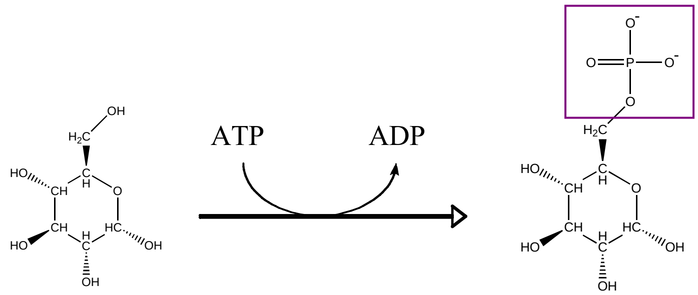
$$\Delta G° = -24 \text{ kJ/mol} - 310 \text{ K } (0.022 \text{ kJ/mol})$$

$$\Delta G° = -31 \text{ kJ/mol of ATP hydrolyzed}$$

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

Consider the following ATP-coupled reaction: the **conversion of glucose to glucose-6-P.**

Why this reaction is important: 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 = -31 kJ/mol for ATP hydrolysis

An enzyme **couples** the glucose to glucose-6-P reaction to ATP hydrolysis.
The net change in free energy = 17 kJ/mol + (-31 kJ/mol) = -14 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.

Example 2) from page 5 of Lecture 18 notes: Enthalpy and hydrogen bonds

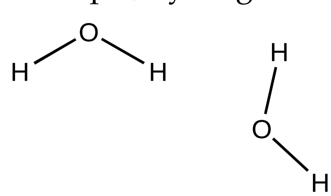
A **hydrogen bond** is an electrostatic interaction between a hydrogen atom in a polar bond (typically a H-F, H-O or H-N bond) and a "hydrogen-bond acceptor", a strongly electronegative atom.

$$\mathrm{X}\text{—}\underset{\delta+}{\mathrm{H}}\cdots\cdots:\underset{\delta-}{\mathrm{Y}}$$

where X = O, N, F
And Y is the hydrogen bond acceptor: N, O, or F

The H-bond acceptor (Y) atom must be small, highly electronegative atom with a lone pair 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.

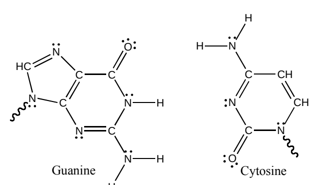
		mean bond enthalpy (in kJ/mol)
OH---O	H-bond	20
H-O	covalent bond	463
OH---N	H-bond	29
NH---N	H-bond	14
H-N	covalent bond	388

Hydrogen bonding can be *inter*molecular (as in the water molecules above) or *intra*molecular. Intramolecular hydrogen bonds in proteins are required for a protein's 3-dimensional shape.

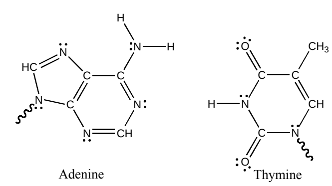
Hydrogen bonds are also important in DNA structure and function.

Hydrogen bonding in DNA

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



3 H-bonds between C and G



2 H-bonds between A and T

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