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5.111 Principles of Chemical Science
Fall 2008

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5.111 Lecture Summary #17

Readings for today: Section 7.1 – Spontaneous Change, Sections 7.2 and 7.8 – Entropy, Sections 7.12, 7.13, and 7.15 – Free Energy.

Read for Lecture #18: Section 7.16 – Free-Energy Changes in Biological Systems. (Assigned sections in chapter 7 are the same for the 3rd and the 4th ed.)

Topics: Thermodynamics

- I. Enthalpies of reactions: calculating ΔH_r° (continued from Lecture #16)
- II. Spontaneous change and free energy
- III. Entropy
- IV. Free energy of formation

Clicker question: review of hybridization

Hybridization in complex molecules. Example: the morphine rule

Morphine, a potent and addictive analgesic (“painkiller”), and related molecules share a characteristic set of four features referred to as the morphine rule:

1) phenyl ring
2) _____ C
3) CH₂CH₂
4) _____ N

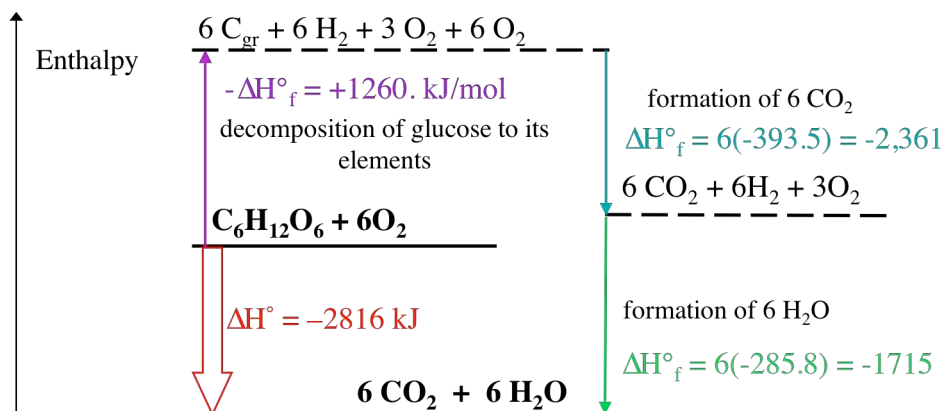
Morphine

Demerol

These molecules mimic the action of (and have structural similarities to) endorphins.

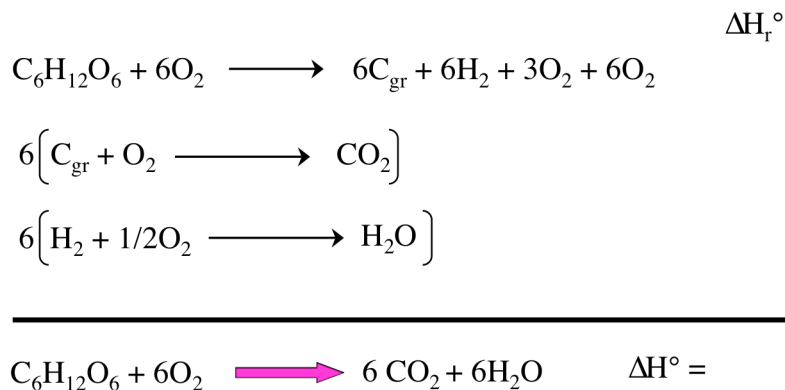
I. ENTHALPIES OF CHEMICAL REACTIONS (continued from Lecture #16) USING HESS’S LAW TO CALCULATE ΔH_r

Enthalpy is a “STATE” FUNCTION, which means ΔH is _____ of path.



Hess's Law: If two or more chemical equations are added to give another chemical equation, corresponding _____ must be added.

ΔH° for glucose oxidation (all values in kJ):



We have covered 3 methods (so far) to calculate ΔH_r° :

1) _____ enthalpies (ΔH or ΔH_B)

$$\Delta H_r^\circ = \Sigma \Delta H_B(\text{_____}) - \Sigma \Delta H_B(\text{_____})$$

2) Standard enthalpies of formation (_____)

$$\Delta H_r^\circ = \Sigma \Delta H_f^\circ(\text{_____}) - \Sigma \Delta H_f^\circ(\text{_____})$$

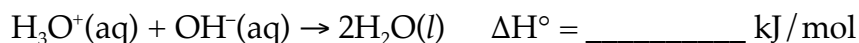
3) Hess's law

*** END OF EXAM #2 MATERIAL ***

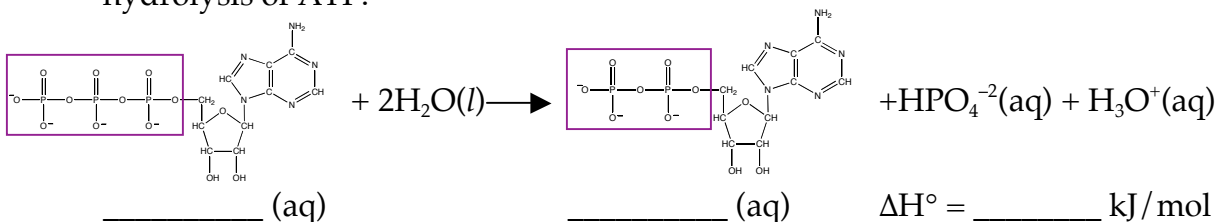
II. SPONTANEOUS CHANGE AND FREE ENERGY

A **spontaneous change** is a process that, given enough time, occurs without the need for outside intervention.

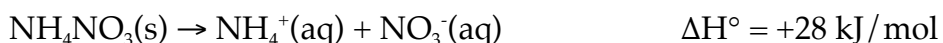
For example, the following reactions are spontaneous at constant pressure:



hydrolysis of ATP:



But so are these ...



Is ΔH the key to spontaneity? _____!

Condition for spontaneity under constant P + T involves GIBBS FREE ENERGY, ΔG.

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

where T = temperature and ΔS = change in entropy, a measure of disorder.

ΔG < 0 _____ process

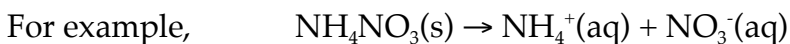
ΔG > 0 _____ process

ΔG = 0 equilibrium

Under constant pressure and temperature, a process is spontaneous when ΔG < 0, not necessarily when ΔH < 0. Why?

$$\underbrace{\Delta G}_{\text{Useful work or FREE energy}} = \underbrace{\Delta H - T\Delta S}_{\text{Amount of reaction energy that gets "stuck"}}$$

Figuring this out was one of the towering achievements of thermodynamics!!



ΔH_r° = +28 kJ/mol ΔS_r° = +109 JK⁻¹mol⁻¹

ΔG° = ΔH° - TΔS°

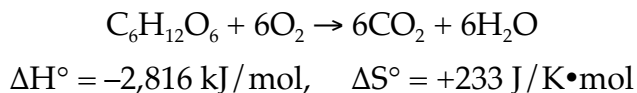
at T = 298 K, ΔG° = _____ - _____ (_____)

ΔG° = _____ kJ/mol - _____ kJ/mol

ΔG° = _____ kJ/mol

ΔG° is negative, even though ΔH° is positive. The reaction is **spontaneous**.

Now consider glucose oxidation at room temperature:



$$\Delta G^\circ = \text{_____} - 298(\text{_____}) = \text{_____} \text{ kJ/mol}$$

ΔG° more negative than ΔH° . This reaction is spontaneous at _____ temperatures.

III. ENTROPY

Entropy, S , is a measure of the _____ of a system.
 ΔS = change in entropy. ΔS is a state function.

ΔS° positive \Rightarrow _____ in disorder

ΔS° negative \Rightarrow _____ in disorder

Disorder of gas ____ liquid ____ solid

In solids, molecules cannot move around freely- they are locked in ordered locations.

Internal degrees of freedom – e.g. multiple molecular configurations, many quantum states that can be occupied - also contribute to entropy

Without calculations, we can predict the sign of ΔS for many reactions. For example, $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$ has a _____ ΔS .

Entropy for reactions, ΔS_r°

can be calculated from **absolute** entropies of products and reactants,

$$\Delta S_r^\circ = \sum S^\circ(\text{_____}) - \sum S^\circ(\text{_____})$$

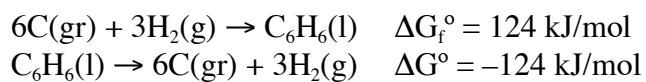
where S° is the absolute standard entropy.

Unlike E or H , where the zero can be selected, S has an absolute zero – the perfect crystal at $T = 0 \text{ K}$ (perfectly ordered, no disorder at all).

For example, consider the decomposition of hydrogen peroxide.

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

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



The reverse reaction is spontaneous, but very, very slow!

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

To calculate ΔG° for a reaction...

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

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