5.111 Lecture Summary #16

Read for Lecture #17: Section 7.1 – Spontaneous Change, Sections 7.2 and 7.8 - Entropy, Sections 7.12, 7.13, + 7.15 – Free Energy. (Section numbers are the same for the 3rd and the 4th ed.)

Topics:

I. Valence bond theory and hybridization (continued from Lecture #15)
Determining hybridization in complex molecules

II. Energies and enthalpies of chemical reactions
A. Bond energy / bond enthalpy
B. Heat of formation

I. VALENCE BOND THEORY AND HYBRIDIZATION (continued from Lecture #15)

DETERMINING HYBIDIZATION IN COMPLEX MOLECULES

To determine the hybridization of a given atom in a molecule,

(# of bonded atoms) + (# of lone pairs) = # of hybrid orbitals

2 hybrid orbitals- _____, 3 hybrid orbitals - _____, 4 hybrid orbitals- sp³

Exception: single-bonded, _____________ atoms. For the purposes of this course, do NOT hybridize single, bonded, terminal atoms.

Example: ascorbic acid (vitamin C)

Identify the hybridization and geometry of each C atom:
Identify the symmetry and name the hybrid or atomic orbitals that constitute the bonds below:

Bonds to carbon b:

- \( \text{C}_b-\text{H} \):
- \( \text{C}_b-\text{C}_c: \sigma(\text{C}2\text{sp}^3, \text{C}2\text{sp}^3) \)
- \( \text{C}_b-\text{O} \):

Bonds to carbon d:

- \( \text{C}_d-\text{O} \):
- \( \text{C}_d-\text{C}_c: \sigma(\text{C}2\text{sp}^2, \text{C}2\text{sp}^3) \)
- \( \text{C}_d-\text{C}_e \):

II. ENERGIES AND ENTHALPIES OF CHEMICAL REACTIONS

A. BOND ENERGY/ BOND ENTHALPY

bond (dissociation) energy, \( \Delta E_{d} \), is the energy required to break a bond.

\[ \Delta H, \text{ bond } \Delta H \] is the change in heat accompanying the dissociation of a bond (measured at constant pressure \( P \)).

\[ \Delta H = \Delta E + \Delta(PV) \]

For gases, \( \Delta H \) & \( \Delta E \) differ by _____ %. For liquids and solids, negligible difference.

\[ \Delta H^\circ = \text{bond enthalpy} \] indicates reactants and products are in the standard state (pure form) at 1 bar for gasses.
Bond enthalpies for C—H bonds (all gases)

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3 + \text{H} & \Delta H^\circ = +438 \text{ kJ/mol} \\
\text{C}_2\text{H}_6 & \rightarrow \text{C}_2\text{H}_5 + \text{H} & \Delta H^\circ = +410 \text{ kJ/mol} \\
\text{CHF}_3 & \rightarrow \text{CF}_3 + \text{H} & \Delta H^\circ = +429 \text{ kJ/mol} \\
\text{CHCl}_3 & \rightarrow \text{CCl}_3 + \text{H} & \Delta H^\circ = +380 \text{ kJ/mol} \\
\text{CHBr}_3 & \rightarrow \text{CBr}_3 + \text{H} & \Delta H^\circ = +377 \text{ kJ/mol}
\end{align*}
\]

\(\Delta H^\circ\) is positive – _______________

The C-H bond enthalpies listed above are all within 8% of the average value (_______ kJ/mol) for C-H bonds. (See Table 6.8 in the text.)

What is the importance of bond enthalpies? The difference between bond enthalpies in products and reactants gives an estimate of the enthalpy of reaction.

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 & \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} & \Delta H_r^\circ = -2816 \text{ kJ/mole} \\
\Delta H^\circ & \text{ is negative - ______________} 
\end{align*}
\]

---

**The oxidation of glucose**

Plants convert carbon dioxide and water into sugar (glucose) and oxygen.

* This process requires energy.  
* We eat plants to get the energy stored in the glucose molecules.

![Image of plant with equation 6CO2 + 6H2O → C6H12O6 + 6O2]

We perform the reverse reaction, the oxidation of glucose, to harness the stored energy.

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 & \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy} & \text{We store this energy in the form of ATP.}
\end{align*}
\]

To calculate \(\Delta H_r^\circ\) for the oxidation of glucose (or for any reaction):

\[
\Delta H_r^\circ = \sum \Delta H_i - \sum \Delta H_j
\]

\(i^{th}\) bond in reactants \(j^{th}\) bond in products

If bonds stronger in products than reactants, \(\Delta H\) is ______________ (__________).

If bonds stronger in reactants than products, \(\Delta H\) is ______________ (endothermic).
B. HEAT OF FORMATION

More accurate approach...use heat of formation - \( \Delta H^\circ_f \)

\[ \Delta H^\circ_f = \Delta H^\circ_r \] for forming 1 mol of compound from pure elements in their most stable form at the standard state = 1 bar and 298.15 K

\[ \begin{align*} 
H_2(g) + \frac{1}{2}O_2(g) & \rightarrow H_2O(l) \quad \Delta H^\circ = -285.8 \text{ kJ/mol} = \Delta H^\circ_f \text{ for } H_2O(l) \\
C_{\text{gr}} + O_2(g) & \rightarrow CO_2(g) \quad \Delta H^\circ = -393.5 \text{ kJ/mol} = \Delta H^\circ_f \text{ for } CO_2(g) \\
O_2(g) & \rightarrow O_2(g) \quad \Delta H^\circ = \text{_________} = \Delta H^\circ_f \text{ for } O_2(g) 
\end{align*} \]

The heat of formation of an element in its most stable state is ____________.

\[ 3O_2(g) + 6C_{\text{gr}} + 6H_2(g) \rightarrow C_6H_{12}O_6 \quad \Delta H^\circ_f = \text{_________. kJ/mol for } C_6H_{12}O_6 \]
We can calculate $\Delta H_r^\circ$ for glucose oxidation (or any other reaction) using $\Delta H_r^\circ$.

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

$\Delta H_r^\circ =$

$\Delta H_r^\circ =$

$\Delta H_r^\circ = \underline{\text{kJ/mol}}$

Same value as experiment because $\Delta H_r^\circ$ is specific to a compound. Table of $\Delta H_r^\circ$ for compounds is small compared to a table of $\Delta H$ for all possible reactions or to a table of individual bond enthalpies for each bond in all possible molecules!

Enthalpy is a “STATE” FUNCTION, which means $\Delta H$ is __________________ of path.

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

$\Delta H^\circ$ for glucose oxidation (all values in kJ):

$$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{C}_\text{gr} + 6\text{H}_2 + 3\text{O}_2 + 6\text{O}_2$$

$$6[\text{C}_	ext{gr} + \text{O}_2 \rightarrow \text{CO}_2]$$

$$6[\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}]$$

$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$

$\Delta H^\circ =$