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 HYBRIDIZATION IN COMPLEX MOLECULES**

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

\[(\# \text{ of bonded atoms}) + (\# \text{ of lone pairs}) = \# \text{ of hybrid orbitals}\]

- 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:

- Cₐ:
- C₍:
- C₆:
- C₈:
Identify the symmetry and name the hybrid or atomic orbitals that constitute the bonds below:

Bonds to carbon b:
- \( C_b\text{-}H: \)
- \( C_b\text{-}C_a: \) \( \sigma(C_2sp^3, C_2sp^3) \)
- \( C_b\text{-}C_c: \) \( \sigma(C_2sp^3, C_2sp^3) \)
- \( C_b\text{-}O: \)

Bonds to carbon d:
- \( C_d\text{-}O: \)
- \( C_d\text{-}C_c: \) \( \sigma(C_2sp^2, C_2sp^3) \)
- \( C_d\text{-}C_e: \)

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.

\[
\Delta H, \text{ bond } = \Delta E + \Delta(PV)
\]

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

\( \Delta H^\circ \) = ________________ 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)

- \( CH_4 \rightarrow CH_3 + H \quad \Delta H^\circ = +438 \text{ kJ/mol} \)
- \( C_2H_6 \rightarrow C_2H_5 + H \quad \Delta H^\circ = +410 \text{ kJ/mol} \)
- \( CHF_3 \rightarrow CF_3 + H \quad \Delta H^\circ = +429 \text{ kJ/mol} \)
- \( CHCl_3 \rightarrow CCl_3 + H \quad \Delta H^\circ = +380 \text{ kJ/mol} \)
- \( CHBr_3 \rightarrow CBr_3 + H \quad \Delta H^\circ = +377 \text{ kJ/mol} \)

\( \Delta H^\circ \) 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.

\[
C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad \Delta H_r^\circ = -2816 \text{ kJ/mole}
\]

\( \Delta H^\circ \) is negative - ________________

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**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.

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

\[
C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy} \quad \text{We store this energy in the form of ATP.}
\]

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

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

If bonds stronger in products than reactants, \( \Delta H \) is _____________ (__________).
If bonds stronger in reactants than products, \( \Delta H \) is _____________ (endothermic).
\[
\text{H} + 6 \text{O}=\text{O} \rightarrow 6 \text{O}=\text{C}=\text{O} + 6 \text{H}-\text{O}-\text{H}
\]

\[
\left[\text{__}(\text{C-H}) + \text{__}(\text{O-H}) + \text{__}(\text{C-O}) + \text{__}(\text{C-C}) + \text{__}(\text{C=O}) + \text{__}(\text{O}=\text{O})\right] - \left[\text{__}(\text{C}=\text{O}) + \text{__}(\text{OH})\right]
\]

- bonds broken (reactants)
- bonds formed (products)

\[
\Sigma \Delta H_i = \underline{\ldots} \text{ kJ/mol}
\]

\[
\Sigma \Delta H_f = \underline{\ldots} \text{ kJ/mol}
\]

\[
\Delta H_r^{\circ} \text{calculated} = 12,452 \text{ kJ/mol} - 15,192 \text{ kJ/mol} = \underline{\ldots} \text{ kJ/mol of C}_6\text{H}_{12}\text{O}_6
\]

\[
\Delta H_r^{\circ} \text{experimental} = -2,816 \text{ kJ/mol}
\]

Agreement within 3%, very good for mean bond enthalpies.

**B. HEAT OF FORMATION**

More accurate approach...use heat of formation - \(\Delta H_f^{\circ}\)

\[\Delta H_f^{\circ} = \Delta H_r^{\circ}\] for forming 1 mol of compound from pure elements in their most stable form at the standard state = 1 bar and 298.15 K

\[
\text{H}_2(\text{g}) + \left(\frac{1}{2}\right) \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -285.8 \text{ kJ/mol} = \Delta H_f^{\circ} \text{for H}_2\text{O}(\text{l})
\]

\[
\text{C}_{\text{gr}} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ = -393.5 \text{ kJ/mol} = \Delta H_f^{\circ} \text{for CO}_2(\text{g})
\]

\[
\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{g}) \quad \Delta H^\circ = \underline{\ldots} = \Delta H_f^{\circ} \text{for O}_2(\text{g})
\]

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

\[
3\text{O}_2(\text{g}) + 6\text{C}_{\text{gr}} + 6\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 \quad \Delta H_f^{\circ} = \underline{\ldots} \text{ kJ/mol for C}_6\text{H}_{12}\text{O}_6
\]
We can calculate $\Delta H_r^\circ$ for glucose oxidation (or any other reaction) using $\Delta H_f^\circ$.

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

$\Delta H_r^\circ =$

$\Delta H_f^\circ =$

$\Delta H_r^\circ = \underline{\text{___________}}$ 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 $\underline{\text{___________}}$ of path.

**Hess’s Law**: If two or more chemical equations are added to give another chemical equation, corresponding $\underline{\text{_______}}$ must be added.

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

$\Delta H_f^\circ$

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

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

6$\left[\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}\right]$

C$_6$H$_{12}$O$_6$ + 6O$_2$ $\rightarrow$ 6 CO$_2$ + 6 H$_2$O $\Delta H^\circ =$