5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #16

Readings for today: : Sections 6.13, 6.15, 6.16, 6.17, 6.18, and 6.20 (Sections 6.14, 6.16, 6.17, 6.18, 6.19, and 6.21 in *3rd ed*) – The Enthalpy of Chemical Change.
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*.)

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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

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

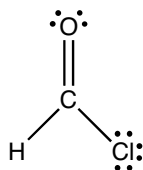**DETERMINING HYBIDIZATION IN COMPLEX MOLECULES**

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- sp^3

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

C-H: σ(C2sp^2, H1s)   C-O: σ(C2sp^2, O   )
C-Cl: σ(C2sp^2, Cl   )   π(C2p$_y$, O   )

Example: ascorbic acid (vitamin C)
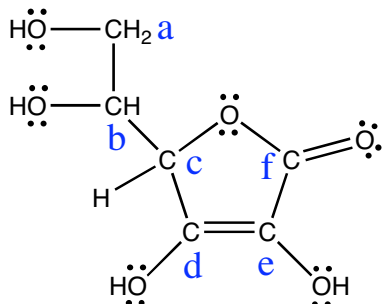
Identify the hybridization and geometry of each C atom:

C$_a$:   C$_d$:

C$_b$:   C$_e$:

C$_c$:   C$_f$:

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Identify the symmetry and name the hybrid or atomic orbitals that constitute the bonds below:
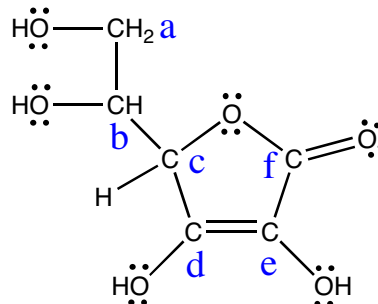
Bonds to carbon b:

    C_b-H:

    C_b- C_a: $\sigma(C2sp^3, C2sp^3)$

    C_b-C_c: $\sigma(C2sp^3, C2sp^3)$

    C_b-O:

Bonds to carbon d:

    C_d-O:

    C_d- C_c: $\sigma(C2sp^2, C2sp^3)$

    C_d-C_e:

II. ENERGIES AND ENTHALPIES OF CHEMICAL REACTIONS

A. BOND ENERGY/ BOND ENTHALPY

bond (dissociation) energy, ΔE_d, is the energy required to break a bond.
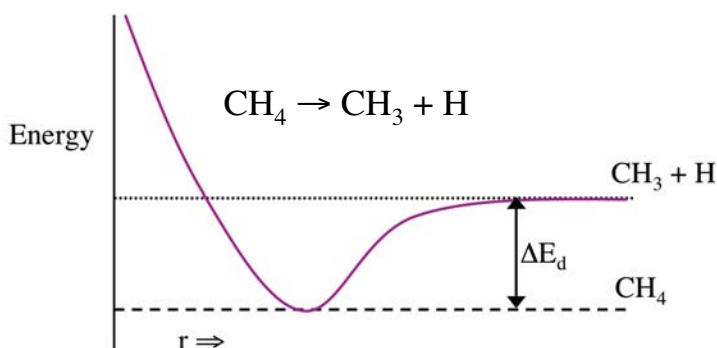
ΔH, bond _____ , is the change in heat accompanying the dissociation of a bond (measured at constant pressure P).

$$\Delta H = \Delta E + \Delta(PV)$$

For gases, ΔH & ΔE differ by _____ %. For liquids and solids, negligible difference.

$\Delta H\,° =$ _____ 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)

$$CH_4 \rightarrow CH_3 + H \qquad\qquad \Delta H° = +438 \text{ kJ/mol}$$
$$C_2H_6 \rightarrow C_2H_5 + H \qquad\qquad \Delta H° = +410 \text{ kJ/mol}$$
$$CHF_3 \rightarrow CF_3 + H \qquad\qquad \Delta H° = +429 \text{ kJ/mol}$$
$$CHCl_3 \rightarrow CCl_3 + H \qquad\qquad \Delta H° = +380 \text{ kJ/mol}$$
$$CHBr_3 \rightarrow CBr_3 + H \qquad\qquad \Delta H° = +377 \text{ kJ/mol}$$

$\Delta H°$ 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.
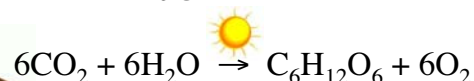
$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad\qquad \Delta H_r° = -2816 \text{ kJ/mole}$$

$\Delta H°$ is negative - _____

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.

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

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

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy$$ We store this energy in the form of ATP.
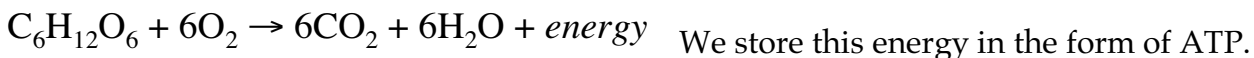
To calculate $\Delta H_r°$ for the oxidation of glucose (or for any reaction):

bond enthalpies

$$\Delta H_r° = \Sigma \Delta H_i - \Sigma \Delta H_j$$
i^{th} bond j^{th} bond
in reactants   in products

If bonds stronger in products than reactants, ΔH is _____ (_____).

If bonds stronger in reactants than products, ΔH is _____ (endothermic).

$+$ 6 O=O $\rightarrow$ 6 O=C=O + 6 H–O–H
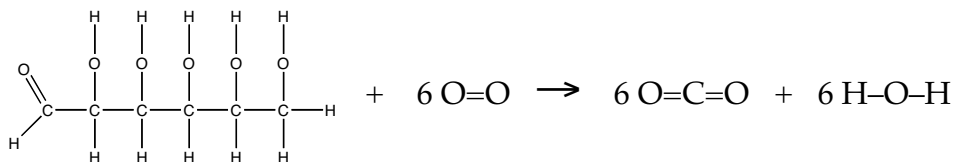
[__(C-H) + __(O-H) + __(C-O) + __(C-C) + __(C=O) + __(O=O)] − [__(C=O) + __(OH)]

bonds broken (reactants)	bonds formed (products)

$\Sigma\Delta H_i =$ _____ kJ/mol $\Sigma\Delta H_j =$ _____ kJ/mol

$\Delta H_r°_{calculated} = 12{,}452$ kJ/mol $- 15{,}192$ kJ/mol $=$ _____. kJ/mol of $C_6H_{12}O_6$

$\Delta H_r°_{experimental} = -2{,}816$ kJ/mol

Agreement within 3%, very good for <u>mean</u> bond enthalpies.

B. HEAT OF FORMATION

More accurate approach…use heat of formation - $\Delta H_f°$

$\Delta H_f° = \Delta H_r°$ for forming 1 mol of compound from pure elements in their most
                stable form at the standard state = 1 bar and 298.15 K

$H_2(g)$ + (1/2)$O_2(g)$ $\rightarrow$ $H_2O(l)$ $\Delta H° = -285.8$ kJ/mol $= \Delta H_f°$ for $H_2O(l)$
stable form **stable form**
of hydrogen **of oxygen**

C_{gr} + $O_2(g)$ $\rightarrow$ $CO_2(g)$ $\Delta H° = -393.5$ kJ/mol $= \Delta H_f°$ for $CO_2(g)$
stable form stable form
of carbon of oxygen

$O_2(g)$ $\rightarrow$ $O_2(g)$ $\Delta H° =$ _____ $= \Delta H_f°$ for $O_2(g)$
stable form
of oxygen

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

$3O_2(g)$ + $6C_{gr}$ + $6H_2(g)$ $\rightarrow C_6H_{12}O_6$ $\Delta H_f° =$ _____. kJ/mol for $C_6H_{12}O_6$

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We can calculate ΔH_r° for glucose oxidation (or any other reaction) using ΔH_f°.

$$\Delta H_r^\circ = \Sigma \Delta H_f^\circ(\underline{\hspace{3cm}}) - \Sigma \Delta H_f^\circ(\underline{\hspace{3cm}})$$
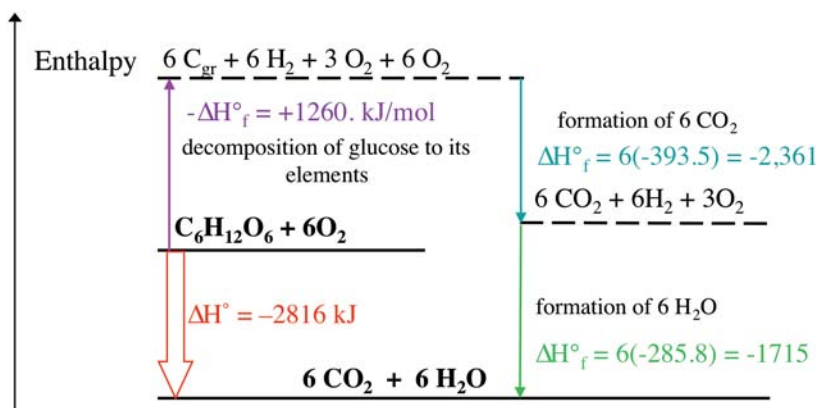
$\Delta H_r^\circ =$

$\Delta H_r^\circ =$

$\Delta H_r^\circ = \underline{\hspace{3cm}}$ kJ/mol

Same value as experiment because ΔH_f° is specific to a compound. Table of ΔH_f° for compounds is small compared to a table of ΔH 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 ΔH is $\underline{\hspace{4cm}}$ of path.

Hess's Law: If two or more chemical equations are added to give another chemical equation, corresponding $\underline{\hspace{2cm}}$ must be added.

Enthalpy $6\,C_{gr} + 6\,H_2 + 3\,O_2 + 6\,O_2$

$-\Delta H^\circ_f = +1260.$ kJ/mol
decomposition of glucose to its elements

formation of 6 CO_2
$\Delta H^\circ_f = 6(-393.5) = -2,361$
$6\,CO_2 + 6H_2 + 3O_2$

$C_6H_{12}O_6 + 6O_2$

$\Delta H^\circ = -2816$ kJ

formation of 6 H_2O
$\Delta H^\circ_f = 6(-285.8) = -1715$

$6\,CO_2 + 6\,H_2O$

ΔH° for glucose oxidation (all values in kJ): $\quad \Delta H_r^\circ$

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6C_{gr} + 6H_2 + 3O_2 + 6O_2$

$6\left[C_{gr} + O_2 \longrightarrow CO_2 \right]$

$6\left[H_2 + 1/2O_2 \longrightarrow H_2O \right]$

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6\,CO_2 + 6H_2O \qquad \Delta H^\circ =$

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