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*.)

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)

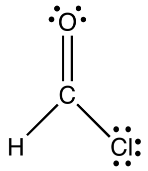
DETERMINING HYBIDIZATION IN COMPLEX MOLECULES

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

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

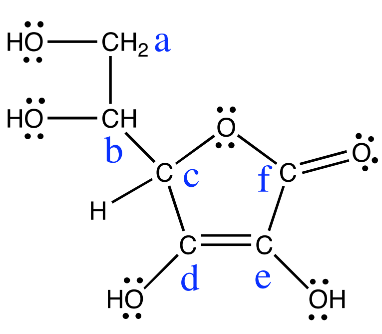
2 hybrid orbitals- _____ , 3 hybrid orbitals - _____ , 4 hybrid orbitals- sp^3

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



C-H: $\sigma(C2sp^2, H1s)$
C-Cl: $\sigma(C2sp^2, Cl \qquad)$
C-O: $\sigma(C2sp^2, O \qquad)$
$\pi(C2p_y, O \qquad)$

Example: ascorbic acid (vitamin C)

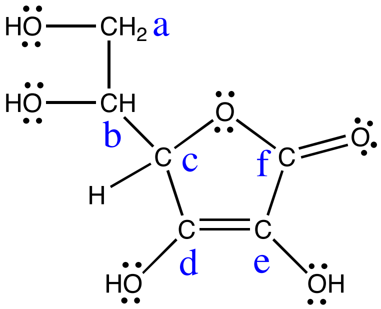


Identify the hybridization and geometry of each C atom:

C_a:
C_b:
C_c:
C_d:
C_e:
C_f:

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:

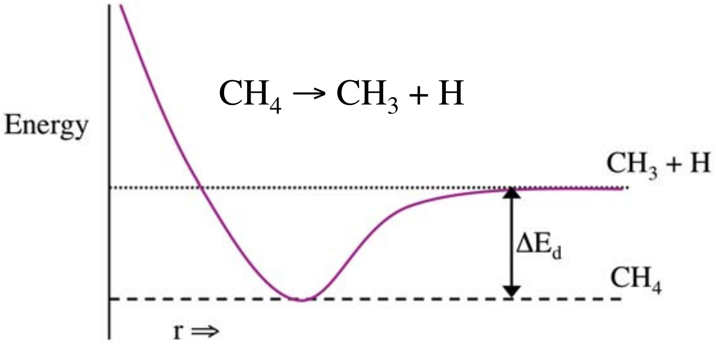
C_d- C_c: $\sigma(C2sp^2, C2sp^3)$

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.

ΔH ° = _________________ 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)

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

ΔH° 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.

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

ΔH° 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.

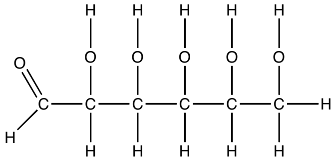
To calculate ΔH_r° for the oxidation of glucose (or for any reaction):

bond enthalpies

$$\Delta H_r^\circ = \underset{\substack{\text{i}^{\text{th}}\text{ bond}\\ \text{in reactants}}}{\overset{\downarrow}{\Sigma \Delta H_i}} - \underset{\substack{\text{j}^{\text{th}}\text{ bond}\\ \text{in products}}}{\overset{\downarrow}{\Sigma \Delta H_j}}$$

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

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



$+ \ 6\,O{=}O \longrightarrow 6\,O{=}C{=}O \ + \ 6\,H{-}O{-}H$

$$\underbrace{[\_\_(C\text{-}H) + \_\_(O\text{-}H) + \_\_(C\text{-}O) + \_\_(C\text{-}C) + \_\_(C{=}O) + \_\_(O{=}O)]}_{\text{bonds broken (reactants)}} - \underbrace{[\_\_(C{=}O) + \_\_(OH)]}_{\text{bonds formed (products)}}$$

$\Sigma\Delta H_i =$ __________ kJ/mol $\qquad \Sigma\Delta H_j =$ __________ kJ/mol

$\Delta H_r{}^\circ{}_{\text{calculated}} = 12{,}452$ kJ/mol – 15,192 kJ/mol = ____________. kJ/mol of $C_6H_{12}O_6$

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

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

B. HEAT OF FORMATION

More accurate approach…use heat of formation - $\Delta H_f{}^\circ$

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

$\underset{\textbf{stable form of hydrogen}}{H_2(g)} + \underset{\textbf{stable form of oxygen}}{(1/2)O_2(g)} \rightarrow H_2O(l)$ $\qquad \Delta H^\circ = -285.8$ kJ/mol $= \Delta H_f{}^\circ$ for $H_2O(l)$

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

$\underset{\textbf{stable form of oxygen}}{O_2(g)} \rightarrow O_2(g)$ $\qquad \Delta H^\circ =$ ______ $= \Delta H_f{}^\circ$ for $O_2(g)$

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

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

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

$\Delta H_r^\circ = \Sigma\Delta H_f^\circ$(________________) - $\Sigma\Delta H_f^\circ$(_________________)

$\Delta H_r^\circ =$

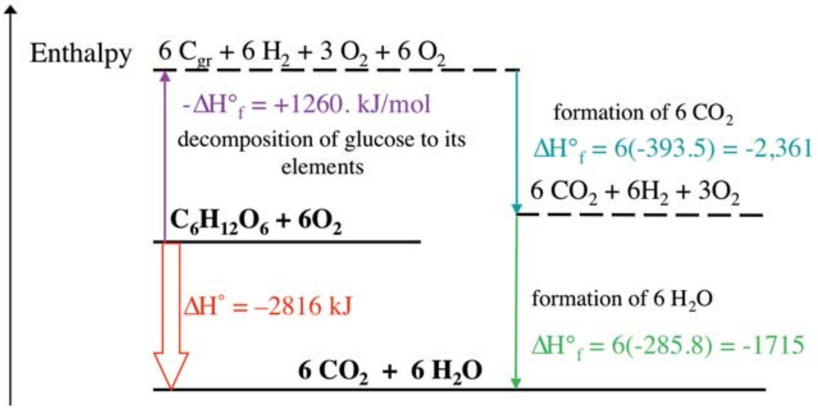
$\Delta H_r^\circ =$

$\Delta H_r^\circ =$ _____________ 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 ___________________ 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): ΔH_r°

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

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

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

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

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