5.111 Lecture Summary #15   Friday, October 10, 2014

Readings for today: Sections 7.13, 7.15, 7.16, 7.17, 7.18, and 7.20 (Sections 6.13, 6.15, 6.16, 6.17, 6.18, and 6.20 in *4th ed*) – The Enthalpy of Chemical Change.
Read for Lecture #16: Section 8.1 (Section 7.1 in *4th ed*) – Spontaneous Change, Sections 8.2 and 8.8 (Sections 7.2 and 7.8 in *4th ed*) - Entropy, Sections 8.12, 8.13, 8.15 (Sections 7.12, 7.13, 7.15 in *4th ed*) – Free Energy.
Announcements: Extra problems for exam 2 will be posted today.

Topics: **Introduction to Thermodynamics**
            A. Bond energy/ bond enthalpy (ΔH_B)
            B. Enthalpies of reaction (ΔH_r)
   C. Methods to calculate ΔH_r

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INTRODUCTION TO THERMODYNAMICS

In the study of a given reaction, **thermodynamics** deals with the _____

associated with the reaction, while **kinetics** deals with the _____

of the reaction (lecture 30).

For example the conversion of diamonds to graphite is thermodynamically favorable.
"Diamonds are forever" is therefore a _____statement.

A. BOND ENERGY/ BOND ENTHALPY
Bond (dissociation) energy, ΔE_d, is the energy required to break a bond.

$CH_4 \rightarrow CH_3 + H$
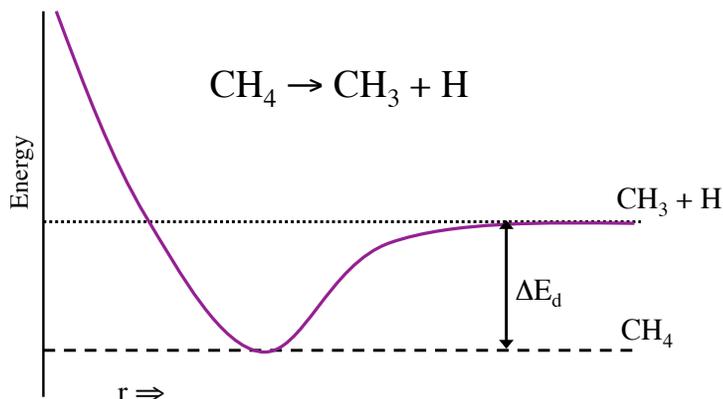
ΔH_B, bond _____ , is the change in heat accompanying the dissociation of a bond (measured at constant pressure P).

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

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

ΔH_B (bond enthalpies) are always positive– it always takes energy (heat) to break a bond. Bond breaking is always endothermic (heat must be added), whereas bond formation is always _____ (heat released).

ΔH_B ° = _____ bond enthalpy. Indicates reactants and products are in the standard state (pure form) at 1 bar for gases.

Bond enthalpies for C—H bonds (all gases)

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

The C-H bond enthalpies listed above are all within 8% of the **mean bond enthalpy** (_____ kJ/mol) for C-H bonds.

What is the importance of bond enthalpies? The difference between bond enthalpies in products and reactants gives an estimate of the **enthalpy of reaction $\Delta H_r°$.**

B. ENTHALPIES OF REACTION
ΔH_r ° = Standard bond enthalpy for a reaction
   Negative $\Delta H_r°$: exothermic reaction
   Positive $\Delta H_r°$: endothermic reaction

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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 store
in the glucose molecules.

$$6CO_2 + 6H_2O \xrightarrow{\;} C_6H_{12}O_6 + 6O_2$$
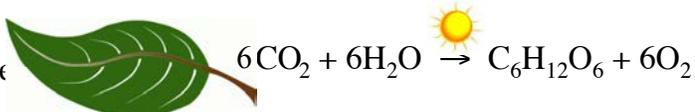
We perform the reverse reaction, the oxidation of glucose, to harness the stored energy.

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

$\Delta H_r° = –2816 \text{ kJ/mol}$ Since $\Delta H_r°$ is negative, the reaction is _____

Thermodynamics tells us that this reaction is exothermic, so heat should be released.
But kinetics tells us that the reaction is _____(so we _____feel the heat when we expose
     sugar to oxygen). In our bodies, catalysts called enzymes speed up this reaction.

C. THERE ARE MULTIPLE WAYS TO CALCULATE $\Delta H_r°$:
 i. Bond enthalpies (ΔH or ΔH_B) $\Delta H_r° = \Sigma\Delta H_B(\text{reactants}) - \Sigma\Delta H_B(\text{products})$
ii. Standard enthalpies of formation ($\Delta H_f°$) $\Delta H_r° = \Sigma\Delta H_f°(\text{products}) - \Sigma\Delta H_f° (\text{reactants})$
iii. Hess's law (combining reaction enthalpies)

i. Calculating ΔH_r° from bond enthalpies (ΔH_B°)

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

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

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

$6\,O=O \rightarrow 6\,O=C=O + 6\,H–O–H$
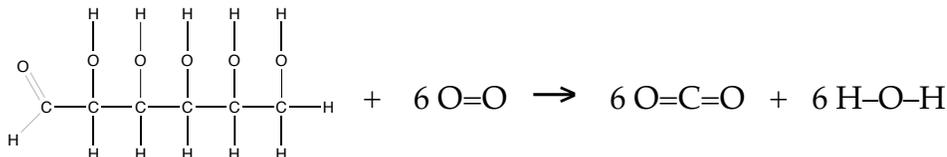
$[\_\_(C\text{-}H) +\_\_(O\text{-}H) +\_\_(C\text{-}O) +\_\_(C\text{-}C) +\_\_(C=O) +\_\_(O=O)] - [\_\_(C=O) +\_\_(OH)]$

bonds broken (reactants)   bonds formed (products)

$\Sigma\Delta H_i =$ _____kJ/mol $\Sigma\Delta H_j =$ _____kJ/mol

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

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

Agreement within 3%, which is very good considering that <u>mean</u> bond enthalpies were used.

ii. Calculating ΔH_r° from HEAT OF FORMATION

More accurate approach…use heat of formation: ΔH_f°

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

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

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

$O_2(g) \rightarrow O_2(g)$ $\Delta H^\circ =$ _____ $= \Delta H_f^\circ \text{ for } O_2(g)$
stable form
of oxygen

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

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

We can calculate $\Delta H_r°$ for glucose oxidation (or any other reaction) using $\Delta H_f°$.

$$\Delta H_r° = \Sigma\Delta H_f°(\underline{\hspace{3cm}}) \quad \Sigma\Delta H_f°(\underline{\hspace{3cm}})$$

$\Delta H_r° = [6\ \Delta H_f°(CO_2) + 6\ \Delta H_f°(H_2O)] - [\Delta H_f°(C_6H_{12}O_6) + 6\ \Delta H_f°(O_2)]$

$\Delta H_r° = [\ 6\ (-393.5) + 6\ (-285.8)\ ] - [\ (-1260.) + 6\ (0)\ ]$ (all in kJ/mol)

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

This is the same value as experiment because $\Delta H_f°$ is specific to a compound.

iii. Calculating a $\Delta H_r°$ from other $\Delta H°$s using HESS'S LAW

Enthalpy is a "STATE" FUNCTION, which means ΔH is $\underline{\hspace{3cm}}$ of path.
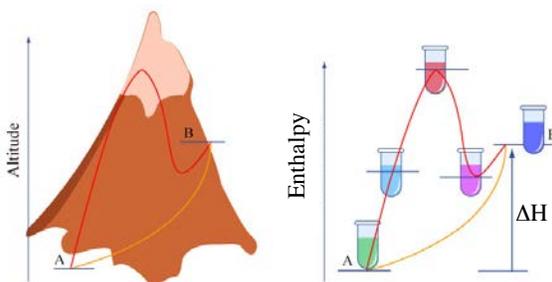
Hess's Law: If two or more chemical equations are added to give another chemical equation, corresponding $\underline{\hspace{2cm}}$ must be added.

Example:
Calculate the $\Delta H_r°$ for glucose oxidation ($C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$), given the following $\Delta H°$ values:

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ C_{gr} + 6\ H_2 + 3\ O_2 + 6\ O_2$ +1260. kJ/mol

$\underline{\hspace{1cm}}(C_{gr} + O_2 \rightarrow CO_2)$ $\underline{\hspace{1cm}}(-393.5\ kJ/mol)$

$\underline{\hspace{1cm}}(H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O)$ $\underline{\hspace{1cm}}(-285.8\ kJ/mol)$

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ $\Delta H_r° = \underline{\hspace{3cm}}$ kJ/mol
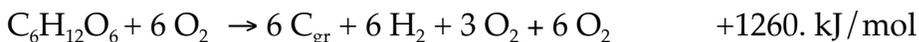
Thus, we have three ways to calculate $\Delta H_r°$, from 1. bond enthalpies 2. Heat of formation   3. Hess's law

5.111 Principles of Chemical Science
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