
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 ($\Delta H_b$)
B. Enthalpies of reaction ($\Delta H_r$)
C. Methods to calculate $\Delta H_r$

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, $\Delta E_d$, is the energy required to break a bond.

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

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

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

$\Delta H_b$ (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° = __________________ 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)

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

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 ΔHr°.

**B. ENTHALPIES OF REACTION**

ΔHr° = Standard bond enthalpy for a reaction

- Negative ΔHr°: exothermic reaction
- Positive ΔHr°: endothermic reaction

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.

\[
\begin{align*}
6\text{CO}_2 + 6\text{H}_2\text{O} & \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \\
6\text{CO}_2 + 6\text{H}_2\text{O} & \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 + \text{energy}
\end{align*}
\]

We store this energy in the form of ATP.

ΔHr° = –2816 kJ/mol Since ΔHr° 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 ΔHr°:**

i. Bond enthalpies (ΔH or ΔH°) \( \Delta H_r° = \Sigma \Delta H_b(\text{reactants}) - \Sigma \Delta H_b(\text{products}) \)

ii. Standard enthalpies of formation (ΔHf°) \( \Delta H_r° = \Sigma \Delta H_f°(\text{products}) - \Sigma \Delta H_f°(\text{reactants}) \)

iii. Hess’s law (combining reaction enthalpies)
i. Calculating $\Delta H_r^\circ$ from bond enthalpies ($\Delta H_b^\circ$)

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

If bonds stronger in products than reactants, $\Delta H_r$ is ____________ (__________).
If bonds stronger in reactants than products, $\Delta H_r$ is ____________ (endothermic).

\[
\begin{array}{c}
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\end{array}
\quad + \quad 6 \text{O}=\text{O} \quad \rightarrow \quad 6 \text{O}=\text{C}=\text{O} \quad + \quad 6 \text{H}–\text{O}–\text{H}
\]

$\Sigma \Delta H_i(\text{reactants}) - \Sigma \Delta H_j(\text{products})$

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

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

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

ii. Calculating $\Delta H_r^\circ$ from HEAT OF FORMATION

More accurate approach…use heat of formation: $\Delta H_f^\circ$

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

$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(l)$  \hspace{1cm} $\Delta H^\circ = -285.8 \text{ kJ/mol} = \Delta H_f^\circ$ for H$_2$O(l)

$\text{C}_{\text{gr}} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  \hspace{1cm} $\Delta H^\circ = -393.5 \text{ kJ/mol} = \Delta H_f^\circ$ for CO$_2$(g)

$\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{g})$  \hspace{1cm} $\Delta H^\circ = \text{_______} = \Delta H_f^\circ$ for O$_2$(g)

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

$3\text{O}_2(\text{g}) + 6\text{C}_{\text{gr}} + 6\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6$  \hspace{1cm} $\Delta H_f^\circ = \text{_______} \text{ kJ/mol for C}_6\text{H}_{12}\text{O}_6$
Hess’s Law: If two or more chemical equations are added to give another chemical equation, corresponding steps must be added.

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

\[
\begin{align*}
C_6H_{12}O_6 + 6O_2 & \rightarrow 6C_6 + 6H_2 + 3O_2 + 6O_2 & +1260. \text{ kJ/mol} \\
(C_6 + O_2 & \rightarrow CO_2) & (-393.5 \text{ kJ/mol}) \\
(H_2 + \frac{1}{2}O_2 & \rightarrow H_2O) & (-285.8 \text{ kJ/mol})
\end{align*}
\]

\( C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad \Delta H_r^\circ = \text{_______________ kJ/mol} \)

Thus, we have three ways to calculate \( \Delta H_r^\circ \), from 1. bond enthalpies 2. Heat of formation 3. Hess’s law