Thermochemistry Calculations

Some Definitions

- $\Delta E$ means an energy change
- $\Delta H$ means an energy change at constant pressure conditions
- $H$ is called *enthalpy* (accent on second syllable)

Some Guidelines

1. If a reaction is reversed then the value of $\Delta H^\circ$ changes sign.

   \[
   \begin{align*}
   2 \text{H}_2 + \text{O}_2 & \rightarrow 2 \text{H}_2\text{O} (l) \\
   \Delta H^\circ & = -571.66 \text{ kJ}
   \\
   2 \text{H}_2\text{O} (l) & \rightarrow 2 \text{H}_2 + \text{O}_2 \\
   \Delta H^\circ & = +571.66 \text{ kJ}
   \end{align*}
   \]

2. If a reaction’s coefficients are doubled (tripled, etc.) then so is its $\Delta H^\circ$ value.

   \[
   \begin{align*}
   \text{C} + \text{O}_2 & \rightarrow \text{CO}_2 \\
   \Delta H^\circ & = -393.51 \text{ kJ}
   \\
   2 \text{C} + 2\text{O}_2 & \rightarrow 2 \text{CO}_2 \\
   \Delta H^\circ & = -787.02 \text{ kJ}
   \end{align*}
   \]

Example of the Guidelines in Action

Given \( \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \), \( \Delta H^\circ = -393.51 \text{ kJ} \) and \( 3 \text{O}_2 \rightarrow 2 \text{O}_3 \), \( \Delta H^\circ = -285.4 \text{ kJ} \),

then calculate \( 3\text{C} + 2\text{O}_3 \rightarrow 3\text{CO}_2 \), \( \Delta H^\circ = ??? \)

Multiply the first reaction by 3 and then add the reverse of the second reaction

\[
\begin{align*}
3 (\text{C} + \text{O}_2 \rightarrow \text{CO}_2) & \Rightarrow 3 \text{C} + 3 \text{O}_2 \rightarrow 3 \text{CO}_2 \\
\Delta H^\circ & = 3(-393.51 \text{ kJ})
   \\
\text{and now add} & 2 \text{O}_3 \rightarrow 3 \text{O}_2 \\
\Delta H^\circ & = +285.4 \text{ kJ}
   \\
\text{The sum, after canceling the "3 O}_2" \text{ terms, is} & \\
3\text{C} + 2\text{O}_3 & \rightarrow 3\text{CO}_2 \\
\Delta H^\circ & = -1465.93 \text{ kJ}
\end{align*}
\]
Enthalpies of Formation

$\Delta H_f^\circ$ means the enthalpy change for forming a substance from its elements, in their most stable states, at a temperature of 25 °C and a pressure of 1 bar.

Example: $\text{C}_{\text{graphite}} + \text{O}_2 \rightarrow \text{CO}_2$ $\Delta H_f^\circ = -393.51$ kJ

Consider a reaction:

Reactants $\rightarrow$ Products

Imagine an energy diagram as follows:

\[
\begin{align*}
\text{Reactants} & \quad \text{Elements in Standard States} \\
\uparrow & \\
\Sigma (\Delta H_f^\circ)_{\text{products}} & \quad \downarrow \Sigma (\Delta H_f^\circ)_{\text{reactants}} \\
& \quad \text{Products} \\
\end{align*}
\]

Have $\Delta H_{\text{rxn}}^\circ = \Sigma (\Delta H_f^\circ)_{\text{products}} - \Sigma (\Delta H_f^\circ)_{\text{reactants}}$

An Example

$\text{C}_3\text{H}_8 + 5 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}$

Have $\Delta H_{\text{rxn}}^\circ = [3 \Delta H_f^\circ(\text{CO}_2) + 4 \Delta H_f^\circ(\text{H}_2\text{O})] - [5 \Delta H_f^\circ(\text{O}_2) + \Delta H_f^\circ(\text{C}_3\text{H}_8)]$

$\Delta H_{\text{rxn}}^\circ = [3 (-393.51) + 4 (-285.83)] - [5 (0) + (-103.85)] = -2220.00$ kJ
Chemical Bonds and Reaction Energies

Energy changes for chemical reactions can be estimated using the energies of chemical bonds. This method depends on the fact that energy is needed to break a bond, but energy is released on making a bond. Also, it is assumed that every type of chemical bond has an unchanging, fixed energy, which is not strictly true but is accurate enough for our purposes. This means that to estimate a reaction's energy change we just count the bonds that break and the bonds that form. Simple addition and subtraction of the relevant bond energies gives an overall energy change.

As an example of the bond dissociation method for calculating reaction energies, consider the combustion of propane (C₃H₈). The reaction is

\[
\text{C}_3\text{H}_8(g) + 5 \text{O}_2(g) \rightarrow 3 \text{CO}_2(g) + 4 \text{H}_2\text{O}(l) + \text{energy}
\]

Now draw a Lewis dot structure of each reactant and product molecule, count the bonds broken and formed, and estimate the energy change. Tables on the next page give bond energy values.

Bonds broken (reactants):

\[
\begin{align*}
\text{C}_3\text{H}_8 & \rightarrow 8 \text{C-H bonds} \rightarrow 8(413) = 3304 \text{ kJ / mol} \\
\text{C}_3\text{H}_8 & \rightarrow 2 \text{C-C bonds} \rightarrow 2(348) = 696 \text{ kJ / mol} \\
5 \text{O}_2 & \rightarrow 5 \text{O=O bonds} \rightarrow 5(497) = 2485 \text{ kJ / mol}
\end{align*}
\]

Bonds formed (products):

\[
\begin{align*}
3 \text{CO}_2 & \rightarrow 6 \text{C=O bonds} \rightarrow 6(743) = 4458 \text{ kJ / mol} \\
4 \text{H}_2\text{O} & \rightarrow 8 \text{O-H bonds} \rightarrow 8(463) = 3704 \text{ kJ / mol}
\end{align*}
\]

Overall Energy Change = \((3304 + 696 + 2485) - (4458 + 3704) = -677 \text{ kJ / mol}

"energy absorbed"  "energy released"

The negative sign means that the reaction releases (produces) energy. Such reactions are called exothermic. The opposite type of reaction, with a positive sign for the energy change, is called endothermic.
Representative Single Bond Energies in kJ / mol

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Representative Multiple Bond Energies in kJ / mol

- O=O 497
- C=O 743
- C=C 612
- C≡C 838

Practice Problems

1. Do the following for C₂H₄ and then for C₂H₅OH. The combustion products of both molecules are CO₂ and H₂O.

   (a) Write and balance the equation for the combustion reaction.

   (b) Use bond energies to estimate the energy change for each combustion reaction. Are the reactions exothermic or endothermic? Explain.

2. Carbon dioxide and water are formed when methane (CH₄) is burned in excess oxygen. However, if there is insufficient oxygen, incomplete combustion occurs and water and CO gas are formed instead.

   (a) Write and balance the reaction for the incomplete combustion of methane, and then determine the reaction's energy change.

   (b) How does the energy change for the incomplete combustion compare to that of the complete combustion of CH₄ per mole of methane consumed?