Work in groups on these problems. You should try to answer the questions without referring to your textbook. If you get stuck, try asking another group for help.

Learning Objectives

• Understand Hess’s Law
• Understand the definition and use of standard enthalpy of formation
• Understand the fundamental relationships of electromagnetic radiation and the electromagnetic spectrum
• Understand the relationship between line spectra and the quantum concept

As we saw last week, enthalpy and internal energy are state functions, which means that the sum of the heats of any set of steps that adds to give an overall reaction will have the same heat as doing the reaction directly. This is Hess’s Law. We will revisit this today and go on to see that if we use a special kind of thermochemical reaction, called the standard enthalpy of formation, we can calculate enthalpies of reactions without having to manipulate a series of individual thermochemical equations for each step.

Success Criteria

• Be able to calculate enthalpy of a target reaction from a series of given reactions
• Be able to apply standard enthalpies of formation to calculate the enthalpy of a reaction
• Be able to do conversions between energy, wavelength, and frequency of electromagnetic radiation
• Be able to correlate state-to-state transitions with region of the electromagnetic spectrum and calculate the energy of a state-to-state transition

Standard Conditions, State Functions and Hess's Law

Remember that the measured value of $\Delta H$ depends on the states of all reactants and products (s, l, g, aq) and the temperature and pressure under which the reaction occurs. In order to make meaningful direct comparisons, it is useful to define a set of standard conditions. By international agreement, standard conditions are defined as $T = 25 \, ^{\circ}\text{C}; \ P = 1 \, \text{atm}$; all substances in their usual states for these conditions (the standard state). The standard state of an element is its most stable state; e.g., $\text{H}_2(g)$, C(s) – graphite, $\text{S}_8(s)$, $\text{P}_4(s)$. For compounds, the standard state is the most prevalent state under standard conditions; e.g., $\text{H}_2\text{O}(l)$, $\text{CO}_2(g)$, $\text{C}_2\text{H}_2(g)$, $\text{C}_6\text{H}_6(l)$.

Enthalpy is a state function, which only depends upon current conditions (the state of the system) for its value, not on how the current state was reached. As applied to $\Delta H = H_f - H_i$, the value of the enthalpy change for any process depends
only on the difference between the final and initial states, not on the path chosen. This means that any set of steps, whether real or imagined, that take the system from the initial state to the final state of interest will have a sum of \( \Delta H \) values for all the steps that is equal to the value of \( \Delta H \) for the overall process done directly. This principle, called **Hess's Law of Constant Heat Summation**, was first established by G. H. Hess in 1840:

\[
\text{The enthalpy change for a reaction is independent of path.}
\]

In applying Hess's Law, a set of given thermochemical equations is manipulated such that they add to give a balanced thermochemical equation for the process of interest (the target equation). In doing this, whenever a given thermochemical equation is multiplied (usually by an integer or rational fraction), its \( \Delta H \) is likewise multiplied. Whenever the direction of a given thermochemical equation is reversed, its \( \Delta H \) value changes sign.

**Q1**

Calculate \( \Delta H^\circ \) for this hydrogenation reaction,

\[
\text{C}_2\text{H}_2(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_4(g)\]

Given:

\[
\text{2 C}_2\text{H}_2(g) + 5 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)\]

with \( \Delta H^\circ = -2599.2 \text{ kJ} \) and

\[
\text{C}_2\text{H}_4(g) + 3 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)\]

with \( \Delta H^\circ = -1410.9 \text{ kJ} \) and

\[
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)\]

with \( \Delta H^\circ = -285.8 \text{ kJ} \).
Standard Enthalpies of Formation: $\Delta H^o_f$

Hess’s Law calculations are done so frequently that it is convenient to have tabulated data for a large number of reactions. The most generally useful data for these kinds of calculations are **standard enthalpies of formation**.

The standard enthalpy of formation, $\Delta H^o_f$, of a compound is the enthalpy change for the reaction in which *one mole* of the compound in its standard state is made from the stoichiometric amounts of its elements in their standard states. For all elements in their standard states, $\Delta H^o_f = 0$, by definition.

For example, the following thermochemical equations define standard enthalpies of formation for $\ce{C2H2(g)}$ and $\ce{C2H4(g)}$, respectively.

\[
\ce{2 C(s) + H2(g) \rightarrow C2H2(g)} \quad \text{(Equation a)} \tag{a}
\]

with $\Delta H^o_f = +226.8 \, \text{kJ}$ and

\[
\ce{2 C(s) + 2 H2(g) \rightarrow C2H4(g)} \quad \text{(Equation b)} \tag{b}
\]

with $\Delta H^o_f = +52.3 \, \text{kJ}$.

Notice that each of these equations gives the heat produced when exactly *one mole* of the product compound is made. There are no thermochemical equations for the formation of substances such as $\ce{C(s)}$ as graphite or $\ce{H2(g)}$ as the gaseous element, because these are their normal elemental states. Their standard enthalpies of formation are set as zero by definition.

Let’s use the two enthalpy of formation equations given above to calculate the enthalpy of the following reaction:

\[
\ce{C2H2(g) + H2(g) \rightarrow C2H4(g)}
\]

with $\Delta H^o = ?$.

You calculated the enthalpy of this reaction in Q1, but now we are going to do it with the thermochemical equations that define $\Delta H^o_f$ for $\ce{C2H2(g)}$ and $\ce{C2H4(g)}$. To do this, we simply need to take the reverse of Equation \ref{a} with the negative of its given enthalpy, and add it to Equation \ref{b}, using its given enthalpy. The resulting sum is:

<table>
<thead>
<tr>
<th>Action</th>
<th>Reaction</th>
<th>$\Delta H^o_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Equation \ref{a}</td>
<td>$\ce{\cancel{2} C(s) + \cancel{1} H2(g) \rightarrow \cancel{2} C2H2(g)}$</td>
<td>$-226.8 , \text{kJ}$</td>
</tr>
<tr>
<td>Equation \ref{b}</td>
<td>$\ce{\cancel{2} C(s) + \cancel{2} H2(g) \rightarrow \cancel{2} C2H4(g)}$</td>
<td>$+52.3 , \text{kJ}$</td>
</tr>
</tbody>
</table>
This is the same answer you obtained in Q1, as expected on the basis of Hess’s Law. But notice that the answer we obtain here is the following sum, where $\Delta H^0_f(H_2) = 0$, because $H_2(g)$ is an element in its standard state:

$$\begin{align} \Delta H^0_{rxn} &= \Delta H^0_f(\text{C}_2\text{H}_4) - \left[\Delta H^0_f(\text{C}_2\text{H}_2) + \Delta H^0_f(\text{H}_2)\right] \\
&= +52.3 \text{ kJ} - \left[-226.8 \text{ kJ} + 0 \text{ kJ}\right] 
\end{align}$$

This is the sum of the enthalpies of formation of the products, multiplied by their stoichiometric coefficients (here, 1), minus the sum of the enthalpies of formation of the reactants, multiplied by their stoichiometric coefficients (here again, both 1). This is a general result, which we can summarize as

$$\Delta H^0_{rxn} = \sum n_p\Delta H^0_p - \sum n_r\Delta H^0_r$$

where $\sum n_p$ and $\sum n_r$ are the stoichiometric coefficients of each of the products and each of the reactants, respectively. [The $\sum$ (Greek sigma) means “take the sum of.”] Note that this relationship can only be used if all the data are enthalpies of formation. For a general reaction

$$aA + bB \rightarrow cC + dD$$

we would have

$$\Delta H^0_{rxn} = \left[c \Delta H^0_f(C) + d \Delta H^0_f(D)\right] - \left[a \Delta H^0_f(A) + b \Delta H^0_f(B)\right]$$

Q2

Write the balanced thermochemical equations that pertain to the standard enthalpies of formation of the given compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^0_{f_i}$ (kJ/mol)</th>
<th>Thermochemical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CCl}_4(g)$</td>
<td>-106.7</td>
<td>$\text{CCl}_4(g)$ \rightarrow $\text{CCl}_4(g)$</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3(s)$</td>
<td>-822.16</td>
<td>$\text{Fe}_2\text{O}_3(s)$ \rightarrow $\text{Fe}_2\text{O}_3(s)$</td>
</tr>
<tr>
<td>$\text{HNO}_3(g)$</td>
<td>-134.31</td>
<td>$\text{HNO}_3(g)$ \rightarrow $\text{HNO}_3(g)$</td>
</tr>
<tr>
<td>$\text{NaHCO}_3(s)$</td>
<td>-947.7</td>
<td>$\text{NaHCO}_3(s)$ \rightarrow $\text{NaHCO}_3(s)$</td>
</tr>
</tbody>
</table>
Q3

Part A:

Given:

\[
\ce{N_2O_4(g) + 1/2 O_2(g) \rightarrow N_2O_5(g)} \]
with \(\Delta H^o = +1.67 \, \text{kJ}\) and

\[
\ce{HNO_3(g) \rightarrow 1/2 N_2O_5(g) + 1/2 H_2O(l) }\]
with \(\Delta H^o = –2.96 \, \text{kJ}\).

Calculate \(\Delta H^o\) for the reaction

\[
\ce{N2O4(g) + H2O(l) + 1/2 O2(g) \rightarrow 2 HNO3(g)}\]

Part B:

Given following standard enthalpy of formation data:

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta H^o_f, \text{ (kJ/mol)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\ce{N2O4(g)})</td>
<td>9.66</td>
</tr>
<tr>
<td>(\ce{HNO3(g)})</td>
<td>–134.31</td>
</tr>
<tr>
<td>(\ce{H2O(l)})</td>
<td>–285.83</td>
</tr>
</tbody>
</table>

Calculate \(\Delta H^o\) for the reaction

\[
\ce{N2O4(g) + H2O(l) + 1/2 O2(g) \rightarrow 2 HNO3(g)}\]

Compare your answer to your answer in Part A.
Q4

Calculate the heat of combustion of methane, CH\(_4\)(g), defined by the following thermochemical equation:

\[
\ce{CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)}\]

Given the following standard enthalpies of formation:

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta H^\circ_f) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\ce{CH4(g)})</td>
<td>–74.85</td>
</tr>
<tr>
<td>(\ce{CO2(g)})</td>
<td>–393.5</td>
</tr>
<tr>
<td>(\ce{H2O(l)})</td>
<td>–285.8 kJ</td>
</tr>
</tbody>
</table>

Q5

Calculate the enthalpy of formation, \(\Delta H^\circ_f\), for benzene, \(\ce{C6H6(l)}\), given that the heats of formation of \(\ce{CO2(g)}\) and \(\ce{H2O(l)}\) are –393.5 kJ and –285.8 kJ, respectively, and that the heat of combustion of \(\ce{C6H6(l)}\) is –3267.7 kJ. To do this, carry out the following steps.

a. Write the balanced thermochemical equation that defines the enthalpy of formation of benzene, \(\Delta H^\circ_f\) for benzene, \(\ce{C6H6(l)}\).

b. Write the balanced thermochemical equation for the heat of combustion of benzene.

c. Based on your answer to question ii, write an expression for the heat of combustion of benzene, \(\Delta H^\circ_{comb}\), in terms of the enthalpies of formation of the reactants and products. Using the data given in the problem, solve this for the unknown value of \(\Delta H^\circ_f\) for benzene, the enthalpy of formation of benzene.