Learning Objectives

- Define Hess's Law and relate it to the first law of thermodynamics and state functions
- Calculate the unknown enthalpy of a reaction from a set of known enthalpies of combustion using Hess's Law
- Define molar enthalpy of formation of compounds
- Calculate the molar enthalpy of formation from combustion data using Hess's Law
- Using the enthalpy of formation, calculate the unknown enthalpy of the overall reaction
- Calculate the heat evolved/absorbed given the masses (or volumes) of reactants.

**Hess's Law**

In the last section, we have seen how we can use calorimetry to determine the enthalpy of chemical reactions and the results of experiments is tabulated and found readily on the web and textbooks. However, the heat of some reactions cannot be figured directly through calorimetry. Hess's Law states that if you can add two chemical equations and come up with a third equation, the enthalpy of reaction for the third equation is the sum of the first two. This is a consequence of the First Law of Thermodynamics, the fact that enthalpy is a state function, and brings for the concept of coupled equations.

**Coupled Equations:** A balanced chemical equation usually does not describe how a reaction occurs, that is, its mechanism, but simply the number of reactants and products that are required for mass to be conserved. In reality, a chemical equation can occur in many steps with the products of an earlier step being consumed in a later step. For example, consider the following reaction in which phosphorous reacts with oxygen to from diphosphorous pentoxide ($\text{P}_2\text{O}_5$) according to the following equation:

$$\text{P}_4 + 5\text{O}_2 \rightarrow 2\text{P}_2\text{O}_5$$

and then the product of that reaction in turn reacts with water to form phosphoric acid according to the following equation:

$$2\text{P}_2\text{O}_5 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$$

$\text{P}_2\text{O}_5$ is an intermediate, and if we add the two equations the intermediate can cancel out. Hess's law states that if two reactions can be added into a third, the energy of the third is the sum of the energy of the reactions that were combined to create the third.

equation 1: $\text{P}_4 + 5\text{O}_2 \rightarrow 2\text{P}_2\text{O}_5 \Delta H_1$
equation 2: $2\text{P}_2\text{O}_5 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4 \Delta H_2$
equation 3: \( P_4 + 5O_2 + 6H_2O \rightarrow 4H_3PO_4 \ \Delta H_3 = \Delta H_1 + \Delta H_2 \)

When we say Enthalpy is a state function, we are saying it does not matter how you go from one state to another, the energy between the initial and final states are the same. Hess's law holds for any state function, and is a result of the conservation of energy. Since equations 1 and 2 added up to equation 3, they represented two paths to the same final state.

**Calculating Enthalpy of Reaction from Combustion Data**

In the next example we will use a table of the heats of combustion to calculate the enthalpy of hydrogenation of ethylene into ethane or \( \text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of Combustion (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H(_2))</td>
<td>-286</td>
</tr>
<tr>
<td>Methane (CH(_4))</td>
<td>-889</td>
</tr>
<tr>
<td>Ethane (C(_2)H(_6))</td>
<td>-1,560</td>
</tr>
<tr>
<td>Propane (C(_3)H(_8))</td>
<td>-2,220</td>
</tr>
<tr>
<td>Carbon</td>
<td>-393.5</td>
</tr>
<tr>
<td>Ethylene (C(_2)H(_4))</td>
<td>-1411</td>
</tr>
</tbody>
</table>

Table 5.7.1 Heats of combustion for some common substances. Note, these are negative because combustion is an exothermic reaction. They are often tabulated as positive, and is is assumed you know they are exothermic. Also, these are not reaction enthalpies, but the energy per mol of substance combusted.

Tips for Hess's Law Calculations

1. Write the equation you want on the top of your paper, and draw a line under it
2. Find equations that have all the reactants and products in them for which you have enthalpies.
3. If an equation has a chemical on the opposite side, write it backwards and change the sign of the reaction enthalpy
4. If the equation has a different stoichiometric coefficient than the one you want, multiple everything by the number to make it what you want, including the reaction enthalpy

From the above table we have the following. Note, the non-integer coefficients are used because these are molar values for the combustion of one mole of the substance that was measured.

Given:

(eq. 1) \( \text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} \ (-286 \text{ kJ/mol}) \)
(eq. 2) \( \text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \) (-1411 kJ/mol)

(eq. 3) \( \text{C}_2\text{H}_6 + 3/2\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \) (-1560 kJ/mol)

Unknown : \( \text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 \)

(eq2) \( \text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \) -1411 kJ/mol

(eq1) \( \text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O} \) -286 kJ/mol

(eq 3) \( 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_6 + 3/2\text{O}_2 \) -(-1560 kJ/mol)

Note, we had to write the third equation backwards, so its sign changed, and that this tells us is that the enthalpy of hydrogenation of ethylene into ethane (adding hydrogen) is -286 -1411 + 1560, or -136 kJ/mol.

What is important here, is that by measuring the heats of combustion scientists could acquire data that could then be used to predict the enthalpy of a reaction that they may not be able to directly measure. This is a consequence of enthalpy being a state function, and the path of the above three steps has the same energy change as the path for the direct hydrogenation of ethylene.

Fig. 5.7.1 Showing Hess's law in terms of energy being conserved as a state function. The color code shows reactants in red letter/grey background, and products in black letters/yellow background. The blue shaded species (C\(_2\)H\(_6\)) functions as an intermediate in terms of the energy cycle, as it is formed in step 3 and consumed in step 4. When we use Hess's law, we are going from \( \text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 \), which is the negative of step 4. That is, step 4 in reverse (going down not up) equals steps 1+2+3. Note step 3 is the reverse of the combustion of C\(_2\)H\(_6\), and so it is positive (endothermic)

This is a very important concept of thermodynamics, and is a consequence that enthalpy is a state function. The change in enthalpy is the same if you go from \( \text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 \), in 1 step (the opposite of step 4), or in three steps. Now the actual work done in the process may be different, but the enthalpy change of the system (reaction) is the same, no
matter which path you take. This allows us to take thermodynamic data from a table and calculate the value of an unknown path if we can devise an alternative path that has known values. Let's recap the process with the following video:

Video Tutor:

Video 5.7.1 (7:00 min YouTube) Showing how to solve above problem while also relating it to Hess's Law and the First Law of Thermodynamics.

In the next section we will look at the enthalpy of formation, which is another path for which there are tables, and calculate the same enthalpy of reaction using those values, instead of combustion data.

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**Standard Enthalpies of Formation**

The **standard enthalpy of formation** $\Delta H^\circ$ is the enthalpy change when 1 mole of a pure substance, or a 1 M solute concentration in a solution, is formed from its elements in their most stable states under standard state conditions. In this class, the standard state is 1 bar and 25°C. Note, if two tables give substantially different values, you need to check the standard states. One of the values of enthalpies of formation is that we can use them and Hess's Law to calculate the enthalpy change for a reaction that is difficult to measure, or even dangerous. We can look at this as a two step
Note the enthalpy of formation is a molar function, so you can have non-integer coefficients. For example, the molar enthalpy of formation of water is:

\[ \text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O}(l) \Delta H_f^0 = -285.8 \text{ kJ/mol} \]

This equation says that 285.8 kJ of energy is exothermically released when one mole of liquid water is formed by reacting one mole of hydrogen gas and 1/2mol oxygen gas (3.011x10^{23} molecules of O_2). Note, ΔH_f^0 of liquid water is less than that of gaseous water, which makes sense as you need to add energy to liquid water to boil it.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enthalpy of Formation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H_2)</td>
<td>0</td>
</tr>
<tr>
<td>Methane (CH_4)</td>
<td>-74.6</td>
</tr>
<tr>
<td>Ethane (C_2H_6)</td>
<td>-84.0</td>
</tr>
<tr>
<td>Ethylene (C_2H_4)</td>
<td>52.4</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>-393.5</td>
</tr>
<tr>
<td>Water (l)</td>
<td>-286</td>
</tr>
<tr>
<td>Water (g)</td>
<td>-241.8</td>
</tr>
</tbody>
</table>

Table 5.7.2: Standard enthalpies of formation for select substances. A more comprehensive table can be found at the table of standard enthalpies of formation, which will open in a new window, and was taken from the CRC Handbook of Chemistry and Physics, 84 Edition (2004).

When reviewing the table of standard formation enthalpies, notice:

- The standard enthalpy of formation for elements in their standard form is zero.
- Most standard enthalpy of formation values are negative, indicating that the formation of most compounds from their elements is an exothermic process. Those compounds that have positive values are most likely unstable.
- You can use this data to help you figure out the relative stabilities of compounds. The more exothermic (more negative) the standard enthalpy of formation, the more stable the compound.

**Calculating Enthalpy of Reaction from Standard Enthalpies of Formation**

The equation we use is a direct consequence of the first law of thermodynamics and application of Hess's law.
\[ \Delta H_{\text{reaction}} = \sum m_i \Delta H^0 \text{(products)} - \sum n_i \Delta H^0 \text{(reactants)} \]

where \( m_i \) and \( n_i \) are the stoichiometric coefficients of the products and reactants respectively.

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**Fig. 5.7.2 Process diagram describing the states involved with using enthalpies of formation to determine enthalpies of reaction.** Note, this is not an energy diagram, but a process diagram, in the sense that the arrows do not indicate the direction of energy transfer. By this we mean that the Y-axis does not indicate the direction of increasing or decreasing energy, only that energy has changed. That is, the process of forming a mole of products from their atoms in their standard elemental state is the standard state molar enthalpy of formation, but it may be endothermic or exothermic. Likewise, the process of breaking apart a mole of reactants into its atoms in their standard state is the negative of its molar enthalpy of formation, which likewise can be endothermic or exothermic.

So what is the Process?

- **Reactants break apart** into their atoms that take their elemental standard state forms. This is the opposite of forming them, so this step is the negative of their enthalpy of formation. You need to multiply by the coefficient to account for all the atoms that are involved in the process.
- **Products form** from their atoms in their elemental standard state forms. This is their enthalpy of formation

So the equation

\[ \Delta H_{\text{reaction}} = \sum m_i \Delta H^0 \text{(products)} - \sum n_i \Delta H^0 \text{(reactants)} \]

Describes the enthalpy change as reactants break apart into their stable elemental state at standard conditions and then form new bonds as they create the products.

Lets apply this to the combustion of ethylene (the same problem we used combustion data for in the above video):

\[ \text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 \text{.} \]

using the above equation, we get

\[ \Delta H_{\text{reaction}} = \Delta H^0 \text{ (C}_2\text{H}_6) - \Delta H^0 \text{ (C}_2\text{H}_4) - \Delta H^0 \text{ (H}_2) \]
\[ \Delta H_{\text{reaction}} = -84 - (52.4) - 0 = -136.4 \text{ kJ}, \]

When we used Hess's Law and some combustion data, we found the enthalpy of the reaction to be -136 kJ. So, we have two ways to obtain the same answer. If you know the enthalpy of formation for each product and reactant (from tabular data), you can use this method to figure out the overall enthalpy of the entire reaction.

So, how do we calculate the molar enthalpy of formation for a mole of substance from its pure elements in the first place? When it is not possible for us to collect this data experimentally, we can use combustion data and Hess's Law. Let's see an example of how we can calculate the enthalpy of formation using combustion data and Hess's Law.

Example \( \PageIndex{1} \)

Acetylene \((C_2H_2)\) cannot be prepared directly from its elements according to the equation

\[
2C(s) + H_2(g) \rightarrow C_2H_2(g)
\]

Calculate \( \Delta H_m \) for this reaction from the following thermochemical equations, all of which can be determined experimentally:

\[
\begin{align*}
C(s) + O_2(g) &\rightarrow CO_2(g) \quad \Delta H_m = -393.5 \text{ kJ} \\
H_2(g) + \frac{1}{2}O_2(g) &\rightarrow H_2O(l) \quad \Delta H_m = -285.8 \text{ kJ} \\
C_2H_2(g) + \frac{5}{2}O_2(g) &\rightarrow 2CO_2(g) + H_2O(l) \quad \Delta H_m = -1299.8 \text{ kJ}
\end{align*}
\]

Solution
a) Since Eq. (1) has 2 mol C on the left, we multiply Eq. (2a) by 2.

b) Since Eq. (1) has 1 mol H₂ on the left, we leave Eq. (2b) unchanged.

c) Since Eq. (1) has 1 mol C₂H₂ on the right, whereas there is 1 mol C₄H₂ on the left of Eq. (2c) we write Eq. (2c) in reverse. We then have

\[
\begin{align*}
2 \text{C(s)} + 2 \text{O}_2(g) & \rightarrow 2 \text{CO}_2(g) & \Delta H_m = 2(-393.5\text{ kJ/mol}) \\
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) & \rightarrow \text{H}_2\text{O}(l) & \Delta H_m = -285.8\text{ kJ/mol} \\
2\text{CO}_2(g) + \text{H}_2\text{O}(l) & \rightarrow \text{C}_2\text{H}_2(g) + \frac{5}{2} \text{O}_2(g) & \Delta H_m = -( -1292.8\text{ kJ/mol}) \\
2\text{C(s)} + \text{H}_2(g) + 2\frac{1}{2} \text{O}_2(g) & \rightarrow \text{C}_2\text{H}_2(g) + \frac{5}{2} \text{O}_2(g) & \\
\end{align*}
\]

Cancelling 5/2 O₂ on each side, the desired result is

\[
2\text{C(s)} + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_2(g) & \quad \Delta H_m = 227.0\text{ kJ/mol}
\]

Video Tutor: This video walks you through the same process. Notice: the answer are slightly different because the tabular data is slightly different.
Enthalpies of Reaction and Stoichiometric Problems

As we have seen, enthalpies of reactions are reported on a mole basis. We don't always have stoichiometric equivalencies of reactants and products. In addition, we have to take into account that there are limiting reagents and excess reagents when calculating how much heat is generated/absorbed by a certain mass of reactants. Let's take a look at how we can carry out this process using the following examples.

Example

Determine the heat released or absorbed when 15.0g Al react with 30.0g Fe$_3$O$_4$(s).

Al(s) + Fe$_3$O$_4$(s) $\rightarrow$ Al$_2$O$_3$(s) + Fe(s)

Solution

Strategy: There are four steps to this problem:

1. Balance Equation
2. Calculate $\Delta H_{\text{reaction}}$ from enthalpies of formation

3. Identify Limiting Reagent- the amount of heat generated/absorbed will depend on the limiting reagent

4. Calculate the heat given off by assuming the complete consumption of the limiting reagent

Steps:

1. $8\text{Al}(s) + 3\text{Fe}_3\text{O}_4(s) \rightarrow 4\text{Al}_2\text{O}_3(s) + 9\text{Fe}(s)$

2. Noting:
   
   $\Delta H^\rho_{\text{Fe}_3\text{O}_4} = -1118.4 \text{kJ/mol}$
   
   $\Delta H^\rho_{\text{Al}_2\text{O}_3} = -1675.7 \text{kJ/mol}$
   
   $\Delta H^\rho_{\text{Al}} = \Delta H^\rho_{\text{Fe}} = 0$

   Using
   
   $\Delta H_{\text{reaction}} = \sum m_i \Delta H^\rho_i (\text{products}) - \sum n_i \Delta H^\rho_i (\text{reactants})$
   
   $\Delta H_{\text{reaction}} = [4(-1675.7)] + 9(0)] - [8(0) + 3(-1118.4)]$
   
   $\Delta H_{\text{reaction}} = -3363.6 \text{ kJ}$

3. 

   \[
   \frac{15.0 \text{ g Al}}{1} \times \frac{1 \text{ mole of Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mole Fe}_3\text{O}_4}{8 \text{ mole Al}} \times \frac{231.54 \text{ g Fe}_3\text{O}_4}{1 \text{ mole Fe}_3\text{O}_4} = 48.3 \text{ g of Fe}_3\text{O}_4
   \]

   It looks like 48.3 grams of Fe$_3$O$_4$ are needed to fully react 15.0 gram of Al. We only have 30.0 grams of Fe$_3$O$_4$. Therefore, Fe$_3$O$_4$ will be the limiting reagent, with the 30.0 grams fully reacting, leaving excess Aluminum behind.

4. The heat generated will then be determined by the limiting reactant, Fe$_3$O$_4$.

   \[
   \frac{30.0 \text{ g Fe}_3\text{O}_4}{1} \times \frac{1 \text{ mole Fe}_3\text{O}_4}{231.54 \text{ g Fe}_3\text{O}_4} \times \frac{-3363 \text{ kJ}}{3 \text{ mole Fe}_3\text{O}_4} = -145 \text{ kJ}
   \]

Example \(\PageIndex{3}\))

Pure ethanol has a density of 789g/L. Using the tables for enthalpy of formation, calculate the
enthalpy of reaction for the combustion reaction of ethanol, and then calculate the heat released when 1.00 L of pure ethanol combusts.

**Solution**

Video Tutor: