Hess's Law

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 does usually does not describe how a reaction occurs, that is, its mechanism, but simply the number of reactants in 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 phosphorous reacts with oxygen to from diphosphorous pentoxide \((2P_2O_5)\)

\[ P_4 + 5O_2 \rightarrow 2P_2O_5 \]

and then the product of that reaction in turn reacts with water to form phosphorus acid

\[ 2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4 \]

In the above equation the \(P_2O_5\) 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.

\[
\begin{align*}
equation 1: \quad & P_4 + 5O_2 \rightarrow 2P_2O_5 \quad \Delta H_1 \\
equation 2: \quad & 2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4 \quad \Delta H_2 \\
equation 3: \quad & P_4 + 5O_2 + 6H_2O \rightarrow 4H_3PO_4 \quad \Delta H_3 = \Delta H_1 + \Delta H_2
\end{align*}
\]

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

\[ C_2H_4 + H_2 \rightarrow C_2H_6 \]
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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of Combustion (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H₂)</td>
<td>-286</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>-889</td>
</tr>
<tr>
<td>Ethane (C₂H₆)</td>
<td>-1,560</td>
</tr>
<tr>
<td>Propane (C₃H₈)</td>
<td>-2,220</td>
</tr>
<tr>
<td>Carbon</td>
<td>-393.5</td>
</tr>
<tr>
<td>Ethylene (C₂H₄)</td>
<td>-1411</td>
</tr>
</tbody>
</table>

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 because these are molar values for the combustion of one mole of the substance that was measured.

(eq. 1) \( \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \) (-286 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)

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

\[ \text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \] -1411 kJ/mol (eq2)
\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \] -286 kJ/mol (eq1)
\[ 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_6 + 3/2\text{O}_2 \] (-1560kJ/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 ($C_2H_6$) 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 $C_2H_4 + H_2 \rightarrow C_2H_6$, 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 $C_2H_6$, 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 $C_2H_4 + H_2 \rightarrow C_2H_6$, 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. 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.
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.

**Standard Enthalpies of Formation**

The standard enthalpy of formation $\Delta H^\circ_f$ 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 process.

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:

$$
\begin{align*}
H_2(g) + \frac{1}{2}O_2 (g) & \rightarrow H_2O(l) \quad \Delta H^\circ_f = -285.8 \text{ kJ/} \\
H_2(g) + \frac{1}{2}O_2 (g) & \rightarrow H_2O(g) \quad \Delta H^\circ_f = -241.6 \text{ kJ/mol}
\end{align*}
$$

This equation says that 85.8 kJ is 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 $(3.011\times10^{23}$ molecules of O$_2$). Note, $\Delta H^\circ_f$ 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.
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.

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

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enthalpy of Formation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H₂)</td>
<td>0</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>-74.6</td>
</tr>
<tr>
<td>Ethane (C₂H₆)</td>
<td>-84.0</td>
</tr>
<tr>
<td>Ethylene (C₂H₄)</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).

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

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

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.

Let's apply this to the combustion of ethylene (the same problem we used combustion data for)

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

Using the above equation, we get

\[
\Delta H_{\text{reaction}} = \Delta H_f^\circ (\text{C}_2\text{H}_6) - \Delta H_f^\circ (\text{C}_2\text{H}_4) - \Delta H_f^\circ (\text{H}_2)
\]

\[
\Delta H_{\text{reaction}} = -84 - (52.4) - 0 = 136.4 \text{ kJ}, \text{ while above we got -136, noting these are correct to the first insignificant digit.}
\]

Using combustion data, calculate the enthalpy of formation of acetylene, \( \text{C}_2\text{H}_2(\text{g}) \)

Calculate the enthalpy of formation for acetylene, \( \text{C}_2\text{H}_2(\text{g}) \) from the following combustion data

\[
\Delta H_{\text{comb}} (\text{C}_2\text{H}_4) = -1300 \text{kJ/mol}
\]
\[
\Delta H_{\text{comb}} (\text{C}) = -394 \text{kJ/mol}
\]
\[
\Delta H_{\text{comb}} (\text{H}_2) = -572 \text{kJ/mol}
\]

Note: in the following video, the enthalpy is correlated to the balanced equation, with integer coefficients, and there is no \( \text{mol}^{-1} \). It is important that students understand that \( \Delta H_{\text{reaction}} \) is for the entire equation, so in the case of acetylene, the balanced equation is

\[
2\text{C}_2\text{H}_4(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \quad \Delta H_{\text{reaction}} (\text{C}_2\text{H}_4) = -2600 \text{kJ}
\]
But when tabulating a molar enthalpy of combustion, or a molar enthalpy of formation, it is per mole of the species being combusted or formed. That is, the equation in the video and the one above have the exact same value, just one is per mole, the other is per 2 mols of acetylene.

6:27 YouTube showing solution to the above problem

**Enthalpies of Reaction and Stoichiometric Problems**

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

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

There are three Tasks to this problem

1. Balance Equation and Identify Limiting Reagent
2. Calculate $\Delta H_{\text{reaction}}$ from enthalpies of formation
3. Calculate the heat given off by the complete consumption of the limiting reagent

1. $8\text{Al(s)} + 3\text{Fe}_3\text{O}_4(\text{s}) \rightarrow 4\text{Al}_2\text{O}_3(\text{s}) + 9\text{Fe(s)}$
\[15g\text{Al} \times \left(\frac{\text{mol Al}}{26.98g}\right) \times \left(\frac{1}{8\text{mol Al}}\right) = 0.069\]
\[30.0g\text{Fe}_3\text{O}_4 \times \left(\frac{1\text{mol Fe}_3\text{O}_4}{231.54g}\right) \times \left(\frac{1}{3\text{mol Fe}_3\text{O}_4}\right) = 0.043\]

So \text{Fe}_3\text{O}_4(s)\text{ is the limiting reagent.}

2. Noting
\[\Delta H_f^0 (\text{Fe}_3\text{O}_4) = -1118.4\text{kJ/mol}\]
\[\Delta H_f^0 (\text{Al}_2\text{O}_3) = -1675.7\text{kJ/mol}\]
\[\Delta H_f^0 (\text{Al}) = \Delta H_f^0 (\text{Fe}) = 0\]

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

3. \[30.0g\text{Fe}_3\text{O}_4 \times \left(\frac{1\text{mol Fe}_3\text{O}_4}{231.54g}\right) \times \left(\frac{-3363kJ}{3\text{mol Fe}_3\text{O}_4}\right) = -145kJ\]

Note, you could have used the 0.043 from step 2,
\[0.043(-3363kJ) = -145kJ\]

Using enthalpies of formation, calculate the heat released when 1.00L of ethanol combuts.

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 combuts.
Video 5.7.2 (4:53min): Calculating heat released by combustion of 1 L of ethanol