**Thermochemistry: The Heat of Neutralization**

Refer to sections 8.8-8.9 in your McMurray/Fay *Chemistry* textbook to review calorimetry and Hess’s Law before coming to the lab.

**Introduction**

Energy is defined as the ability to do work. One form of energy is heat, defined as thermal energy flowing from an object at a higher temperature to an object at a lower temperature. For example, a piece of molten iron placed in water will lose (give off) heat while the water will gain (absorb) heat until the two have reached thermal equilibrium (the temperatures of the two substances will be the same).

Most physical and chemical changes are either endothermic or exothermic. Endothermic reactions absorb energy or heat from the surroundings and result in a lower temperature. These reactions will feel cool or cold to the touch because they are absorbing heat energy from your hand. Exothermic reactions release or give off energy or heat to the surroundings and result in a higher temperature. These reactions (if they are not too violent) will feel warm or hot to the touch because they are releasing heat to your hand.

The amount of heat exchanged during a reaction is called the heat of reaction, \( q \). The enthalpy change of a reaction, \( \Delta H \), is the heat of a reaction at constant pressure, usually calculated in units of kJ/mol. Endothermic reactions are assigned a positive enthalpy value (\( \Delta H > 0 \)) and exothermic reactions are assigned a negative enthalpy value (\( \Delta H < 0 \)). Most reactions occur in several steps, with energy **required** (\( \Delta H > 0 \)) to break bonds, and energy **released** (\( \Delta H < 0 \)) as new bonds are formed. If a reaction can be written as the sum of several individual reactions, the enthalpies of the individual reactions will add up to give the enthalpy for the overall reaction. The overall \( \Delta H \) of a reaction is the algebraic sum of the individual steps and is independent of the pathway or mechanism between reactants and final products. This is Hess’s Law of Heat Summation (\( \Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \ldots \)), commonly called Hess’s Law.

Hess’s Law is quite useful because there are many reactions for which the heat of reaction cannot be easily measured experimentally. Generally, experiments to measure the amount of heat generated or absorbed in a reaction are carried out in a calorimeter. A calorimeter is a closed-system reaction chamber that prevents a reaction (the system) from exchanging heat with the environment (the surroundings) so temperature changes within the reaction chamber can be used to calculate the amount of heat transferred during a reaction.

Some reactions are too violent and dangerous to perform in a closed calorimeter system. Other reactions generate so much heat that simple calorimeters cannot be used. In such cases, it is practical to examine a series of reactions whose net effect is the desired reaction, but whose heats of reaction are more easily measured. The desired heat of reaction can then be calculated by applying Hess’s Law as illustrated in the following example.

**Example:** Calculate the enthalpy of the formation of sulfurous acid (\( \text{SO}_2 (g) + \text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{SO}_3 (aq) \)) using the following equations and given enthalpies:

1. \( 2\text{H}_2\text{SO}_3 (aq) \rightarrow 2\text{H}_2\text{S} (g) + 3\text{O}_2 (g) \) \( \Delta H = 408 \text{ kJ} \)
2. \( \text{S} (s) + \text{O}_2 (g) \rightarrow \text{SO}_2 (g) \) \( \Delta H = -297 \text{ kJ} \)
3. \( \text{H}_2\text{O} (l) + \text{S} (s) \rightarrow \frac{1}{2} \text{O}_2 (g) + \text{H}_2\text{S} (g) \) \( \Delta H = 155 \text{ kJ} \)

According to Hess’s Law, you can combine the above reactions in a way that will result in the desired reaction and calculate its enthalpy change as illustrated below. In the final equation, you want \( \text{H}_2\text{SO}_3 (aq) \) as a product, so you reverse equation (1) and multiply it by \( \frac{1}{2} \) to obtain one mole of \( \text{H}_2\text{SO}_3 (aq) \) as a product.

\[
\text{(1) } \text{H}_2\text{S} (g) + \frac{3}{2} \text{O}_2 (g) \rightarrow \text{H}_2\text{SO}_3 (aq) \quad \Delta H = - (408 \text{ kJ}) \times \frac{1}{2}
\]
Similarly with equation (2), you want \( \text{SO}_2 \) (g) on the reactant side, so you reverse the reaction and change the sign of \( \Delta H \).

\[
(2) \quad \text{SO}_2 (g) \rightarrow \text{S} (s) + \text{O}_2 (g) \quad \Delta H = -(-297 \text{ kJ})
\]

These equations are then combined with the third equation, and the corresponding enthalpy changes are added to yield the desired \( \Delta H \). Note that S (s), \( \text{O}_2 \) (g) and \( \text{H}_2\text{S} \) (g) cancel when these reactions are added together.

\[
\begin{align*}
(1) \quad & \text{H}_2\text{S} (g) + \frac{3}{2} \text{O}_2 (g) \rightarrow \text{H}_2\text{SO}_3 (aq) \quad \Delta H = -204 \text{ kJ} \\
(2) \quad & \text{SO}_2 (g) \rightarrow \text{S} (s) + \text{O}_2 (g) \quad \Delta H = +297 \text{ kJ} \\
(3) \quad & \text{H}_2\text{O} (l) + \text{S} (s) \rightarrow \frac{1}{2} \text{O}_2 (g) + \text{H}_2\text{S} (g) \quad \Delta H = +155 \text{ kJ}
\end{align*}
\]

\[
\text{SO}_2 (g) + \text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{SO}_3 (aq) \quad \Delta H = +248 \text{ kJ}
\]

In this experiment, you will use a coffee-cup calorimeter to determine the heat of neutralization when \( \text{NaOH} \) (aq) is added to \( \text{HCl} \) (aq). You will also measure the heat of dissolution of \( \text{NaOH} \). Then you will apply Hess’s law to compare the measured and calculated values for the neutralization of \( \text{HCl} \) solution with solid \( \text{NaOH} \).