HEAT OF FORMATION OF AMMONIUM NITRATE

OBJECTIVES FOR THE EXPERIMENT

The student will be able to do the following:

1. Calculate the change in enthalpy (heat of reaction) using the Law of Hess.
2. Find heats of reaction using a coffee-cup (open) calorimeter.
3. Calculate the heat capacity of a coffee-cup calorimeter.
4. Calculate the amount of heat involved in a specific temperature change of water.

BACKGROUND

The heat of formation of ammonium nitrate is the heat liberated when one mole of solid ammonium nitrate forms at constant pressure from its component elements in their standard states.

\[ \text{N}_2(g) + 2\text{H}_2(g) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{NH}_4\text{NO}_3(s) \quad \Delta H = \Delta H_f \text{NH}_4\text{NO}_3(s) \]

Even though this reaction does not take place, we still would like to know the value so it could be used in calculations of \( \Delta H_s \) for reactions that do take place. For example, we could use the heat of formations for ammonium nitrate, dinitrogen monoxide, and water to calculate the \( \Delta H \) for the following reaction.

\[ \text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(l) \]

\[ \Delta H_{\text{rxn}} = \Delta H_f \text{N}_2\text{O}(g) + 2 \times \Delta H_f \text{H}_2\text{O}(l) - \Delta H_f \text{NH}_4\text{NO}_3(s) \]

Because the reaction for the heat of formation of ammonium nitrate does not take place, we cannot determine it directly in the laboratory. Like many heats of reaction, we can determine this value indirectly using the Law of Hess. We will determine the heats of reaction for four reactions whose equations can be summed to yield the equation for the heat of formation of ammonium nitrate. The sum of the heats of reaction for each equation will yield the heat of formation of ammonium nitrate.

\[ \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{H}_2(g) \rightarrow \text{NH}_3(aq) \quad \Delta H_f \text{NH}_3(aq) = -81.17 \text{ kJ/mole} \]
\[ \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{HNO}_3(aq) \quad \Delta H_f \text{HNO}_3(aq) = -206.0 \text{ kJ/mole} \]
\[ \text{NH}_3(aq) + \text{HNO}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(aq) \quad \Delta H_{\text{neut}} \]
\[ \text{NH}_4\text{NO}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(s) \quad -\Delta H_{\text{solution}} \]

\[ \text{N}_2(g) + 2\text{H}_2(g) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{NH}_4\text{NO}_3(s) \]

\[ \Delta H_f \text{NH}_4\text{NO}_3(s) = \Delta H_f \text{NH}_3(aq) + \Delta H_f \text{HNO}_3(aq) + \Delta H_{\text{neut}} + (-\Delta H_{\text{solution}}) \]

The heat of formation of aqueous ammonia is \(-81.17 \text{ kJ/mole}\), and the heat of formation of aqueous nitric acid is \(-206.0 \text{ kJ/mole}\). You will determine the heat of neutralization and the heat of solution experimentally using an open or coffee-cup calorimeter.

You can determine the amount of heat involved in a reaction from the amount of heat exchanged with the rest of the system. If the reaction evolves heat, its heat of reaction is negative. The rest of the system absorbs an equal amount of heat, and its heat value is positive. If the reaction absorbs heat, its heat of reaction is positive. The rest of the system gives off an equal amount of heat, so its heat value is negative. Thus, the heat of the
reaction is always equal to the opposite of the heat of the system. In this experiment, heat can be exchanged with the calorimeter, the products of the reaction, the water in which the reactants were dissolved, and the surroundings.

\[ q_{\text{reaction}} = -q_{\text{solution}} = -[q_{\text{calorimeter}} + q_{\text{product}} + q_{\text{water}} + q_{\text{surroundings}}] \]

We will assume that the heat exchanged with the products and surroundings is negligible. You can calculate the heat exchanged with the calorimeter from the heat capacity of the calorimeter and its change in temperature. You can calculate the heat exchanged with the water from the specific heat of water, 0.00418 kJ/g °C, the water’s mass, and the change in temperature of the water.

\[ q_{\text{reaction}} = -[q_{\text{calorimeter}} + q_{\text{water}}] \]

\[ q_{\text{rxn}} = -[C_{\text{cal}} \Delta T_{\text{cal}} + \frac{0.00418 \text{ kJ}}{\text{g} \cdot \degree \text{C}} m_w \Delta T_w] \]

The change in temperature is the same for the calorimeter and the water.

\[ q_{\text{rxn}} = -[C_{\text{cal}} + \frac{0.00418 \text{ kJ}}{\text{g} \cdot \degree \text{C}} m_w] \Delta T \]

To determine the heat of reaction, we must first determine the heat capacity of the calorimeter. We will do this by measuring the heat absorbed by the calorimeter when 75 mL of hot water is added to 75 mL of cold water in the calorimeter. When the hot water combines with the cold water in the calorimeter, it loses heat to the cold water and the calorimeter.

\[ q_{\text{hot water}} = -[q_{\text{calorimeter}} + q_{\text{cold water}}] \]

\[ \frac{0.00418 \text{ kJ}}{\text{g} \cdot \degree \text{C}} m_{\text{hot}} \Delta T_{\text{hot}} = -[C_{\text{cal}} \Delta T_{\text{cal}} + \frac{0.00418 \text{ kJ}}{\text{g} \cdot \degree \text{C}} m_{\text{cold}} \Delta T_{\text{cold}}] \]

The changes in temperature for the cold water and the calorimeter are the same.

You can calculate the masses of water from the volumes of water added. Assume that the density of water is 1.0 g/mL. You can determine the changes in temperature from measurements of the initial and final temperatures. Thus, the only unknown in the above equation is the heat capacity of the calorimeter. You can solve the equation for \( C_{\text{cal}} \) and calculate its value from the experimental data.
PROCEDURE FOR THE DETERMINATION OF THE HEAT CAPACITY OF THE CALORIMETER

1. Heat about 300 mL of deionized water to about 85 °C. Use the thermometer from your drawer to determine the approximate temperature.

2. Add 75 mL of room temperature deionized water to the clean and dry calorimeter.

3. Put the stirring bar into the water and put the cups onto the magnetic stirrer.

4. Place a thermometer into the thermometer clamp, through the lid, and into the water. Be sure it is well above the stirring bar. Don’t start the bar spinning yet.

5. Record the temperature of the room temperature water to 0.1 °C. Raise the lid to allow you enough room to add the hot water. Start the stirring bar spinning.

6. Warm a 100-mL graduated cylinder by adding about 100 mL of your hot water to the cylinder, letting it sit for about one minute, and pouring the water down the drain.

7. Transfer about 75 mL of hot water to the heated graduated cylinder. Record the volume of hot water to ±1 mL on the data sheet.

8. Measure the temperature of the hot water to 0.1 °C. Record this on the data sheet.

9. Add the hot water to the cold water.

10. Lower the lid and thermometer onto the cups.

11. Adjust the thermometer so that it is well above the stirring bar.

12. Record the highest temperature reached by the water in the calorimeter.

13. Calculate the heat capacity of your calorimeter.

PROCEDURE FOR THE DETERMINATION OF THE HEAT OF NEUTRALIZATION

1. Dry your calorimeter.

2. Measure 75 mL of the 1.50 M ammonia solution into the calorimeter.

3. Record its temperature to 0.1 °C before you start the stirring bar spinning. We will assume that the nitric acid solution has the same temperature.

4. Start the stirring bar spinning, and pour 75 mL of the nitric acid solution into the calorimeter and quickly replace the lid. Be sure that the thermometer is well above the stirring bar. Continue stirring.

5. Record the highest temperature reached.

6. Pour the solution down the drain, rinse the inner cup with distilled water, and wipe it dry.

7. Calculate the heat at constant pressure, \( q_p \), and the molar heat of neutralization, \( \Delta H_{\text{neut}} \).

PROCEDURE FOR THE DETERMINATION OF THE HEAT OF SOLUTION

1. Weigh out about 10 g of NH\(_4\)NO\(_3\) on a piece of weighing paper. Record the mass to 0.001 g.

2. Pour 150 mL of water into the calorimeter and record the water temperature to 0.1 °C.

3. Start the magnetic stirrer, add the ammonium nitrate, and lower the lid and thermometer onto the calorimeter. Be sure that the thermometer is well above the stirring bar.

4. The temperature might fluctuate more than in the previous procedures, but it should stabilize at a lower temperature than the initial temperature. Record this temperature to 0.1 °C.

5. Pour the solution in the sink. Clean and dry the calorimeter.

6. Calculate the heat at constant pressure, \( q_p \), and the molar heat of solution, \( \Delta H_{\text{soln}} \).
### REPORT SHEET FOR THE HEAT OF FORMATION OF AMMONIUM NITRATE

#### HEAT CAPACITY OF THE CALORIMETER

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Volume cold water</td>
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<tr>
<td>Mass cold water</td>
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<td>Volume hot water</td>
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<td>Mass hot water</td>
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<td>Temperature cold</td>
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<td>Change in temperature hot</td>
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<td>$C_{cal}$</td>
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Show your calculations for the heat capacity of the calorimeter here.

#### HEAT OF NEUTRALIZATION

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<table>
<thead>
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<tbody>
<tr>
<td>Volume 1.50 M NH$_3$</td>
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<tr>
<td>Volume 1.50 M HNO$_3$</td>
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<tr>
<td>Initial T</td>
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<tr>
<td>Mass water</td>
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<tr>
<td>$q_{neut}$</td>
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<td>Molar $\Delta H_{neut}$</td>
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Show your calculations here. Watch your significant figures and signs.
HEAT OF SOLUTION

<table>
<thead>
<tr>
<th>Mass of NH₄NO₃</th>
<th>Volume water</th>
<th>Initial T</th>
<th>Final T</th>
<th>Change in temperature</th>
<th>Mass water</th>
<th>q_{soln}</th>
<th>Molar ΔH_{soln}</th>
</tr>
</thead>
</table>

Show your calculations here. Watch your significant figures and signs.

CALCULATION OF THE HEAT OF FORMATION OF AMMONIUM NITRATE

\[ \Delta H_f \text{ of ammonium nitrate} \]

Show your calculations here. Watch your significant figures and signs.