Experiment 3: The Enthalpy of Reaction for the Dissolution of Salts

I. Introduction

You will need a flash drive for this lab to save your data from the laptop computer.

The enthalpy of reaction is generally the easiest of the thermodynamic functions to measure. It can be measured by performing a reaction in a constant-pressure calorimeter. A calorimeter is a device that measures a change of heat energy due to reaction as a change in temperature of the water in the calorimeter and the calorimeter itself.

We will be using a coffee cup calorimeter (shown in Figure 1), which will turn out to give a fairly accurate value for the enthalpy of reaction providing that the data is taken precisely.

A. The Energy Transfer Process

There is one key concept that is worth describing: the energy transfer process. Let’s consider the dissolving of NH₄NO₃ in water. Suppose we added 5 g of NH₄NO₃ to 40 mL of room temperature water already in the calorimeter. We then used a temperature probe to monitor the temperature of the water over time. When NH₄NO₃ dissolves,

\[
\text{NH}_4\text{NO}_3(s) \leftrightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq) \quad (1)
\]

The reaction is endothermic, meaning that the reaction will take in heat energy as it occurs. If this is true, the only sources of heat energy in the calorimeter are

(i) the solution and
(ii) the coffee cup calorimeter itself (consisting of cups, lid, probe, etc.)

Both of these get colder as energy is taken from them to dissolve the solid NaNO₃.

In thermodynamic terms, the system is the calorimeter and its contents, in this case including all of the water/salt. The surroundings are everything outside of the calorimeter (the rest of the room, the lab bench, etc.). We assume that the system is closed and does not exchange energy with the surroundings; therefore, any energy taken in by the reaction must be taken from the water and the coffee cup calorimeter.

Mathematically, the sum of the energies of the reactants, water and calorimeter must be zero,

\[
\begin{align*}
\text{Energy Balance:} & \quad q_{\text{Rxn}} + q_{\text{soln}} + q_{\text{cal}} = 0 \\
\end{align*}
\]

Where:

\(q_{\text{Rxn}}\) is the amount of energy involved in the dissolving reaction,

\(q_{\text{soln}}\) is the amount of energy transferred to or from (from in this case) the solution and

\(q_{\text{cal}}\) is the amount of energy transferred to or from (again from in this case) the calorimeter.
Therefore, by simply rearranging the above equation,

\[ q_{\text{Rxn}} = - (q_{\text{soln}} + q_{\text{cal}}) \]  

(3)

The difference in sign accounts for the fact that the dissolving reaction for \( \text{NH}_4\text{NO}_3 \) takes in energy while the water and calorimeter give off energy.

The energy involved in the dissolving reaction \( q_{\text{Rxn}} \) is related to the molar enthalpy of reaction \( \Delta H_{\text{rxn}} \) by the following equation,

\[ q_{\text{Rxn}} = (\Delta H_{\text{rxn}}) \text{ (mol salt)} \]  

(4)

where the moles of salt can be determined from the weight and molar mass of salt.

Once \( q_{\text{Rxn}} \) is determined, then calculating the enthalpy of reaction is straightforward. To determine \( q_{\text{Rxn}} \), however, requires that both \( q_{\text{w}} \) and \( q_{\text{cal}} \) be determined. The amount of energy transferred from the water is,

\[ Q_{\text{soln}} = m_{\text{soln}} C_{\text{soln}} \Delta T \]  

(5)

where:

- \( m_{\text{soln}} \) is the mass of the solution (water and salt combined)
- \( C_{\text{soln}} \) is the specific heat of the solution (we will assume it is the same as water, 4.184 J/g°C),
- \( \Delta T \) is the temperature change of the solution/calorimeter.

The mass of the solution and the temperature change of the solution will both be measured experimentally.

The amount of energy transferred from the calorimeter will be represented by,

\[ q_{\text{cal}} = C' \Delta T \]  

(6)

where:

- \( \Delta T \) is the temperature change of the solution/calorimeter (same value as above) and
- \( C' \) is the calorimeter constant.

Although we can measure the mass of the calorimeter, there is no simple “specific heat” of the calorimeter that can be used to calculate the energy transferred from the calorimeter. This is because it is a mixture of things and not a pure substance with a specific heat that can be looked up in a table. What is assumed is that some energy is being transferred from the calorimeter and that the larger the temperature change of the water/calorimeter (\( \Delta T_c \)), the more energy is transferred from the calorimeter. This is similar to assuming that if you get an actual ice-cold soda: the colder the soda, the colder the cup gets.

The value of the calorimeter constant, \( C' \), will be set at 10.5 J/°C for the automated system and \( C' \) will be set at 17.5 J/°C for the manual system.

Putting equations 3, 4, 5 and 6 together,

\[ (\Delta H_{\text{rxn}}) \text{ (mol salt)} = - (m_{\text{soln}} C_{\text{soln}} \Delta T + C' \Delta T) \]  

(7a)

Rearranged this becomes:

\[ (\Delta H_{\text{rxn}}) = - \frac{(m_{\text{soln}} C_{\text{soln}} \Delta T + C' \Delta T)}{\text{ (mol salt)}} \]  

(7b)

where the mol of salt can be determined from the grams of salt, the mass of water is measured and the temperature change is obtained through graphical analysis. Then solve for \( \Delta H_{\text{rxn}} \).
B. Graphical Analysis: What is Happening in Figure 2

As the salt is dissolving, heat energy is being used to dissolve the NH₄NO₃ (an endothermic process) Heat is being taken from the water/calorimeter, so the temperature of the water/calorimeter is decreasing.

After all of the salt dissolves (or as much as can dissolve), the temperature of the water/calorimeter starts to increase because the water/calorimeter is gaining energy (warming back to room temperature) from the surroundings. Truly, the system is not isolated from the surroundings and there is a heat exchange between the system (water/calorimeter) and the surroundings (the rest of the room, the lab bench, etc.).

C. Graphical Analysis: Practically

We will try to get around all of these issues by using graphical analysis to determine the temperature change if all of the salt had dissolved instantaneously at the second that we put the salt into the water/calorimeter. We do this by drawing a vertical line at the time that the salt was added and drawing a sloped line through the data points over which the temperature is linearly returning to room temperature.

The graphical analysis allows us to create a process for which the system is isolated from the surroundings if all of the salt dissolves at the instant it is put into solution. So, the system is not truly isolated, but the graphical analysis allows the calculations to compensate for if it was isolated.

II. Sample Calculations

A. Determining the Temperature Change (ΔT₁)

1. Plot calorimeter temperature (y-axis) versus time (x-axis). It should look roughly like Figure 2. (Data Analysis lines may be drawn by hand.)

To prepare this plot:

1. It is necessary to change the limits on the y-axis. To do this in Excel, double click on the numbers of the y-axis, click on the three vertical bars icon and change the options under axis options to make the limits so that the data takes up the whole plot and the plot takes up an entire page (my plot is really too small to accurately determine the temperatures).

2. Include major gridlines every 1 degree and minor gridlines every 0.2 degrees.

Detailed instructions on creating graphs in Excel are included in the introduction section of the lab manual.
3. Include a complete title and labels for the axes.

4. Then hand-draw the data analysis lines to determine the change in temperature:
   a. Draw a vertical line on the plot at the instant the salt was added.
   b. Draw a line that extends approximately from the point at the longest time back through
   the “straight line” part of the data to cross the vertical line already drawn.

5. Graphically determine the temperature $T_f$ where the two lines cross.

6. Graphically determine the temperature $T_i$ at which the salt was added.

7. Determine $\Delta T$.

III. Experimental Procedure

A. Equipment needed

   From stockroom: 1 thermometer, laptop, Xplorer GLX w/ temperature probe
   Equipment in Lab: 2 Styrofoam coffee cups, lids, mortar & pestle
   Chemicals in lab: water, solid KNO$_3$, NaNO$_3$

B. Disposal

   Place all solutions in the appropriate waste container. (usually found in the fume hood)

C. Experimental considerations

   1. All water is deionized water for this experiment.

   2. Because we will be sharing two or three balances, remember to always zero the balance before
      weighing. If you spill some salt, please clean up the balance area before returning to your station.

   3. Each time a weighing boat or mortar and pestle is used, make sure to clean it by wiping it out with
      a paper towel. Do not wash it with water.

   4. Laptop computers must be checked out and the log filled out upon return of the computer. Place
      the laptop on an elevated platform such as a notebook to prevent any accidental spill from hurting
      the laptop.

D. Before Starting Experimental Work (Before Class)

   1. In your notebook, enter the experiment title, date, your name and name of partner. Number each
      page.

   2. Write the purpose of the lab.

   3. Draw a schematic for a coffee cup calorimeter, labeling all of the parts.

   4. Write an executive summary of each procedure described in this lab. Include enough detail that
      you could attempt the lab without this instruction sheet. (The steps for operation of the GLX may
      be cut and pasted into your notebook.)


   1. Measure out approximately 5 grams of sodium nitrate. (The exact amount is not critical. You do
      not need to record the weight. You will reweigh it after you crush it in step 2.)

   2. Use a mortar and pestle marked for use with sodium nitrate to crush the salt. Then pour the salt
      onto a clean weighing paper or weighing boat and record the exact mass of salt and weighing boat
      in Table 1.
3. Open the digital thermometer and it will turn on automatically. Place a piece of tape on the probe section of the thermometer at a height that will keep the tip approximately ¼ inch above the bottom of the cup to prevent accidentally piercing the cup. (See picture.)

4. Weigh a clean, dry Styrofoam cup pair with lid. Add approximately 40 mL of room-temperature deionized water (from your wash bottle) to the cup and determine the water’s mass by weighing the cup, lid and water together. Record your data in Table 1.

5. Insert the thermometer through the hole in a lid.

6. **Begin recording the temperature of the water inside the calorimeter every 20 sec** in Table 2. Be sure to record the temperature to the nearest 0.1°C. **Do not hold the thermometer directly or you will transfer heat from you hand!**

7. After about three minutes, or when the temperature has stabilized (whichever is longer) add the salt to the calorimeter, while vigorously swirling to attempt to dissolve the salt as quickly as possible, and continue to record the temperature of the calorimeter every 20 seconds for an additional 6 minutes. Record the mass of the weighing boat (and any salt left in it) after adding the salt in Table 1. Then determine the mass of salt that was actually transferred to the calorimeter.

Most salts have endothermic dissolving reactions. For these, the temperature will decrease initially then begin to increase. Keep recording until the temperature increases in a fairly linear manner even if this is longer than 6-8 minutes. (Check with your instructor if you are unsure if it is ok to stop data collection.)

8. Examine the solution in the calorimeter. Record whether or not all of the salt dissolved.

   Did all of the salt dissolve? __________ (If not, repeat the experiment with less salt.)

9. Place the salt water in the appropriate container in the back of the room to recover the salt.

10. Wipe off the probe, close the digital thermometer to turn it off and return it to its original box.

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**F. Procedure 2.** Set-up of Xplorer GLX Data Collection System

1. Plug the A/C power adapter into the Xplorer GLX handset (“the unit”) using the port labeled 15V DC, 1A on the right-hand side of the unit to be sure there is constant power available during the entire experiment. Be sure to press in the plug so that it is flush against the unit. The unit will turn on automatically.

2. Plug the temperature probe (Thin white wire with jack on the end) into temperature sensor 1 on the upper left side of the unit.

3. **Adjust the sample collection rate** by first going to the home screen (press the button that looks like a house) and then press F4 to make adjustments to the temperature sensor. This will bring up another dialog box like the one below. **Press the check mark** (✔) to select the highlighted Sample Rate Unit. Press the down arrow to change from “Samples/s” to “seconds” and then ✔ again.
4. Arrow down to select **Sample Rate**, press the plus (++) key once to increase the sample rate to 2 seconds, then press the **home** key to accept the sensor modifications, and **F1 (Graphs)** to be ready for data collection.

G. **Procedure 3.** Automated Determination of the Heat of Reaction for Dissolving of Potassium Nitrate.

1. Measure out approximately 5 grams of potassium nitrate. (The exact amount is not critical. You do not need to record the weight. You will reweigh it after you crush it in step 2.)

2. Use a mortar and pestle marked for use with potassium nitrate to crush the salt. Then pour the salt onto a clean weighing paper or weighing boat and record the exact mass of salt and weighing boat.

3. Weigh a clean, dry Styrofoam cup pair with lid. Add approximately 40 mL of room-temperature deionized water (from your wash bottle) to the cup and weigh the cup, lid and water together. Determine the water's mass by subtraction. Record your data in Table 1.

4. Insert the temperature probe through a hole in the lid making sure that the tip of the sensor probe is on the bottom of the cup and place the lid on the top cup. Tape the probe in place to the top of the lid.

5. Press the **start/stop** button (It looks like a “play” button, ▶️) to start recording the temperature of the water inside the calorimeter. Next press **F1 (Auto Scale)** to make the graph fill the screen. **Do not touch the wire for the temperature probe once the experiment has started, as this will affect the temperature readings!**

6. After about two minutes, or when the temperature has stabilized (whichever is longer), add the salt to the calorimeter **without stopping data collection** and without taking the temperature-measuring device out of the solution. Vigorously swirl the solution to attempt to dissolve the salt as quickly as possible, and record the temperature of the calorimeter while continuing to swirl for an additional 4 minutes for most experiments. When you have a clearly linear section of data that is headed back towards room temperature, you may stop data collection by pressing the **start/stop** button again.
7. Record the mass of the weighing boat (and any salt left in it) after adding the salt in Table 1. Then determine the mass of salt that was actually transferred to the calorimeter.

Most of the salts have endothermic dissolving reactions. For these, the temperature will decrease initially then begin to increase. Keep recording until the temperature increases in a fairly linear manner even if this is longer than 6-8 minutes. (Check with your instructor if you are unsure if it is ok to stop data collection. If the temperature is still going down, then keep recording. Good data generally has a pretty linear region of increasing temperature.)

8. Examine the solution in the calorimeter. **If all of the salt did not dissolve, repeat experiment with less salt.**

9. Place the salt water in the appropriate container in the back of the room to recover the salt.

10. **Save your data** by transferring it to an Excel file using your flash drive.

   - Start by pressing the **home** key to get back to the main menu.
   - Then press **F2 (Table)** to get to your data in a tabular form.
   - Press the **check mark (✓)**
   - Press the arrow keys (if necessary) until **temperature** is highlighted
   - Press the **checkmark (✓) again.**
   - **Arrow down to 3 (data properties)**
   - Press the **check mark (✓) to get to the next screen.**
   - Be sure that numeric style is set to “**fixed Decimals**”
   - **Arrow down to Number of Digits**
   - Increase the value to **3** using the **+ and - keys.**

   - **Press F1 (OK) to accept.**

   - **If the second column does not show the time data:**
     - Press the **check mark (✓)**
     - **Arrow** to the second column heading (-----)
     - Press the **checkmark (✓) again.**
     - **Arrow down to time**
     - Press the **checkmark (✓) again.

   - **INSERT A FLASH DRIVE** in the USB port on the right side of the GLX.
   - **Press F4 (Tables)**
   - **Arrow down to Export All Data**
   - Press the **check mark (✓) to select this option.**
- The generic file name “GLXport.txt” OR “GLXportRunX.txt” should be highlighted.
- **Press the checkmark (✓) and edit the name** (the key will delete characters) to something meaningful (using T9 texting), and **Press the checkmark** again to accept.
- **Press F1 (OK)** to transfer your data. A message will show up on the screen letting you know when the export is complete.

11. Importing the data into Excel.
- Remove your flash drive from the Xplorer GLX.
- Turn on one of the laptop computers and open Excel.
- Insert the flash drive into one of the USB ports on the laptop computer.
- In Excel, select file/open and then navigate to the flash drive.
  You will need to change the file type to all files in the dialog box at the bottom in order for the file to show up since this is a tab-delimited file and not an Excel file.
- Select the GLX export file and then click open.
  The Text Import Wizard should open.
- Make sure that the delimited (not fixed width) option is selected.
- Select Options to start the import at row 2, and click on next.
- In step 2, be sure that the “Tab” delimiter is checked and that the data is now shown in columns.
- Click finish.

H. Data necessary to determine ΔH°rxn. These are NOT ΔH°; these are ΔH°f.

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔH°f(kJ/mol)</th>
<th>Species</th>
<th>ΔH°f(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃(s)</td>
<td>−494.6</td>
<td>NO₃⁻(aq)</td>
<td>−207.4</td>
</tr>
<tr>
<td>NaNO₃(s)</td>
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<td>SO₄²⁻(aq)</td>
<td>−909.3</td>
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<tr>
<td>Na⁺(aq)</td>
<td>−240.1</td>
<td>K⁺(aq)</td>
<td>−250.4</td>
</tr>
</tbody>
</table>

IV. Further Instructions

A. In-Class Work

The graph and calculations for one of the two salts should be completed before leaving. **You must show your completed graph, including your data analysis lines and estimate of ΔT to your instructor before continuing on to the calculations.** (If ΔT is estimated incorrectly, you will have to repeat all of the calculations!) The work for the second salt can be done at home.

Graph paper for the manual graph of the first salt will be provided by your instructor. If you do not complete it during class time, remember to take a piece of graph paper home with you.
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B. Required Graphs and Calculations

Graphs

1. Prepare a hand written graph for Procedure 1.

2. Prepare a graph using Excel for Procedure 3.

In order to get complete credit for your graphs, they must:
   a) include a complete title
   b) have axes labeled with units
   c) have useful, easy to read scales
   d) fill most of the page
   e) have proper graphical analysis lines shown
   f) have the initial and final temperatures identified and labeled (i.e., \( T_i = \_\_ \)).

Calculations

1. Using the \( T_f \) and \( T_i \) values from your graphs, calculate \( \Delta H_{\text{rxn}} \) for each salt.
   Show all calculations.

2. Calculate \( \Delta H_{\text{rxn}} \) based on literature values given in the section H of the lab for each salt.
   Show all calculations.

3. Calculate the percent error between experimental and literature values of \( \Delta H_{\text{rxn}} \) for each salt.

C. Discussion Items

In your notebook, after completion of all experimental work and calculations, create the heading Discussion Items, copy the following questions, and provide appropriate answers.

1. Why must we use an alternate formula to calculate the contribution to the total energy exchange from the calorimeter? (Why can’t we use the standard equation \( q = m c \Delta T \))

2. Which procedure do you feel gave you the more accurate results, the manual or the automated procedure? Give explicit reasons (data) to support your opinion.

3. What is the sign of \( \Delta S \) in these reactions? Give 2 reasons for your conclusion.
   a) based on general trends in \( \Delta S \).
   b) based on your experimental data for \( \Delta H \) and the equation for the Gibbs Free Energy \( \Delta G = \Delta H - T \Delta S \), and following a set of logic steps.

D. Experimental Summary:

In your notebook, after completion of all experimental work and calculations, create the heading Experimental Summary.

1. Write a summary paragraph describing what was done and what was learned in this experiment, including any issues that were encountered and dealt with.

2. Present a table that summarizes what was determined from this experiment.
   (Hint: it should have at least 3 entries for each salt.)
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E. Tables:

Table 1: Gravimetric Data

<table>
<thead>
<tr>
<th><strong>Sodium Nitrate</strong></th>
<th><strong>Potassium Nitrate</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of cups, lid, and water</td>
<td>Mass of cups, lid, and water</td>
</tr>
<tr>
<td>Mass of cups and lid</td>
<td>Mass of cups and lid</td>
</tr>
<tr>
<td>Mass of water (calculated)</td>
<td>Mass of water (calculated)</td>
</tr>
<tr>
<td>Mass of salt and weighing boat (after crushing step)</td>
<td>Mass of salt and weighing boat (after crushing step)</td>
</tr>
<tr>
<td>Mass of weighing boat (after transfer of salt)</td>
<td>Mass of weighing boat (after transfer of salt)</td>
</tr>
<tr>
<td>Mass of salt added to water (calculated)</td>
<td>Mass of salt added to water (calculated)</td>
</tr>
</tbody>
</table>

Table 2: Temperature data for Sodium Nitrate

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<th>Time (sec)</th>
<th>Temp. (°C)</th>
<th>Time (sec)</th>
<th>Temp. (°C)</th>
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</thead>
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