

Heats of Reaction

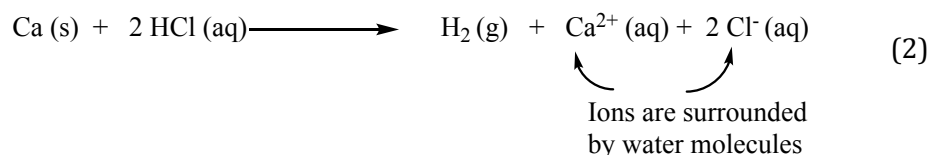
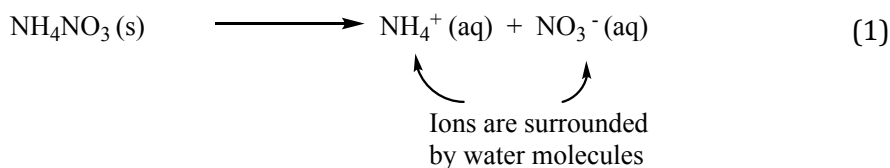
Applications of thermochemistry



Introduction

A significant percentage of the energy we consume every day is produced in chemical reactions like the combustion of fossil fuels. Studying energy and its transformations in chemical reactions is a vitally important field of chemistry for social, economic, and environmental reasons. During a chemical reaction, an input of energy is required to break chemical bonds and energy is released in the form of heat when bonds form. When solids are dissolved in solution, energy can also be released or absorbed. The net energy change from these different types of processes will determine whether a reaction is endothermic or exothermic.

Under conditions of constant pressure, the energy change of a reaction is called the **heat of reaction** or **enthalpy change (ΔH)**. By convention, if heat is released, the reaction is termed **exothermic** and ΔH is negative. If heat is absorbed, the reaction is said to be **endothermic** and ΔH is positive. The amount of heat either absorbed or released during a reaction can be measured by monitoring the changes in temperature of the reacting solution over time in a container that insulates the reaction from the surrounding environment. In this experiment, you will measure the heat of reaction for two processes: 1) solvation of ammonium nitrate in which the ions separate and are surrounded by water; and 2) a redox reaction that produces hydrogen gas and ions that are surrounded by water.



Scientific questions:

1 - How do changes to the reactants in the two chemical reactions, the solvation of ammonium nitrate and the reaction of calcium and hydrochloric acid, explain the change in temperature of the solutions? (During each reaction, bonds in the reactants are broken and new bonds are formed.)

2 - How can changes in bonding explain the temperature change and heat flow of the solution?

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The enthalpy change of a reacting solution, $\Delta H_{\text{solution}}$, is determined by measuring the temperature change ($\Delta T = T_{\text{final}} - T_{\text{initial}}$) and the mass of the solution. The product of the specific heat, the mass of solution, and the temperature change of the system will give the enthalpy change for the reaction:

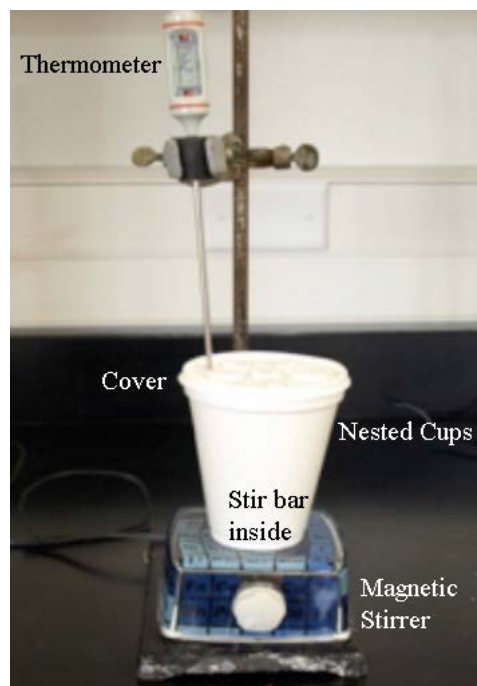
Heat of **solution**:

$$\Delta H_{\text{solution}} = (\text{specific heat of water}) \times (\text{grams of solution}) \times (\Delta T)$$

In order to determine the change in temperature (ΔT), you will need to know the initial temperature of the solution (before the reaction) and the final temperature, at zero time, after mixing. The final temperature, however, cannot be measured directly with a thermometer and must be extrapolated from trends of cooling or warming that are measured over time.

In order to measure the temperature trend over a period of time, you will need to perform these reactions in a container that can effectively insulate the reaction from the rest of the environment. This is possible with a **double Styrofoam cup calorimeter** (illustrated here.)

While the calorimeter prevents heat exchange with the environment, the Styrofoam cups do not create a perfectly isolated system. During a reaction, some heat can be absorbed by the Styrofoam material of the cup. Therefore, you have to correct for the amount of heat the cup will “steal” from the reaction, before you can accurately determine the heat of reaction. This correction value is called the **calorimeter constant** or **heat capacity** of the calorimeter. Every Styrofoam cup calorimeter in the lab will have a slightly different value.



The calorimeter constant is used to determine the enthalpy change ($\Delta H_{\text{calorimeter}}$) experienced by the calorimeter during each experimental reaction you are trying to measure. When the calorimeter constant is known, the true heat of reaction can be calculated by adding the enthalpy change of the calorimeter back to the calculated heat of solution:

Heat of **reaction**:

$$\Delta H_{\text{reaction}} = - (\Delta H_{\text{calorimeter}} + \Delta H_{\text{solution}})$$

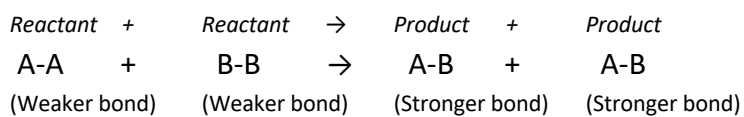
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Materials:

| <u>Chemicals:</u> | <u>Equipment and Supplies:</u> |
|--|--|
| <ul style="list-style-type: none">• 1.0 M Hydrochloric acid (HCl)• Ammonium nitrate (NH₄NO₃)• Calcium metal (Ca)• Deionized Water | <ul style="list-style-type: none">• Styrofoam cup calorimeter• One-hole stopper• Thermometer• Graduated cylinder• Magnetic stirrer• Magnetic stir bar• Balance |

Pre-Lab Assignment:

1. Please write a short summary of the experiment you will perform today.
2. Please prepare a safety table that lists the chemicals, their hazards, and the precautions you will take when handling them.
3. What are the limitations of a Styrofoam cup calorimeter in measuring heats of reactions?
4. What is the difference between the heat of reaction and the heat of solution?
5. Consider the following reaction:



- a. For this chemical reaction, describe the reactants and products in terms of stability. Explain how bond strength and chemical work are connected to stability.
 - b. For this chemical reaction, place "+q" on one side of the equation to illustrate heat flow. Explain how you made your choice.
 - c. For this chemical reaction, would you expect the temperature to increase or decrease? Explain the evidence used to make your prediction about the reaction.
6. What data will you collect during this experiment? How will you use this data to determine:
 - a. The reaction temperature at time zero (instantaneously after mixing).
 - b. The amount of energy is lost to the experimental equipment.
 - c. Whether your reaction is endothermic or exothermic.

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Procedure:

Part 1. Determine the **calorimeter constant** of your Styrofoam cup calorimeter.

1. Obtain one calorimeter (consisting of two Styrofoam cups, one inside the other, and a plastic lid), a magnetic stirrer, a stir bar and a digital thermometer. Set up the calorimeter as shown in the illustration on page 2. Punch two small holes in the plastic lid of the cup, one for the thermometer and the other for an opening to the outside. The cup needs to be as well sealed as possible but there needs to be an opening to the atmosphere. All steps using the calorimeter should be done in the hood.
2. Use a graduated cylinder to obtain exactly 50.0 mL of room temperature water and add it to your calorimeter. Allow this to stir for a few minutes in order for the apparatus to come to thermal equilibrium, then measure and record the temperature of the water in the calorimeter to the nearest 0.1°C. Record the exact temperature of this room temperature water in your notebook.
3. Use the graduated cylinder to measure 50.0 mL of water into a small beaker and heat with a Bunsen burner until it is about twenty degrees (20°C) **above** room temperature (probably around 40°C). Stir with a glass rod to mix the hot water thoroughly and then measure the exact temperature right before you do step 4.
4. Locate a way to keep time by seconds (using your cell phone or the clock in the room). When you're ready to keep time, pour the hot water into the calorimeter with the room temperature water (make sure the stir bar is going), replace the lid, start the clock, and insert the thermometer. Try to start measuring temperature and time measurements as soon as you mix! After recording the initial temperature immediately after mixing, record the temperature every five seconds until it reaches a maximum and then every 15 seconds for at least two minutes more until you notice a consistent pattern of cooling as the mixture returns to room temperature. Do not stop recording the temperature before you observe a cooling (downward) trend for at least one minute.
5. Empty your calorimeter, dry all the parts completely, and allow everything to return to room temperature. While you wait, use your data to calculate your calorimeter constant (see the following directions and example).
6. Use the time vs. temperature data for mixing to determine the calorimeter constant.
7. The first step in determining the calorimeter constant is to use your data to find the final temperature (T_{final}) of the mixed water. T_{final} is impossible to measure directly because you can't actually accurately measure the temperature the INSTANT they are mixed, so we've got to extrapolate what this value is by using the pattern that emerges as the mixed water cools down over time. By plotting the time vs. temperature data, we can extrapolate back to time zero. Plot your temperature vs. time data using Excel or another graphing program. It should look something like this:

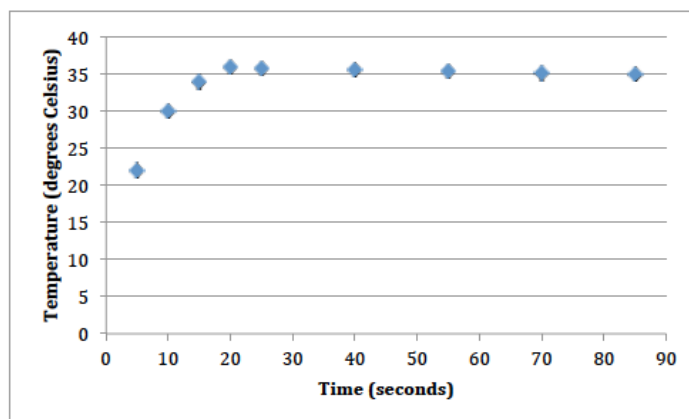


Figure 1. Temperature vs. time data after mixing hot and room temperature water in calorimeter

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- Next, identify the highest temperature that the mixture ever reached (in the example in Figure 1, it's 36.0 °C and happens after 20 seconds). From this point on, the mixture cools down in relatively consistent way. Identify where this cooling trend begins in your own data.
- The pattern of this cooling can be modeled by using a trend line called a cooling curve. We can use the equation of this line ($y = mx + b$) to extrapolate back to the temperature at time zero by finding the y-intercept. The y-intercept will tell us what temperature the mixture was the INSTANT it was mixed at time zero. This value is the final temperature (T_{final}), not to be confused with the last temperature that was recorded (at 85 seconds in Figure 1).
- Using Excel, plot a trend line for the cooling. Figure 2 shows an example of a trend line plot for the cooling curve. The equation of the trend line indicates that the y-intercept is 36.214. That means that T_{final} is 36.2 °C.

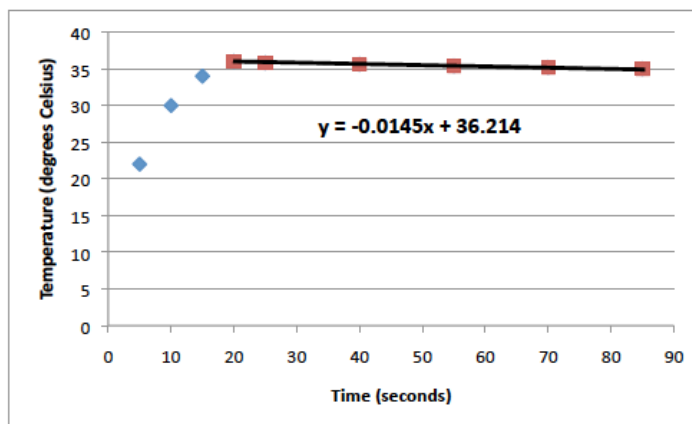


Figure 2. Cooling curve of hot and room temperature water after mixing

- To create a perfectly closed system, a barrier is needed that prevents any heat exchange outside of the system and the surroundings, including the barrier itself. Imagine if we mixed 50 mL of hot water and 50 mL of cold water in this perfectly closed system. The heat can't go anywhere beyond the system and surroundings and so we'd expect that the hot water would lose EXACTLY as much heat as the cold water gains. Therefore, the absolute value of the enthalpy change (ΔH) of the hot water should be equal to the enthalpy change of the cold water.
- The Styrofoam barrier of your calorimeter cannot perfectly insulate the system and will absorb some heat. By calculating the enthalpy change for the hot water and the cold water and comparing them, we can find out how much heat the calorimeter absorbs:
- The heat lost by the hot water is:

$$\Delta H_{\text{lost}} = (\text{specific heat of water}) \times (\text{grams of solution}) \times (\Delta T_{\text{lost}})$$

$$\Delta T_{\text{lost}} = (\text{the extrapolated final temperature at time zero}) - (\text{the initial temperature of the hot water})$$

The heat gained by the cold water is:

$$\Delta H_{\text{gain}} = (\text{specific heat of water}) \times (\text{grams of solution}) \times (\Delta T_{\text{gain}})$$

$$\Delta T_{\text{gain}} = (\text{the extrapolated final temperature at time zero}) - (\text{the initial temperature of the cold water})$$

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14. Calculate these values for your data. The absolute value of the hot water's enthalpy change should be larger than the absolute value of the cold water's enthalpy change, indicating that the calorimeter has absorbed some of the heat.
15. Next, we can find the enthalpy change ($\Delta H_{\text{calorimeter}}$) of the calorimeter. $\Delta H_{\text{calorimeter}}$ is equal to the difference between the heat lost by the hot water and the heat gained by the cold water. Because ΔH_{lost} is a negative quantity, $\Delta H_{\text{calorimeter}}$ can be expressed as follows:

$$\Delta H_{\text{calorimeter}} = - (\Delta H_{\text{lost}} + \Delta H_{\text{gain}})$$

16. Finally, with the enthalpy change we can calculate the calorimeter constant or heat capacity of the calorimeter ($C_{\text{calorimeter}}$). The heat gained by the calorimeter, $\Delta H_{\text{calorimeter}}$, is divided by the change in the temperature of the calorimeter. Since the temperature of the calorimeter increased to T_{final} , the change in temperature will be ΔT_{gain} .

$$C_{\text{calorimeter}} = \Delta H_{\text{calorimeter}} / \Delta T_{\text{gain}}$$

Why do we need this value?

The calorimeter constant tells you how many joules of heat the calorimeter will absorb per each degree Celsius you measure in your future experimental reactions. It allows you to determine an enthalpy change for the calorimeter in each experiment and correct the heat of solution value you calculate to determine the heat of reaction.

Before you continue, show your instructor your calorimeter constant. If you calculated a negative value, something has gone wrong!

Below is an example of how to determine a calorimeter constant:

To determine the calorimeter constant of a calorimeter, a student added 50 mL hot water to 50 mL of colder room temperature water and the temperature vs. time data was collected and plotted.

Initial temperature of 50 mL hot water: 38.2 °C

Initial temperature of 50 mL of cold water: 21.2 °C

Extrapolated final temperature after mixing: 29.2 °C

Density of water: 1 g/mL; Specific heat of water: 4.184 J/g•°C

The heat lost by the hot water:

$$\Delta H_{\text{lost}} = (50 \text{ g}) \times (4.184 \text{ J/g}\cdot\text{°C}) \times (29.2 - 38.2 \text{ °C}) = - 1883 \text{ joules}$$

The heat gained by the cold water:

$$\Delta H_{\text{gain}} = (50 \text{ g}) (4.184 \text{ J/g}\cdot\text{°C}) (29.2 - 21.2\text{°C}) = + 1674 \text{ joules}$$

The heat lost to the calorimeter is the difference between the heat lost by the hot water and the heat gained by the cold water:

$$\Delta H_{\text{calorimeter}} = - (- 1883 + 1674) \text{ joules} = + 209 \text{ joules}$$

Therefore, the calorimeter constant of this calorimeter is:

$$C_{\text{calorimeter}} = + 209 \text{ joules} / (29.2 - 21.2\text{°C}) = + 26.1 \text{ joules/°C}$$

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Part 2. Reaction of Calcium and Hydrochloric acid

1. Pour 100.0 mL of 1.0 M HCl into the calorimeter. Allow the solution to reach thermal equilibrium while stirring with the stir bar and record this as the initial temperature.
2. Weigh out about 1 g (± 0.01 g) of calcium.
3. Be ready to start recording the temperature. Add the calcium to the HCl in the calorimeter, quickly replace the lid, insert the thermometer, and start the timing.
4. Record the temperature every 5 seconds for one minute and then every 15 seconds for at least two minutes or until you notice the temperature is steadily declining from the highest point it reached.
5. Clean and dry the calorimeter for the next reaction.

Part 3. Reaction of Solvation: Ammonium nitrate + water

1. Pour 100.0 mL of distilled water (room temperature) into the calorimeter. Allow the water to reach thermal equilibrium while stirring with the stir bar and record this as the initial temperature.
2. Weigh out about 5 g (± 0.01 g) of ammonium nitrate, NH_4NO_3 .
3. Be ready to start recording the temperature. Add the ammonium nitrate to the calorimeter, quickly replace the lid, insert the thermometer, and start the timing.
4. Record the temperature every 5 seconds for one minute and then every 15 seconds for at least two minutes more until you see the temperature start to steadily increase from its lowest point.

Part 4. Calculate the heat of reaction for both reactions. For this part, you may return to the breakout room.

1. Pick another group to team up with. Acquire their data for each reaction and provide them with the numbers you recorded. Make sure to record their calorimeter constant because it will be different from your own. Together answer the following questions and then move on to analyzing your data in your original group.

Q: What is different about the two reactions? What did the temperature do? Looking at the data, identify where each reaction reached its lowest or highest temperature.

Q: Can you tell just from looking at the temperature vs. time data whether each reaction is exothermic or endothermic? Why or why not?

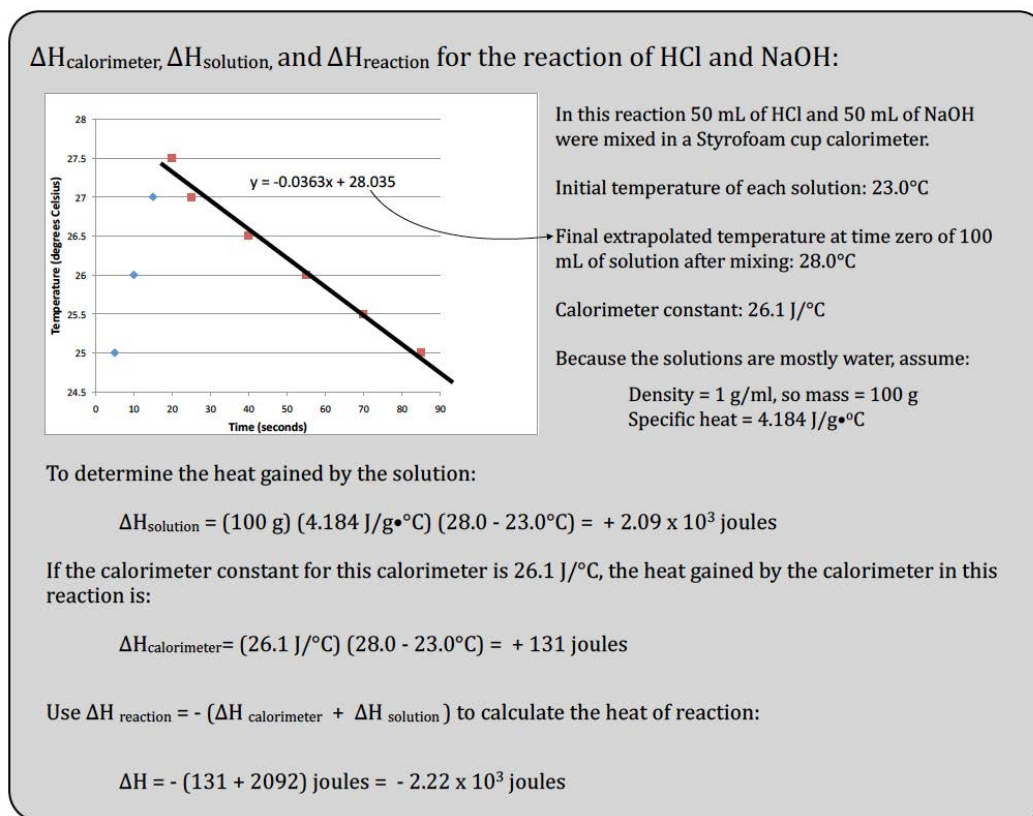
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2. For each reaction, working together in a group, calculate:
 - a) The enthalpy change of the calorimeter ($\Delta H_{\text{calorimeter}}$)
 - b) The enthalpy change of the solution ($\Delta H_{\text{solution}}$)
 - c) The enthalpy change of the reaction ($\Delta H_{\text{reaction}}$)

To do this, you will first need to plot the temperature vs. time data. Use a spreadsheet program like Excel to generate a scatter plot.

3. Next, you will need to create a cooling or heating curve by finding the minimum or maximum temperature recorded for each reaction. Fit a trend line to the cooling or heating trend and determine the temperature at time zero (the y-intercept of the equation for the line). Remember, this is the final temperature of each reaction.

Below is an example calculation of the heat of reaction of an acid and base:



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Rubric for lab report (due next lab meeting) (Use the Gen Chem lab report template)

| | |
|---|--|
| <p>Introduction: (10 pts)</p> | <p>This section provides a short introduction or summary to the report, and should include:</p> <ul style="list-style-type: none"> Title of the report Author name (your name) Lab partner name (if you had partner(s)) Date of experiment Overview: A few sentences describing what the lab experiment was about <p>We also recommend including your section and TA name (optional)</p> |
| <p>Data, Results, Evidence: (25 pts total)</p> | <p>This section organizes data, results, and evidence. The goal of the section is to describe what you did and what data were collected. Observations can be important data to use in analysis. See additional instructions in the Template for Submission of Lab Reports (in ICN Resources).</p> <p>This section should include:</p> <ul style="list-style-type: none"> Procedure: Reference the laboratory procedure that was downloaded and the date it was accessed (Heats of Reaction, InterChemNet, accessed: 12/8/2019. Any changes in procedures should be noted.) Graph and Trend Line for Hot and Cold Water: Provide the temperature vs. time graph for mixing the hot and cold water. Provide the equation for the trend line of the cooling curve for mixing the hot and cold water. Use the extrapolated value of T_{final} to calculate the calorimeter constant. Temp vs Time Graphs with Trend Lines for Each Reaction: Provide the temperature vs. time graph for each reaction. Provide the equation for the trend line of the cooling or heating curve for each reaction. Use the extrapolated value of T_{final} to calculate the heat of solution, the enthalpy changes of the calorimeter, and the heat of reaction. Show all calculations. Observations: include observations and notes to help explain any chemistry. <p>Notes: To receive full credit, your calculations should be clearly labeled, including proper units with appropriate number of significant figures. Data from outside sources can be used in this section to support data obtained.</p> |
| <p>Analysis of Evidence (Reasoning):</p> <p>Scientific explanations that use evidence and appropriate chemistry concepts to construct claims. (30 pts total)</p> | <p>In this section, your data, results, and evidence, including observations, are analyzed to help explain the chemistry that occurs in the experiment. Your analysis will be a major support for any claims you make. See additional instructions in the Template for Submission of Lab Reports (in ICN Resources).</p> <ul style="list-style-type: none"> Explain the Calorimeter Constant: Explain how you experimentally determined and calculated the calorimeter constant and what this value means. Why must T_{final} be extrapolated? Why must the calorimeter constant be calculated before determining heats of reactions? Analyze Each Reaction: Explain how you used the temperature vs. time data for each reaction to calculate the heat of solution, enthalpy change of the calorimeter, and heat of reaction. Address the First Scientific Question: How do changes to the reactants in the two chemical reactions, the solvation of ammonium nitrate and the reaction of calcium and hydrochloric acid, explain the change in temperature of the solutions? (During each reaction, bonds in the reactants are broken and new bonds are formed.) Address the Second Scientific Question: How can changes in bonding explain the temperature change and heat flow of the solution? <p>Note: Data from outside sources can be discussed in this section to support analysis.</p> |
| <p>Claim(s): Statement(s), derived from evidence, using scientific reasoning. (15 pts total)</p> | <p>This section is to present claims. It is advantageous to directly connect evidence (from your lab investigation and outside sources) that you utilize in your discussion to develop your claims. See additional instructions in the Template for Submission of Lab Reports (in ICN Resources).</p> <p>Addressing the scientific question as part of your claim may be useful.</p> |