

Experiment 9: Enthalpy of Formation of Magnesium Oxide

Objective: In this experiment, a simple calorimeter will be constructed and calibrated, and Hess' law of constant heat summation will be used to determine the enthalpy of formation of magnesium oxide, MgO.

Introduction

Mark is a chemist who has just been hired by Flashbulbs Are Us, a relatively new company founded just three years ago in 1954. Flashbulbs are a popular source of light for photographers. In the flashbulbs manufactured by Flashbulbs are Us, magnesium foil is placed in an atmosphere of oxygen contained within a glass bulb. An electric current (generated by a battery) is passed through the metal, and the magnesium burns with an intense white light. Mark thinks there would be advantages to switching from glass to plastic to house the contents of the flashbulb. The flashbulbs would be easier to transport and less hazardous to the customers since the plastic is more difficult to break. In choosing a specific plastic for the housing, he needs to select a material which can withstand the heat generated by the magnesium metal as it burns. To tackle this problem, Mark first needs to determine how much heat is produced by the combustion of magnesium.

When magnesium is burned in oxygen, a large quantity of heat is released which results in a large, negative $\Delta H^\circ_{\text{rxn}}$ value:



The change in enthalpy of this reaction is quite difficult to measure directly by experiment. However, Mark realizes that he can obtain the heat of reaction indirectly by measuring the enthalpies of other reactions and using Hess' law.

Virtually all chemical processes involve energy transfer of one type or another, and the branch of chemistry that explores this transfer is called **thermochemistry** (see Tro, Chapter 6). The **energy change** of a reaction, symbolized by the expression ΔU_{rxn} , is the sum of energy which is transferred as both heat, q , and work, w :

$$\Delta U_{\text{rxn}} = q + w \quad \text{Eq. 1}$$

For a reaction that occurs at constant pressure, the term **enthalpy** is used, which is the sum of the energy of all the atoms and molecules *plus* the work of displacing the environment, that is, the PV work:

$$H = U + PV \quad \text{Eq. 2}$$

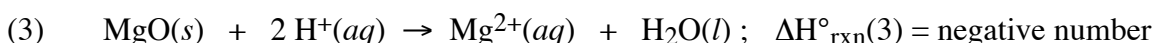
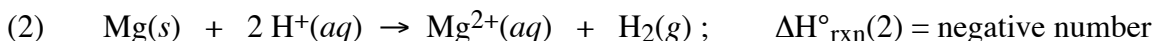
Thus, the **enthalpy change** for a chemical reaction at constant pressure is defined by the following equation:

$$\Delta H_{\text{rxn}} = \Delta U_{\text{rxn}} + P\Delta V_{\text{rxn}} \quad \text{Eq. 3}$$

In the case of an enthalpy change which takes place at *1 atm of pressure*, we use the notation $\Delta H^\circ_{\text{rxn}}$.

In accordance with **Hess' Law**, enthalpy changes for chemical reactions are additive. If two chemical equations are added together to form a third equation, the enthalpy change of the third equation, $\Delta H^\circ_{\text{rxn}}(3)$, is equal to the sum of $\Delta H^\circ_{\text{rxn}}(1)$ and $\Delta H^\circ_{\text{rxn}}(2)$. When applying Hess' law, it is important to establish a convention for the signs, (+) or (-), of the enthalpy changes. An **exothermic** reaction is one which *releases* energy and is assigned a *negative* value. An **endothermic** reaction is one which *absorbs* energy and is assigned a *positive* value. The additive property of $\Delta H^\circ_{\text{rxn}}$ values will be applied in this experiment in order to determine the enthalpy change associated with the burning of magnesium metal in air.

For the combustion of magnesium, reaction (1), one possible set of reactions is:



Reaction (1) is equal to reaction (2) minus reaction (3) plus reaction (4):

$$\Delta H^\circ_{\text{rxn}}(1) = \Delta H^\circ_{\text{rxn}}(2) - \Delta H^\circ_{\text{rxn}}(3) + \Delta H^\circ_{\text{rxn}}(4) \quad \text{Eq. 4}$$

The enthalpy of formation of liquid H_2O has been measured and is given by:

$$\Delta H^\circ_{\text{rxn}}(4) = \Delta H^\circ_{\text{f}}(\text{H}_2\text{O}) = -285840 \text{ Joules/mole} = -285.84 \text{ kJ/mol}$$

The enthalpies of reactions (2) and (3) are measurable quantities. Heat is *released* by the addition of excess strong acid to one mole (24.3 g) of Mg, thus the quantity $\Delta H^\circ_{\text{rxn}}(2)$ will be a negative number. Similarly, the addition of excess strong acid to one mole (40.3 g) of MgO will release heat, and $\Delta H^\circ_{\text{rxn}}(3)$ will also be negative.

Measuring the Heat Capacity of a Calorimeter

Mark knows that he'll need to use a **calorimeter** to measure the heat effects of the magnesium reactions. A **calorimeter** is a reaction vessel that is well insulated in order to prevent heat transfer between the reaction and its surroundings. As heat is evolved by the reaction inside the calorimeter, the temperature of the contents increases, and it is this temperature change which is measured and related to the enthalpy of the reaction. Thus, all heat effects that are observed in the calorimeter should be the result only of the ΔH° value of the reaction or process occurring in the calorimeter.

The relationship between the amount of heat absorbed by a system, Q , and the resulting change in temperature, $\Delta T = T_{\text{final}} - T_{\text{initial}}$, may be expressed in terms of the total **heat capacity** of the system at constant pressure, C_p :

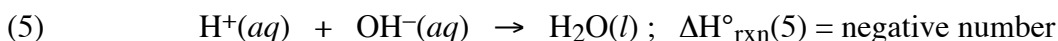
$$Q = (C_p) \cdot \Delta T \quad \text{Eq. 5}$$

However, heat *released* is equal to $-\Delta H$:

$$-\Delta H = -Q = -(C_p) \cdot \Delta T \quad \text{Eq. 6}$$

A calorimeter must be calibrated to determine its **heat capacity**, that is, the amount of heat required to raise the temperature of the calorimeter itself by *one* degree Celsius or Kelvin. The calibration can be accomplished by carrying out a reaction which

has an accurately known heat of reaction and measuring its effect on the calorimeter. One of the most widely used reactions for this purpose is the heat of neutralization of a strong acid by a strong base:



Reaction (5) *releases* a large amount of heat, around 57000 J/mole, therefore, $\Delta H^\circ_{\text{rxn}}(5)$ will be large and negative. The value for $\Delta H^\circ_{\text{rxn}}(5)$ will vary with the temperature at which the reaction is carried out, and can be found in Table 1.

Table 1. Values of $\Delta H^\circ_{\text{rxn}}(5)$ at temperatures between 18 and 30°C

Temperature (°C)	$\Delta H^\circ_{\text{rxn}}(5)$ (kJ/mol)
18	-58.62
19	-58.42
20	-58.22
21	-58.01
22	-57.81
23	-57.61
24	-57.41
25	-57.20
26	-57.00
27	-56.80
28	-56.60
29	-56.39

From Table 1, take the value corresponding to the *final* temperature of your reaction solution as your $\Delta H^\circ_{\text{rxn}}(5)$ value.

In the neutralization reaction, sodium hydroxide, NaOH, will be present in an excess amount so that even though the solution may be contaminated with Na₂CO₃ (from the slow absorption of CO₂ from the atmosphere), enough OH⁻ will be available to react with all of the hydrochloric acid, HCl, added. In this case, we call HCl the **limiting reagent**; thus, the number of moles of water formed in the neutralization is determined by the number of moles of HCl used. Therefore, the actual heat released can be calculated from the following expression:

$$(-Q) = [\Delta H^\circ_{\text{rxn}}(5)] \cdot (\text{moles of HCl}) \quad \text{Eq. 7}$$

using the appropriate value of $\Delta H^\circ_{\text{rxn}}(5)$ from Table 1.

Because no calorimeter is free from heat leaks, it is possible that you will see some heat loss to the surroundings reflected in your data. Figure 1 shows a temperature vs. time plot for a calorimetric experiment in which the reaction was exothermic. After the initial sharp rise in temperature when the reaction is begun (at time of mixing, $t = 0$ seconds), the temperature begins to decrease due to heat loss from the calorimeter. As the temperature equilibrium becomes complete, the loss becomes steady and the

temperature decrease linear. Extrapolation of this linear portion of the curve back to $t = 0$ seconds gives an accurate value for the maximum temperature attained, T_f , if equilibrium were to take place instantaneously with no thermometer lag.

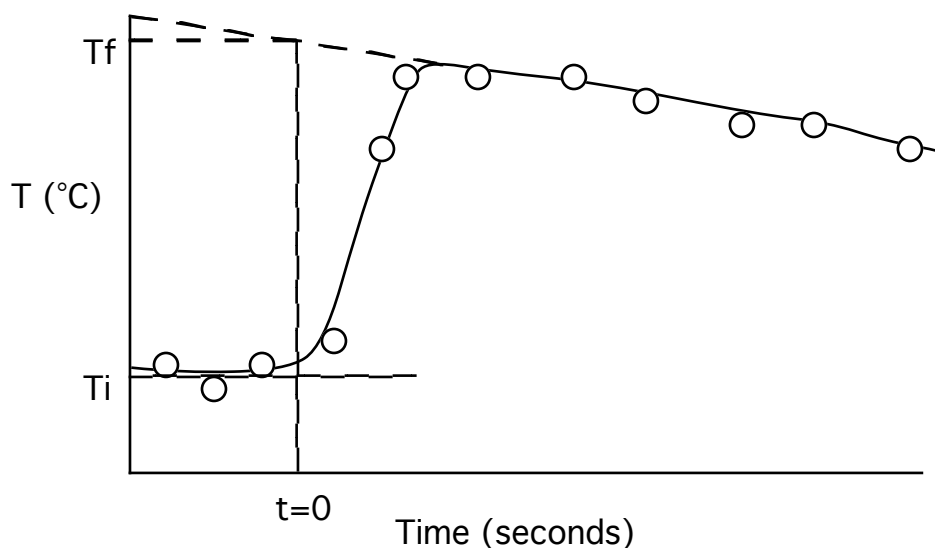


Figure 1. Determining T_f from a plot of temperature as a function of time.

Once T_f has been determined from the plot, it is possible to calculate the heat capacity of the calorimeter. You will record the temperatures of the acid (HCl) and the base (NaOH) before beginning the experiment, and these will be denoted by T_a and T_b , respectively. All of the heat that is liberated by the reaction will be equal to the heat which is absorbed by the calorimeter *and* its contents:

$$\text{heat liberated by reaction} = \text{heat absorbed by acid} + \text{heat absorbed by base} + \text{heat absorbed by calorimeter}$$

Each of the above terms can be expressed by experimental parameters:

$$\text{heat liberated by the reaction (kJ)} = -[\Delta H^\circ_{\text{rxn}}(5)] \cdot (\text{moles of HCl})$$

$$\text{heat absorbed by the acid (kJ)} = (C_{p, \text{aq}}) \cdot (V_a) \cdot (T_f - T_a)$$

$$\text{heat absorbed by the base (kJ)} = (C_{p, \text{aq}}) \cdot (V_b) \cdot (T_f - T_b)$$

$$\text{heat absorbed by the calorimeter (kJ)} = (C_{p, \text{cal}}) \cdot (T_f - T_b)$$

where V_a = mL of acid at temperature T_a , V_b = mL of base at temperature T_b and $(C_{p, \text{aq}})$ denotes the heat capacity of the aqueous solutions. Substituting these expressions into the original equation, the following is obtained:

$$-[\Delta H^\circ_{\text{rxn}}(5)] \cdot (\text{moles of HCl}) = (C_{p, \text{aq}}) \cdot (V_a) \cdot (T_f - T_a) + (C_{p, \text{aq}}) \cdot (V_b) \cdot (T_f - T_b) + (C_{p, \text{cal}}) \cdot (T_f - T_b) \quad \text{Eq. 8}$$

Solving for the heat capacity of the calorimeter, ($C_{p, \text{cal}}$):

$$(C_{p, \text{cal}}) = \frac{-[\Delta H^{\circ}_{\text{rxn}}(5)] \cdot (\text{moles HCl}) - (C_{p, \text{aq}}) \cdot (V_a) \cdot (T_f - T_a) - (C_{p, \text{aq}}) \cdot (V_b) \cdot (T_f - T_b)}{(T_f - T_b)}$$

Eq. 9

In **Eq. 9**, the quantities T_a , T_b , T_f , V_a and V_b are measured experimentally, and the number of moles of HCl used is calculated from the known concentration and volume used. To an acceptable degree of accuracy, all the aqueous solutions involved in the experiment are assumed to have a heat capacity, ($C_{p, \text{aq}}$), of 0.00418 kJ/mL·Kelvin (that is, 4.18 Joules are needed to raise the temperature of 1 mL of solution 1°K). The calorimeter constant, ($C_{p, \text{cal}}$), can thus be calculated and used in determining enthalpy changes of reaction which take place within the calorimeter.

To measure $\Delta H^{\circ}_{\text{rxn}}$ values for reactions (2) and (3) of the magnesium oxidation sequence, weighed amounts of solid magnesium and solid magnesium oxide will be added to excess HCl. In these cases, the solid material will be the limiting reagent. The equation used to calculate the enthalpy is a simplified version of **Eq. 8**:

$$-\Delta H^{\circ}_{\text{rxn}}(x) = \frac{(C_{p, \text{aq}}) \cdot (V_a) \cdot (T_f - T_a) + (C_{p, \text{cal}}) \cdot (T_f - T_a)}{(\text{number of moles of limiting reagent})}$$

Eq. 10

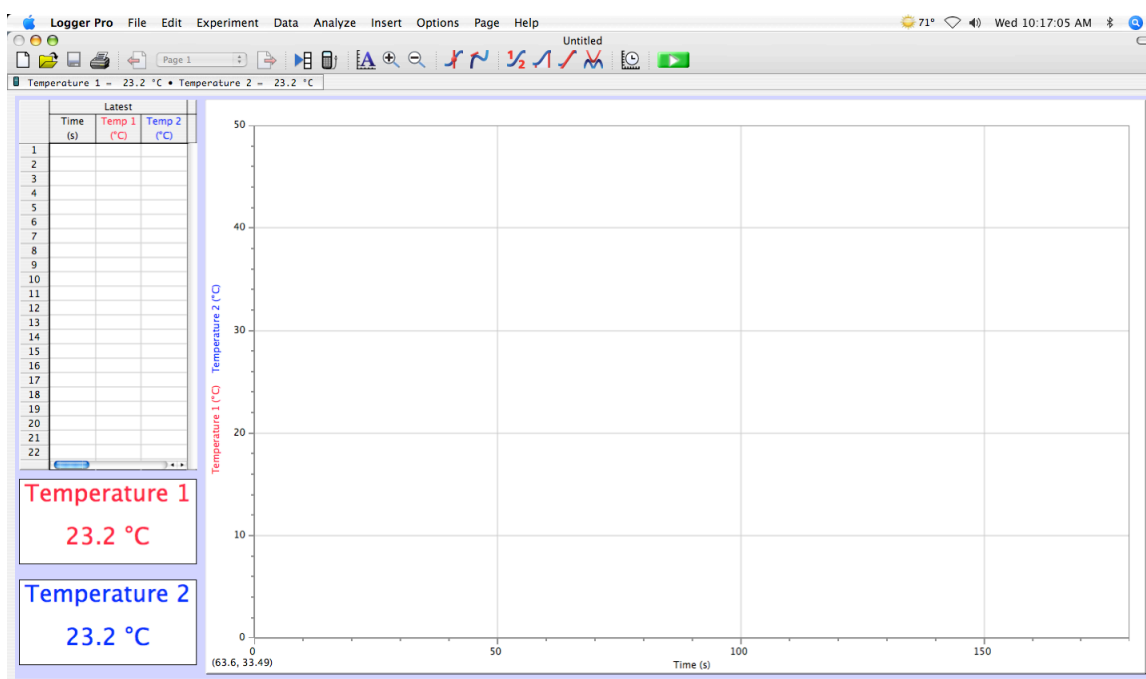
The number of moles of limiting reagent is calculated from the mass of reagent weighed out divided by its molar mass.

From the values that are calculated for $\Delta H^{\circ}_{\text{rxn}}(2)$ and $\Delta H^{\circ}_{\text{rxn}}(3)$ and the given value for $\Delta H^{\circ}_{\text{rxn}}(4)$, the molar enthalpy of formation of solid MgO, $\Delta H^{\circ}_{\text{rxn}}(1)$, can be calculated using **Eq. 4**.

Procedure (you do not need to outline instructions for using the LoggerPro software)

Instead of a thermometer, a temperature probe interfaced to a computer will be used to acquire the temperature readings in this experiment. The temperature probe has an uncertainty of $\pm 0.1^\circ\text{C}$. These probes should not be allowed to sit in acidic or basic solution for longer than 10 minutes. Rinse the probe with water immediately after each experiment. Two students will use the same computer, but each student will have his/her own temperature probe and will obtain his/her own set of data to evaluate. Two temperature probes should already be plugged into the interface box and each inserted through a hole in the center of a cap. Choose a probe and record the number of the channel into which it is plugged. You must use the *same* probe for all measurements.

To log onto the computer, type “student” for the name and type “chemistry” for the password, then click on **Log In**. Click on the **Applications** folder at the bottom of the screen. In the window that opens, click on the button labeled **Logger Pro** to open the Logger Pro software. When two temperature probes are plugged into the interface box, the following picture should appear on the screen:



Pull down the **Experiment** menu and choose **Data Collection....** Change the length of the experiment to 500 seconds. Change the Sampling Rate to 1 samples/second. Click on **Done**. Click once on the number at the very top of the y-axis so that a box appears around the number. Type in 40 and press return. You are now ready to collect data.

Wear safety glasses at all times.

The computer will collect the data for both your and your partner's temperature probes simultaneously; therefore, you should carry out the steps of the experiment at approximately the same time.

Measuring (C_p , cal)

Obtain three Styrofoam cups and one cap. Do **not** write directly on the cups—use labels. Place 20.0 mL of standardized HCl solution (~ 1 M; *record* exact molarity written on the label) in one of the cups. Calculate the number of moles of HCl which are now in the cup. Rinse off the probe with distilled water, wipe it dry with a paper towel and place the cap through which it is inserted onto the cup that contains HCl. Be sure the probe is far enough down that the tip is immersed in the solution, but that it is not touching the bottom of the cup.

Assemble a "calorimeter" by nesting the other two Styrofoam cups together (see Figure 2, below). Place 30.0 mL of 1.0 M NaOH solution in your calorimeter and cover it with the other cap. Place the calorimeter in a 400 mL beaker to prevent it from tipping over. Wait five minutes to allow the solutions to reach thermal equilibrium.

Watch the temperature readings that appear below the data table (this is the temperature of the HCl solution). When the temperature appears to have stabilized, record in your lab notebook the temperature (to the nearest tenth of a degree) of *your* HCl solution.

Remove the cap from the calorimeter (the nested cups). Remove the cap and temperature probe from the cup that contains HCl solution, rinse the probe with distilled water and dry it with a paper towel. Place this cap on the calorimeter, thus placing the temperature probe into the NaOH solution.

Click on the **green button** with an arrow, found at the top of the screen, to begin collecting data. Allow the computer to collect readings for 10 to 12 seconds while the probe is in the NaOH solution. Continue to collect the data (do *not* click on the **red button**) and carry out the following steps in rapid succession and at approximately

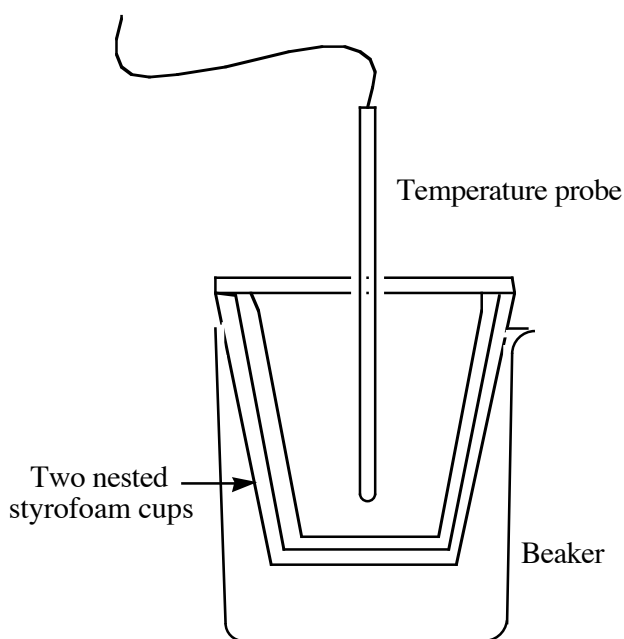


Figure 2. Construction of a calorimeter

the same time as your partner:

- Remove the cap from the cup that contains HCl solution.
- Remove the cap from the calorimeter. *Do **not** pull the tip of the probe out of the NaOH solution.*
- Add the HCl solution to the calorimeter all at once while stirring with the probe.
- Replace the cap with the probe onto the calorimeter (again, make sure the probe is in the solution but does not touch the bottom of the cup) and *swirl* the calorimeter.

Allow the computer to continue to collect data as you swirl the calorimeter until the temperature has reached its maximum and starts to decline as in Figure 1 (p. 4). You should collect data for about 5 minutes. When you have collected a sufficient amount of data, click on the **red button** to stop the data collection. Remove the temperature probe from the solution in the cup and rinse it thoroughly with water.

Important step! Saving your data:

- Save your data by pulling down the **File** menu and selecting **Save As...**
- In the dialog box that appears, the word **Documents** should be displayed in the drop down menu in the middle of the box. If it is not, scroll through the menu on the left, and choose Documents.
- Next to the words **Save as:**, type over the word “untitled” with the name of your file (example: CpCalLAO). You should include your initials in the name you choose.
- Click on **Save**.
- To find your file later, you will have to go to the **Documents** folder. It should have the suffix .cmbl at the end of the file name.

You can now adjust the parameters on the graph. To view just one of the plots (yours or your partner's), click and hold on the y-axis label. Select Temperature 1 from the pop-up menu. Click on the **AutoScale** button in the Toolbar which looks like this:



The computer will choose maximum and minimum values for the x - and y -axes such that the plot fills the graph completely. If you do not like the limits for the axes that the computer has chosen, it is possible to change them by simply clicking once on each of the numbers at the ends of the axes, typing in the desired limits and pressing return. It will be easier to determine the value for T_f later if the y -axis limits are whole numbers. Choose the maximum values to be slightly greater than the highest temperature or time recorded, and choose a temperature minimum that is slightly lower than the lowest temperature. The minimum time recorded should be 0 seconds.

Adjust other graph parameters using **Graph Options...** found under the **Options** menu. Be sure that a check mark appears in the box next to Connect Points, and type in an appropriate title for the graph in the box under Title. Your initials should appear in parentheses at the end of the title (so you can identify your printout). Click on **OK**.

To print the graph, pull down the **File** menu and choose **Printing Options...** Click in the box next to Print Footer to make sure a check mark appears, then type in your name (and a comment about the plot, if desired). Now pull down the **File** menu and choose **Print Graph...** (*not Print...*). Click on **OK**. In the next dialog box, click on **Print**. The printer is located in the support room. Your name should appear at the bottom of the page.

Repeat the procedure for adjusting and printing the second plot, this time selecting Temperature 2 from the y-axis pop-up menu. Be sure to change the title, this time putting the second person's initials at the end.

It is possible to print the table of time and temperature readings that the computer collected, however, it is *not* necessary to do so for this experiment. If for some reason you would like a printout of the data, choose **Print Data Table...** from the **File** menu.

Measuring $\Delta H^\circ_{rxn}(2)$

Obtain about 120 mL of 2 M HCl in a clean, dry flask. Rinse out the calorimeter cup and dry it thoroughly with a paper towel. Clean your graduated cylinder and pre-rinse it with the solution to be measured. Carefully measure 50.0 mL of the 2 M HCl and transfer it into the calorimeter. Replace the cap and temperature probe, making sure the tip is submerged in the liquid.

Measure 30 mm of magnesium ribbon (approximately 0.056 g), and scour it lightly with sandpaper to remove surface oxide. Wind the ribbon into a loose coil so that it can fall completely into the calorimeter cup. Weigh the ribbon accurately and record the mass. Be sure to weigh the ribbon *after* you have scoured it.

Pull down the **Experiment** menu and select **Store Latest Run**. Under the **Data** menu, choose **Hide Data Set** followed by **Run 1**. You can now collect a new data set. Click once on the number at the end of the x-axis, type in 500 and press return. Click once on the number at the bottom of the y-axis, type 0 and return, then click on the upper limit, type 40 and return. Select **All of the Above** from the y-axis pop-up menu. Click on the **green button** and allow the computer to collect temperature readings for 10-12 seconds on the 2 M HCl solution in the calorimeter. Remove the cap, and with the probe still in the solution, add the magnesium ribbon with stirring. Replace the cap and *swirl* the calorimeter as the computer continues to collect data for about 5 minutes or so. Remove the temperature probe from the solution in the cup and rinse it thoroughly with water.

Follow the procedures given above to **save, adjust, re-title** and **print** your plot.

Measuring $\Delta H^\circ_{rxn}(3)$

In a small, clean, dry sample vial place 0.2 to 0.25 grams of granular magnesium oxide. Record the total mass of the bottle and its contents.

Again, rinse and dry the calorimeter cup, add 50.0 mL of 2 M HCl and replace the cap and temperature probe.

Pull down the **Experiment** menu and select **Store Latest Run**. Under the **Data** menu, choose **Hide Data Set** followed by **Run 2**. Change the limits on the x-axis to 0 and 500, and change the limits on the y-axis to 0 and 40. Make sure both Temperatures 1 and 2 are displayed on the y-axis, then click on the **green button** and allow the computer to collect temperature readings for 10-12 seconds on the 2 M HCl solution in the calorimeter. Remove the cap, and with the probe still in the solution, add the MgO solid to the HCl all at once. *Be careful to avoid letting the solid adhere to the walls of the cup.* Replace the cap and swirl the calorimeter as the computer continues to collect data for about 5 minutes or so. Remove the temperature probe from the solution in the cup and rinse it thoroughly with water.

Follow the procedures given above to **save, adjust, re-title** and **print** your plot.

Re-weigh the empty sample vial to obtain the weight of MgO that was added.

Rinse the temperature probe and the cups with water before leaving the lab. When you are ready to leave, pull down the **Logger Pro** menu and choose **Quit Logger Pro**. Pull down the Apple menu and select **Logout**.

You should leave the laboratory with printouts of the three plots that you produced today. However, you should also store a copy of your data file(s) using either www.bc.edu/myfiles or by e-mailing the file(s) to yourself (see Storing and Retrieving Your Lab Files on page 14 of the notebook/manual). If you need to adjust any of your plots after your lab period is over, you can use the computers in the chemistry teaching labs when the rooms are not occupied (MWF 9:00-12:45 or TuTh 12:00-1:15).

A note on displaying multiple data sets:

If you would like to view one of your earlier plots, simply pull down the **Data** menu and choose **Show Data Set** followed by the **Run #** that you wish to display. It is possible to have several sets of data displayed simultaneously. The Runs are numbered sequentially in the order in which they were acquired, with the most recent Run being called **Latest**. Simply use the **Hide Data Set** and **Show Data Set** commands to view the desired plot or plots. You may have to re-adjust the plot display parameters (such as axes scales, etc.). Use the y-axis label to display one or both temperature plots, as desired. Options also appear under the **Data** menu to delete one or more sets of data.

If at any point you have trouble displaying or printing the proper plot or axis limit, try the following:

- Click on the y-axis label and select **More....**
- In the window that appears, scroll through the list, clicking on the boxes until the box(es) corresponding only to the data that you wish to display has/have a check mark. Note: You do not want a check mark to appear next to Time anywhere in this list.

Calculations

1. Determine the T_f ($\pm 0.1^\circ\text{C}$) from your plot for *Measuring* (C_p, cal) by the extrapolation method shown in Figure 1. Calculate the heat capacity, (C_p, cal), of the calorimeter using **Eq. 9**. This value is usually small (less than 20 J/Kelvin or 0.020 kJ/Kelvin). It is such a small value that it is of the same order of magnitude as the experimental error; consequently, the calculation could yield a small negative number. Should this be the case, simply assign (C_p, cal) the value of 0.0 kJ/Kelvin.
2. Using the plot from *Measuring* $\Delta H^\circ_{\text{rxn}}(2)$, determine T_f , and calculate $\Delta H^\circ_{\text{rxn}}(2)$ using **Eq. 10**.
3. Treat the data obtained for $\Delta H^\circ_{\text{rxn}}(3)$ in a similar manner by determining T_f and calculating $\Delta H^\circ_{\text{rxn}}(3)$ using **Eq. 10**.
4. Substitute the values you obtained for $\Delta H^\circ_{\text{rxn}}(2)$ and $\Delta H^\circ_{\text{rxn}}(3)$, along with the given value for $\Delta H^\circ_{\text{rxn}}(4)$, into **Eq. 4** to calculate the heat of formation of magnesium oxide, $\Delta H^\circ_{\text{rxn}}(1) = \Delta H^\circ_f(\text{MgO})$.

Questions

1. Comment on the effectiveness of your calorimeter. What evidence, if any, did you see that indicates heat was lost from the calorimeter to the surroundings during the course of the experiment?
2. The flashbulb that Mark is attempting to modify contains 0.62 g of magnesium metal.
 - a) Based on the heat of formation of magnesium oxide that you obtained, how many kJ of energy are released by the flashbulb contents?
 - b) Assume the energy released by the reaction is completely absorbed by the plastic. If 10.4 g of plastic material having a specific heat of $8.7 \text{ J/g}^\circ\text{C}$ has been used to manufacture the bulb, what will be the temperature of the plastic after the flashbulb goes off? Assume the bulb is at room temperature, 20°C , before ignition.
3. A student rinsed the calorimeter cup with water but did not dry it before determining $\Delta H^\circ_{\text{rxn}}(3)$; consequently, a significant amount of water was present in the cup before the hydrochloric acid was poured in. How would this error affect the final result for the heat of formation of magnesium oxide?
4. List the important sources of error in this experiment and explain what effect each would have on the results. Discuss in particular any errors which you may have made.