

Enthalpy of Formation of Magnesium Oxide

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BACKGROUND

In this laboratory, we will introduce one of the most often used techniques in thermochemistry, calorimetry. Although we often think of calorimetry in terms of finding the number of calories in a certain amount of food, calorimetry is valuable to the chemist in measuring basic thermodynamic data. Along with learning calorimetry techniques, you will use the data you collect, other reaction enthalpies, and Hess's Law, to determine ΔH_f° for MgO(s).

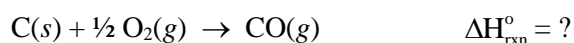
Read and/or review the thermochemistry chapter in your textbook.

Enthalpy and Hess's Law

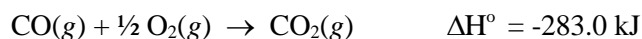
The enthalpy change, $\Delta H_{\text{rxn}}^\circ$, of a chemical reaction is called the enthalpy of reaction or the heat of reaction and represents the amount of heat gained or lost by the reaction system as the reaction proceeds from reactants to products. The standard (molar) enthalpy of formation, ΔH_f° , is defined as the $\Delta H_{\text{rxn}}^\circ$ when one mole of a compound is formed from its elements in their reference form and in their standard states.

Enthalpy is a state function; the enthalpy change of a reaction is independent of its path and depends only on the initial and final states of the reactants and products. This principle, applied to enthalpy, is known as Hess's Law. *Hess's Law states that the enthalpy change of a reaction is the same whether it occurs in one step or in many steps.*

For example, the enthalpy change for the reaction between carbon and oxygen to form carbon monoxide:

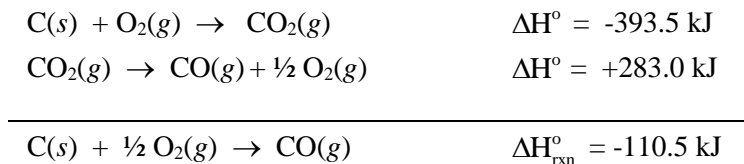


cannot be directly measured since carbon dioxide is also a product of this reaction (there is no way to run this reaction to ONLY give CO). However, to obtain the desired heat of reaction, we can react carbon and carbon monoxide in large excesses of oxygen to form carbon dioxide and measure the enthalpies of these reactions:



According to Hess's Law, we can combine the above two reactions in a manner that will give the desired reaction. Note that if we reverse the second reaction and add it to the first reaction, we will obtain the desired reaction (see below) when the two reactions are then added together. Since we reversed the second reaction, the sign on ΔH° must also be changed.

Adding the resultant reactions yields the desired reaction and adding the resultant ΔH 's yields the desired $\Delta H_{\text{rxn}}^{\circ}$. The same chemical species on opposite sides of the arrow can be canceled. Note how the two reactions lead to the desired reaction and how the $\Delta H_{\text{rxn}}^{\circ}$ is obtained from the individual ΔH° 's for the two reactions.

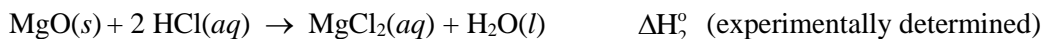


Heat of Reaction

In this laboratory, you will determine ΔH_f° of $\text{MgO}(s)$, which corresponds to $\Delta H_{\text{rxn}}^{\circ}$ for the following reaction:



This reaction is extremely exothermic and therefore very difficult to accurately measure calorimetrically. However, we can apply Hess's law to find the heat of formation for MgO by combining a series of reactions that are much safer and more suitable for a calorimetry experiment. For example, these three reactions may be used:



Using the techniques presented in the CO example above, you can combine these equations to find $\Delta H_{\text{rxn}}^{\circ}$ for formation of one mole of $\text{MgO}(s)$:



Correctly figuring out how to add the equations together to get the reaction shouldn't pose a problem; however, before we can obtain the value of $\Delta H_{\text{rxn}}^{\circ}$, we need to **experimentally** determine the values of ΔH_1° and ΔH_2° values using calorimetry.

Calorimetry

Almost any type of container can be used as a calorimeter, but to collect good data we must account for all heat absorbed or evolved by the chemical process. Therefore, we want a container that traps the heat in a location where it can be measured rather than spreading the heat around. In this experiment you will use Styrofoam cups, since they are excellent at trapping heat (an insulator).

The important thing to remember when conducting thermochemistry experiments is you *must account for all heat gained or lost* during a reaction. For example, if an exothermic reaction occurs in a well-insulated calorimeter, the heat can be transferred two places: (1) the reaction mixture, which can be measured as a temperature rise, and (2) the walls of the calorimeter. In this experiment we will assume the cup is a perfect insulator and as such, no heat is transferred between the calorimeter and the surroundings. Therefore, the following statement and equation applies:

heat absorbed/released by rxn =

heat absorbed/released by calorimeter + heat absorbed/released by the reaction mixture

$$-q_{\text{rxn}} = q_{\text{cal}} + q_{\text{liq}}$$

(where q is heat)

NOTE: This equation DOES NOT necessarily mean that the reaction in the calorimeter is exothermic. The (-) sign indicates that the heat lost by the chemical reaction must be exactly equal to the total heat gained and vice-versa.

Now let's examine each of the terms in the equation.

Heat from Reaction (q_{rxn}): In **this** experiment, q_{rxn} is equivalent to $n \Delta H_{\text{rxn}}^{\circ}$ where n is the number of moles of the limiting reactant that are used in the experiment and $\Delta H_{\text{rxn}}^{\circ}$ is the enthalpy change of the reaction.

Heat Absorbed by the Calorimeter (q_{cal}): For our calorimeter, the heat simply changes the temperature of the calorimeter. We can replace q_{cal} by $C_{\text{cal}} \Delta T$, where C_{cal} is the heat capacity of the calorimeter (calorimeter constant) and ΔT is the temperature change. Note the heat capacity is the amount of heat required to raise the temperature of a substance by 1°C . The units of heat capacity are usually $\text{J}/^{\circ}\text{C}$. Thus we need the heat capacity of the calorimeter, C_{cal} , which is specific for each calorimeter. You will find C_{cal} for your calorimeter by performing a reaction for which $\Delta H_{\text{rxn}}^{\circ}$ is known. It should be noted C_{cal} shouldn't be negative, unless it is very warm in the room.

Heat Absorbed by Reaction Mixture (q_{liq}): This term is equal to $(m)(c)(\Delta T)$. The mass of the solution is represented by m . Specific heat is represented by c and is the heat capacity per gram. Specific heats allow the heat absorbing capabilities of different substances to be compared.

The specific heat for water is 4.184 J/(g°C), however when solutes are dissolved in it the specific heat changes. For the NaOH and HCl reaction, the specific heat of the solution, c , is 4.025 J/(g°C) while for the Mg and MgO reactions with HCl, c is equal to 3.862 J/(g°C). Using these terms we obtain:

$$-n \Delta H_{\text{rxn}}^{\circ} = C_{\text{cal}}\Delta T + (m)(c)(\Delta T)$$

where:

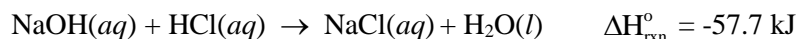
- n = number of moles of the limiting reactant that are used in this experiment
- $\Delta H_{\text{rxn}}^{\circ}$ = enthalpy change (heat) of the reaction
- C_{cal} = calorimeter constant (specific for your calorimeter)
- ΔT = temperature change resulting from the reaction
- m = mass of the solution
- c = specific heat of the solution

Note we used $q = (m)(c)(\Delta T)$ for the liquid in the calorimeter because we know its exact composition. For the calorimeter itself, however, a heat capacity, C_{cal} , was used because the exact calorimeter composition, shape, and size may vary from calorimeter to calorimeter.

The Calorimeter Constant

Every calorimeter is different, not only due to its composition, but also its size and shape. These factors determine the calorimeter's ability to absorb heat. As a result, every calorimeter will have a different C_{cal} . Therefore we must determine the unique value of C_{cal} before we can use it in the calorimetry equation and find the values of ΔH_1° and ΔH_2° .

Now let's apply this concept to your experiment. First the calorimeter must be "calibrated" to find C_{cal} . This calibration is accomplished by producing a known quantity of heat from a reaction and measuring ΔT . The following reaction will be used to determine C_{cal} .



Since $\Delta H_{\text{rxn}}^{\circ}$, the specific heat, the volumes and molarities of the NaOH and HCl solutions, and ΔT (experimentally determined) are known, the only unknown in the equation is C_{cal} , which you can now calculate. Once the value of C_{cal} is known, you can use it in the calorimetry equation to determine your values for ΔH_1° and ΔH_2° .

Measuring the Temperature Change

You will need to find ΔT , the temperature change for the reaction mixture and the calorimeter. However, you will not be able to simply measure the maximum temperature because the temperature may never actually reach the theoretical maximum. This irregular behavior is due to the calorimeter's inability to absorb heat as quickly as the reaction is producing it. To find ΔT at time=0, extrapolate to the maximum temperature for each of your experiments.

You will use the temperature probe to measure the temperature as a function of time. You will also be using Logger Pro on the computer to generate the graph and analyze your data. Your graph should look like the one shown in **Figure 1**. Notice the temperature vs. time plot is irregular until it stabilizes on a slowly decreasing temperature line. Ideally, you want the maximum temperature that would be produced if the reaction happened instantaneously at the time of mixing (time = 0), not some time later when the reaction mixture and the calorimeter have cooled slightly due to leaks in our "adiabatic" system. The proper method to obtain ΔT is depicted in **Figure 1**.

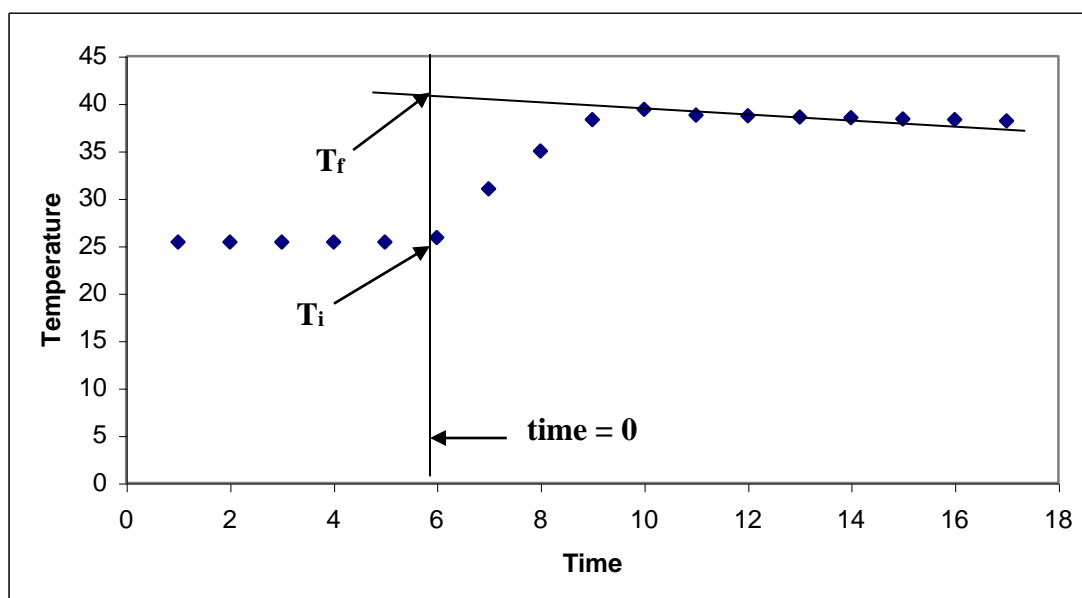


Figure 1. Temperature Extrapolation.

The rate of cooling is used to extrapolate back to what the maximum temperature should have been. This is the intersection of the extrapolation line with the y-axis (time = 0, or when the reactants were originally mixed). Finally: $\Delta T = T_f - T_i$.

EXPERIMENTAL PROCEDURE

Getting Started

1. **Obtain stock solutions:** Use two clean beakers to get stock solutions of 1 M HCl and 1 M NaOH from the appropriate shelf. Record the exact molarity of HCl and NaOH as labeled on the containers. WARNING! HCl is corrosive, clean up spills immediately.
2. **Weigh Mg solid:** The top-loading balances are delicate instruments. Do not spill any chemicals on the balance. If you do spill chemicals, clean them up immediately. To weigh a chemical, place a clean, small piece of paper on the top of the balance. Press the TARE button to ZERO the balance. Add the solid slowly onto the paper until the proper mass has been weighed. Weigh 0.20 g to 0.30 g of the Mg turnings to the nearest milligram on the top-loading balance. Record the exact mass of Mg used on your lab data sheet.
3. **Weigh the MgO solid:** Following the directions in step 2 above weigh 0.50 g to 0.60 g of MgO solid. Record the exact mass of MgO used on your data sheet.

A. Determining the Calorimeter Constant

1. Plug the temperature probe into the Go!Link.
2. Plug the Go!Link into the USB port of the computer.
3. Start up Logger Pro on the computer by double clicking on the Logger Pro icon
4. Choose: Experiment ; Data Collection. In the collection tab choose: Time Based. The Sample at Time Zero box needs to be checked and the Repeat box should not be checked. Enter 1500 s for Duration. You can always stop collecting data, but you can't add in more time once you have started. Enter 1 sample/s for Sampling Rate. Done.
5. Each of the three experiments will generate a graph of temperature (y-axis) vs. time (x-axis). Title the graph and check that the axes are labeled appropriately. You will need to be careful to keep track of which experiment is being run. Double click on the data table title on the left of the screen. For this part of the experiment replace "Data Set" or "Latest" with HCl/NaOH.
6. Using a 50-mL graduated cylinder, measure 50 mL of the 1 M HCl solution. Pour the HCl into the Styrofoam calorimeter. Insert the temperature probe into the calorimeter cup. The temperature probe's tip must be in the HCl solution but not touching the sides or bottom of the cup.
7. Rinse the graduated cylinder successively with tap water, deionized water, and 5.0 mL of 1 M NaOH solution. Measure 50 mL of the 1 M NaOH solution into the graduated cylinder.
8. With the temperature probe in the HCl solution and the plastic cover on the cup, begin measuring and recording the temperature of the HCl solution for at least one minute by touching the data collection button (white triangle in green rectangle) on the upper portion of the computer screen. This will establish T_i . Since the NaOH in the graduated cylinder has been sitting in the room for the same length of time as the HCl, we will assume its T_i is the same.

9. Gently lift the lid off of the calorimeter and pour in the NaOH. **Do NOT stop data collection at this time. You will lose important data!** Immediately replace the lid and gently swirl the calorimeter while taking data. Observe the temperature until a maximum is reached, then **continue taking data for one or two more minutes to obtain plenty of data points for the extrapolation of T_f** . Touch the stop data collection button (white square in red rectangle) on the upper portion of the computer screen when you want to stop collecting data.
10. You now have the data you need to calculate the calorimeter constant, C_{cal} . Remember, the total mass of the solution is the sum of masses of the HCl and NaOH solutions. This mass can be determined by subtracting the weight of the calorimeter from the total weight of calorimeter/solution assembly.
11. Use the table and the cursor to determine T_i and record the value in the report sheet. Notice the x and y values for the cursor crosshair are given on the lower left of the screen.
12. Drag the cursor over the linear portion of the graph that occurs after the solutions have been mixed (see Figure 1). Choose: Analyze; Linear Fit. A line should appear as well as a box containing the equation for the line. If necessary, the box can be dragged so that it does not cover up the graph.
13. Move the cursor crosshair along the line until the x coordinate (lower left of screen) is the time of mixing (time = 0 ; Figure 1). The y value at this point is T_f . Record the value in the report sheet.
14. Choose: Experiment ; Store Latest Run.

Although the calorimeter contents will differ in the three parts of the experiment, the data collection and analysis procedures you use will be the same in all three parts of the experiment.

B. Enthalpy (Heat) of Reaction of Mg and HCl

1. Double click on the data table title on the left of the screen. For this part of the experiment replace "Data Set" or "Latest" with Mg/HCl.
2. Clean and dry your calorimeter. Be sure to the Data Collection information is still correct (Part A; Step 4). Using a graduated cylinder, add 100 mL of 1 M HCl solution. As before, measure and record the temperature of this solution for at least one minute to establish T_i .
3. Gently lift the lid off the calorimeter and put in the Mg turnings. Immediately replace the lid and gently swirl the calorimeter while taking data. Collect the temperature data until a maximum is reached; then continue taking data for one or two more minutes to obtain plenty of data points for the extrapolation of T_f .
4. You now have the data you need to determine ΔH_{rxn}° for the Mg/HCl reaction (ΔH_f°). Use the graph to obtain T_i and T_f as you did previously. Record these values on the report sheet. Remember, the total mass of the solution is the sum of the masses of the HCl solution and the Mg and can be obtained by weighing.
5. Choose: Experiment ; Store Latest Run.

C. Enthalpy (Heat) of Reaction of MgO and HCl

1. Double click on the data table title on the left of the screen. For this part of the experiment replace “Data Set” or “Latest” with MgO/HCl.
2. Clean and dry your calorimeter. Be sure to the Data Collection information is still correct (Part A; Step 4). Using a graduated cylinder, add 100 mL of 1 M HCl solution. As before, measure and record the temperature of this solution for at least one minute to establish T_i .
3. Gently lift the lid off the calorimeter and pour in the MgO solid. Immediately replace the lid and gently swirl the calorimeter while taking data. Collect the temperature data until a maximum is reached; then continue taking data for one or two more minutes to obtain plenty of data points for the extrapolation of T_f .
4. You now have the data you need to determine $\Delta H_{\text{rxn}}^\circ$ for the MgO/HCl reaction (ΔH_2°). Use the graph to obtain T_i and T_f as you did previously. Record these values on the report sheet. Remember the total mass of the solution is the sum of the masses of the HCl solution and the MgO and can be obtained by weighing.

The curves for all three experiments should be visible on the same graph.

- a. Choose: Analyze ; Autoscale ; Autoscale.
- b. If necessary, click on the graph to remove the linear analysis shaded areas and move the analysis boxes around to visually clean up the graph.

Each lab partner’s report must have a Logger Pro generated printout of a single graph containing the plots and linear analysis for all three runs of the experiment.

Once you are ready to print out the graph, Click: File ; Print. Change the “orientation” to landscape under properties. Be sure that the names of all lab partners are entered in the “Name” section and that the date box is checked.

When you are done, return your bin to Lab Services

SAFETY NOTES

1. Avoid skin contact with the hydrochloric acid and sodium hydroxide solutions.
2. Swirl (do not shake) the calorimeters gently to avoid spilling the contents.
3. If you spill any chemicals on the lab benches, clean it up IMMEDIATELY with a damp sponge.