
Calorimetry—Measuring Heat of Formation

Part A: Introduction to Calorimetry

The goal in Part A of this experiment is to determine the heat capacity of a calorimeter. Once this value is known, your calorimeter can be used in Part B of the experiment to determine the heat of formation of magnesium oxide.

All chemical and physical processes are accompanied by heat changes. The measurement of heat changes in physical and chemical processes is called **calorimetry**. Heat changes may be measured by carrying out the process in an insulated vessel where the heat exchange between the system being observed and its surroundings is minimized. This type of system is called a **calorimeter**. The insulated vessel contains a temperature measuring device and a magnetic stirring bar.

The energy associated with the temperature changes in a substance can be expressed two ways. **Specific heat**, C_{sp} , is defined as the amount of energy in joules required to raise the temperature of one gram of that substance by one degree Celsius:

$$\text{specific heat} \quad C_{\text{sp}} = \frac{q}{m(\Delta T_{\text{°C}})} \quad (\text{EQ 9.1})$$

Where q is the quantity of heat, $\Delta T_{\text{°C}}$ is the temperature change in degrees Celsius, and m is the mass of the substance in grams.

The term **heat capacity**, C_s , is used if a particular object, such as a particular calorimeter, is being used repeatedly. Heat capacity is defined as the amount of energy required to raise the temperature of that object one degree Celsius:

$$\text{heat capacity} \quad C_s = \frac{q}{\Delta T_{\text{°C}}} \quad (\text{EQ 9.2})$$

The heat capacity of your calorimeter will be determined in this part of the experiment so that you can use your calorimeter in the following experiment, “Determination of Enthalpy of Formation”. The following example illustrates this procedure to determine the heat capacity of a calorimeter.

EXAMPLE 9.1

A 50.0 mL sample of warm tap water at 50.2 °C is mixed with 62.0 mL of cooler tap water in the calorimeter, which is at 21.4 °C. The final temperature of the system after mixing is 33.7 °C. The density of the water is 1.00 g/mL, and the specific heat of the tap water is 4.184 J/g°C. Determine the heat capacity, C_p , of the calorimeter system.

If there was no heat transfer from the hot water to the calorimeter, all of the heat would be conserved in the liquid. Therefore, all of the heat lost by the warm water would equal the heat gained by the cool water. This, however, is not what is observed because some of the heat from the warm water is used to raise the temperature of the calorimeter system.

The change in temperature is simply

$$\Delta T = T_{\text{final}} - T_{\text{initial}} \quad (\text{EQ 9.3})$$

As mentioned, the heat, q , lost by the warm water is gained by both the cool water and the calorimeter, hence the negative sign represents a heat loss and a positive sign is a heat gain

$$-q_{\text{warm}} = q_{\text{cool}} + q_{\text{calorimeter}} \quad (\text{EQ 9.4})$$

By substituting the expressions for specific heat (equation 9.1) and heat capacity (equation 9.2), equation 9.4 can be expressed as

$$-(\Delta T_{\text{warm}})(m_{\text{warm}})(C_{\text{sp}}) = [(\Delta T_{\text{cool}})(m_{\text{cool}})(C_{\text{sp}})] + C_p(\Delta T_{\text{cool}}) \quad (\text{EQ 9.5})$$

Using the data from this example gives:

$$\Delta T_{\text{cool}} = 33.7 \text{ °C} - 21.4 \text{ °C} = 12.3 \text{ °C} \quad (\text{EQ 9.6})$$

$$\Delta T_{\text{warm}} = 33.7 \text{ °C} - 50.2 \text{ °C} = -16.5 \text{ °C} \quad (\text{EQ 9.7})$$

$$-[-16.5 \text{ °C})(50.0 \text{ g})\left(4.184 \left(\frac{\text{J}}{\text{g} \cdot \text{°C}}\right)\right)] = [(12.3 \text{ °C})(62.0 \text{ g})\left(4.184 \frac{\text{J}}{\text{g} \cdot \text{°C}}\right)] + C_p(12.3 \text{ °C}) \quad (\text{EQ 9.8})$$

Now the heat capacity of our calorimeter can be calculated:

$$3452 \text{ J} = 3191 \text{ J} + C_p(12.3 \text{ °C})$$

$$C_p = 21.2 \frac{\text{J}}{\text{°C}} \quad (\text{EQ 9.9})$$

Procedure: Part A

The following operations are typical for determining the heat capacity of a calorimeter. The temperature of a known mass of water is recorded; the temperature should be approximately room temperature. Another sample of water, whose mass and temperature is measured, is added to the first water sample. The second water sample should be approximately 50 °C higher than the original sample. By carefully monitoring the temperature changes upon mixing the hot and cool water samples, we can determine how much of the heat was transferred to the cool water and how much of the heat was transferred to the calorimeter; refer to equation Equation 9.4.

We will use a temperature probe called a thermistor to measure the temperature changes during this experiment. Your instructor will assist you in setting up and operating the thermistor. After you have collected your data with the thermistor, we will use it to help analyze the data.

Obtain a calorimeter, a magnetic stir bar, a stirring plate and a thermistor. The temperature throughout the experiment as a function of time will be tabulated during the experiment. Measure all masses to the nearest 0.1 g and all temperatures to the nearest 0.1°C.

1. While one partner is performing Step 2 the other should be preparing the thermistor apparatus as directed by your instructor.
2. Wipe out any water or solid debris from the inside of the calorimeter. Measure 50.0 mL of tap water into a graduated cylinder and pour this into a dry, tared calorimeter cup. Weigh the contents of the calorimeter after the water has been added to obtain the mass of water actually transferred to the cup. Add a stir bar and place the cover on the calorimeter then insert the thermistor. Click **Start** on the apparatus screen. Turn on the stirring plate and allow the system to reach a constant temperature.
3. Measure approximately 50 mL of tap water and pour it into a clean 250 mL beaker. Weigh the beaker and its water and record this mass. Gently heat the water to approximately 50-55 °C. Remove from heat and place your thermometer in the beaker and record the temperature of the hot water. It is essential that you obtain the actual temperature of the hot water just before you add the hot water to the calorimeter.
4. Add the hot water without splashing to the calorimeter. Stir gently to prevent splashing.
5. The thermistor apparatus will commence temperature and time measurements automatically. Observe the temperature and time measurements until a maximum temperature has been reached. Continue recording temperature and time readings until the temperature decreases by 2 °C below the maximum temperature or after 10 minutes have elapsed since the maximum temperature was observed.
6. While you are waiting for the maximum temperature to be reached, weigh the empty (wet) beaker to obtain the actual mass of hot water that was added to the calorimeter. Be sure to use the same balance each time that you weigh a particular piece of glassware. **Compare this mass to the mass of the water in the calorimeter.**
7. Weigh the water in the calorimeter.
8. Repeat steps 2-6 at least two more times and calculate the average heat capacity and the standard deviation for your calorimeter.
9. Consult with your instructor to determine if you have good precision for your calorimeter heat capacity.

Part B: Introduction to Measuring the Heat of Formation of Magnesium Oxide

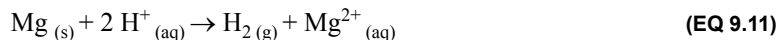
In Part B, the heat of formation of magnesium oxide will be determined. The heat capacity of your calorimeter that you calculated from Part A will be used in this part of the experiment.

The **enthalpy of formation**, ΔH_f , of a substance is the heat absorbed when one mole of it is formed from the elements in their most stable forms at constant pressure. In some cases, elements may be combined in a calorimeter to form the desired product and thus the ΔH_f may be measured directly. In other cases, the elements may not combine completely to form the desired product, or there may be other difficulties with the direct determination. In these cases, ΔH_f may be obtained indirectly by combining results from reactions that may be successfully measured:

$$\Delta H_{\text{rxn}} = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants} \quad (\text{EQ 9.10})$$

A direct determination of the ΔH_f for Mg^{2+} ion and an indirect determination for MgO will serve to illustrate the possibilities.

Consider the reaction of magnesium and HCl:



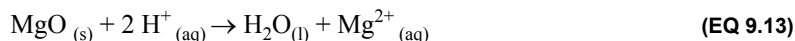
Since the ΔH_f for H^+ and H_2 are zero by definition under these conditions, the ΔH for this reaction is the ΔH_f for Mg^{2+} . The variations in temperature, pressure, and concentration occurring during this experiment will not cause significant errors. So, the ΔH_{rxn} would be the sum of the heat from the reaction of Mg and HCl and the heat from the calorimeter:

$$\Delta H_{\text{rxn}} = \frac{-(q_{\text{solution}} + q_{\text{calorimeter}})}{n} \quad (\text{EQ 9.12})$$

Using Equation 9.1, Equation 9.2, and Equation 9.12 allows one to calculate ΔH_{rxn} .

For MgO , the elements will combine directly, but the reaction is not easily accomplished and measured in a calorimeter, so an indirect approach will be followed.

Consider the reaction of MgO with 1 M HCl:



The ΔH for this reaction will be measured in your calorimeter. When this information is combined with known values for ΔH_f of Mg^{2+} and $\text{H}_2\text{O}_{(l)}$, the desired ΔH_f value for MgO can be determined.

Calorimetry

If a reaction occurs in a calorimeter, the heat released during the reaction will be detected as an increase in temperature, and the amount of heat will be the total heat capacity of the calorimeter and its contents multiplied by the temperature change. The temperature change should be obtained by taking data and graphing the temperature as a function of time from before the reaction until well after the reaction is complete. A thermistor apparatus will be used to capture the temperature changes during this process; the set-up and operations will be similar to that used in previously.

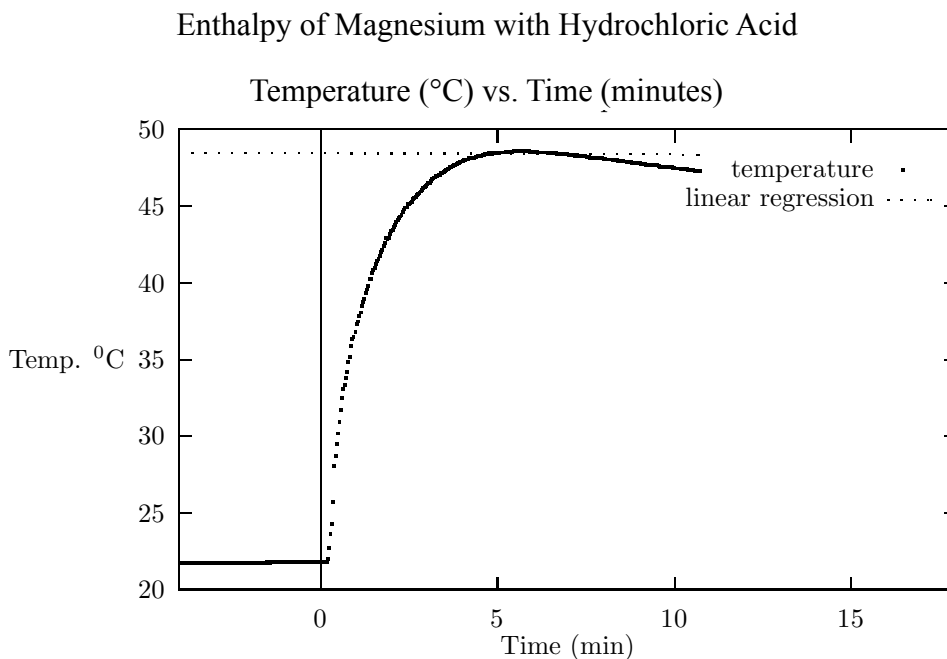
The calorimeter has a heat capacity of approximately 18 J/°C. If your calculated heat capacity from Experiment 9 is close to this value, then use your determined value for heat capacity. If you calculated a heat capacity much different than this value, use 18 J/°C for your heat capacity. The heat capacities of Mg and MgO are negligibly small and can be ignored. The 0.8 M HCl (the average value during reaction) has a specific heat of 4.07 J g⁻¹°C⁻¹, and a density of 1.01 g/mL.

Procedure: Part B

Reaction of Mg with HCl

1. Calibrate the thermistor as you did in “Heat Capacity of the Calorimeter.”

2. Weigh approximately 0.5 g of Mg to the maximum precision; record this mass in your notebook.
3. Add 100.0 mL of 1.0 M HCl to the calorimeter and begin stirring. Click the `Start` button to begin data collection. At this point you want to see the temperature stabilize and produce a nearly straight line on the graph of the thermistor apparatus screen. This may take 2-5 minutes.
4. Add the Mg and continue to stir. It is important that you add the metal into the solution. Any material that sticks to the sides of the calorimeter will introduce error into your results. You will notice the temperature increase on the display as the Mg reacts with the acid.
5. After the temperature remains constant or begins to drop slowly (5-10 minutes), click `Stop` and then `Save Data`.
6. Name your file with a **unique name** and save it to a flash drive. You want to obtain a graph in which the final temperature has been obtained by extrapolation of the first-order line-fit (see Figure 9.1 on page 75).

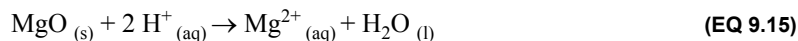
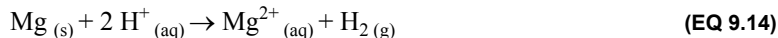
FIGURE 9.1

Reaction of MgO with HCl

Weigh out approximately 0.8 g of MgO. Clean out the calorimeter from the previous reaction and be sure to use a new aliquot of HCl for this reaction. Then repeat the procedure given above for the first reaction of Mg and HCl. Obtain a graph with the final temperature calculated from the curve-fit function as before.

Calculations and Data Treatment

1. By definition ΔH_f° for H^+ , O_2 and H_2 are zero. Therefore, the ΔH for reaction 9.14 is equal to the ΔH_f for Mg^{2+} . The ΔH for reaction 9.17 can now be determined using the data from reactions 9.14-9.16. ΔH for reaction 9.16 can be found in your text.



2. Make graphs and determine the corrected temperatures for each run. Be sure to completely and correctly label all graphs.
3. Calculate ΔH for each reaction using the amounts of reagents that you measured for your reactions.
4. Calculate ΔH per mole of Mg and MgO for each trial.
5. Calculate the percent error for each of your values.
6. Tabulate your values for ΔH_f for Mg^{2+} and MgO along with the literature values for each and their percentage errors.