

Experiment 12A

FV 2/13/09

CALORIMETRY: THE ENTHALPY OF FORMATION OF MgO

MATERIALS: 12 oz. Styrofoam cup with lid, thermometer, 100 mL graduated cylinder, weighing boat, 1.0 M HCl, 1.0 M NaOH, magnesium, magnesium oxide, copper wire, stir motor, stir bar.

PURPOSE: The purpose of this experiment is to determine the enthalpy of formation of magnesium oxide, *i.e.*, ΔH_f for the reaction:



LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Construct and use a calorimeter.
2. Determine the heat capacity of a calorimeter.
3. Calculate the enthalpy of a reaction from calorimetry data.
4. Apply Hess's Law to calculate the enthalpy change associated with a reaction.
5. Use a spreadsheet program for data manipulation, graphing, and regression analysis.

DISCUSSION:

Elemental magnesium is one of the principal components of flares used to illuminate nighttime activities, or to aid in signaling one's location to aircraft and ships. Your instructor may ignite a strip of magnesium ribbon to demonstrate the combustion of magnesium in air. It will be evident that a great deal of light energy is released from this reaction. A direct method for measuring the heat produced by this reaction would be extremely difficult, especially if it were to be carried out in pure oxygen as required for a bomb calorimetry experiment. Thus, we shall resort to an indirect method in this experiment as discussed below.

Some chemical reactions (including the one above) are associated with the evolution of thermal energy and are called *exothermic* reactions. When there is an absorption of energy in a chemical reaction, the process is called *endothermic*. The magnitude of the energy change is determined by the particular reaction as well as the amount of product(s) formed. The thermal energy transferred in a balanced chemical reaction carried out at constant pressure is called the *enthalpy of reaction* (or heat of reaction) and is given the symbol ΔH_{rxn} . ΔH_{rxn} is often expressed in units of kJ/mole where mole refers to the amount of a reactant or a product involved in the reaction. In general, the reactant or product must be specified.

In this experiment, you will measure the enthalpy changes of several exothermic reactions utilizing a simple calorimeter. This calorimeter consists of an insulated vessel, a thermometer, and a lid (which is loose fitting to allow the pressure to remain constant). This constitutes an open system because the calorimeter is not truly isolated from its surroundings so matter and energy can be transferred between the system and the surroundings. A Styrofoam cup will be used as the insulated vessel in this experiment to help retain the heat. The energy given off by any reaction carried out in the calorimeter is absorbed by both the calorimeter and the solvent (water). This causes an increase in the temperature of the calorimeter and solvent that can be measured by a thermometer.

The heat, q , that is absorbed by the calorimeter and solvent is calculated from the equation:

$$q_{\text{calorimeter}} = C \cdot \Delta T \quad (1)$$

where C is the heat capacity of the calorimeter and solvent, and ΔT is the change in temperature of the water (the solvent) in the calorimeter. Heat capacity is defined as the amount of energy required to raise the temperature of an object by 1°C. In this experiment, the vessel and the amount of solvent remain constant, so C is a constant.

Enthalpy is an extensive quantity, so the amount of heat generated by the reaction is given by the expression:

$$q_{\text{reaction}} = n \cdot \Delta H \quad (2)$$

where n is the number of moles of a specific reactant or product and ΔH is the enthalpy change of the reaction in kJ/mol. Since the energy of the universe is conserved, the total energy change of the system (the reaction) and surroundings (calorimeter and solvent) is equal to zero. These relationships can be combined as shown in equation (3).

$$q_{\text{system}} + q_{\text{surroundings}} = q_{\text{reaction}} + q_{\text{calorimeter}} = n \cdot \Delta H + C \cdot \Delta T = 0 \quad (3)$$

This equation can be rearranged to determine either C or ΔH as shown in equations (4) and (5).

$$C = -n \cdot \Delta H / \Delta T \quad (4)$$

$$\Delta H = -C \cdot \Delta T / n \quad (5)$$

For exothermic reactions, $\Delta H < 0$ and $\Delta T > 0$.

A. Determination of the Heat Capacity of the Calorimeter and Solvent

Before measuring the enthalpy change of a reaction, it is necessary to first determine the heat capacity of the calorimeter being used. This is done by measuring the temperature change, ΔT , that occurs when a known reaction is carried out in the calorimeter. For this experiment, the reaction:



is performed to provide this calibration. Knowing the value of ΔH for this reaction and the number of moles (n) of product formed, the heat capacity (C) can be calculated using equation (4). With the value of C known, the calorimeter can be used to determine the ΔH for other reactions by carrying out the reaction in the same calorimeter, measuring ΔT and using equation (5).

The main experimental problem in calorimetry is obtaining an accurate value of ΔT . The initial temperature, T_i , of the reactants can be determined directly using a thermometer. However, it is difficult to obtain a precise value for the final temperature, T_f (the instantaneous temperature when the reactants are mixed together and react). This is an open system, so heat exchange will occur between the room and the contents of the calorimeter, unlike an isolated system such as a bomb calorimeter. An open system allows the reaction to proceed at constant pressure at the sacrifice of the loss of generated heat to the surroundings. This occurs both during the reaction and after its completion. The rate of heat exchange depends upon the insulating properties of the calorimeter, the rate of reaction, and the effectiveness of mixing the reactants. A correction for this heat exchange is made by an *extrapolation* process using a temperature vs. time curve (see Figure 1). First, a plot of the temperature readings as a function of time for the reaction is generated. By extrapolating only the linear portion of the curve (e.g., the points including and after the maximum temperature) back to zero time (the time when the reactants were mixed in the calorimeter), T_f is obtained. The T_f value determined in this manner will be the temperature that the calorimeter and the solvent would have reached, had the reaction occurred instantaneously and with no heat exchange to the room. This value should be used for the calculation of change in temperature, ΔT . Consult [Appendix O](#) for specific instructions for extrapolation using Microsoft Excel.

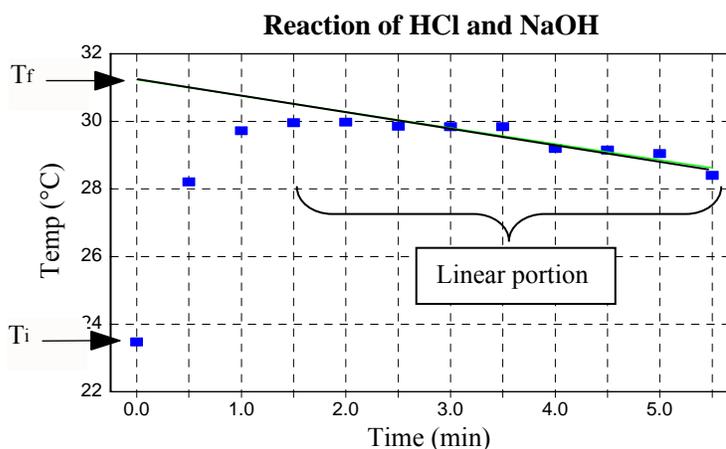
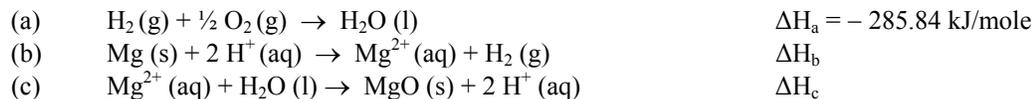


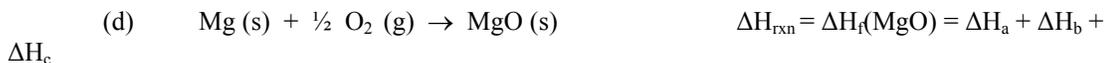
Figure 1. Determining temperature change from calorimetry data

B. Determination of the Enthalpy of Formation of MgO

The calibrated calorimeter will be used to determine the enthalpy of formation of magnesium oxide by application of Hess's law. Consider the following reactions:



By adding equations (a), (b), and (c) we obtain



which represents the formation of MgO(s) from the elements in their standard states. By definition, the enthalpy change associated with equation (d) is the enthalpy of formation of MgO(s) and is symbolized by $\Delta H_{\text{f}}(\text{MgO})$.

Reaction (a) represents the formation of liquid water from its constituent elements. The enthalpy change for this reaction, symbolized ΔH_{a} above, is the standard heat of formation of liquid water (or $\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O})$) and is a known quantity. ΔH_{b} and ΔH_{c} will be determined experimentally by measuring the temperature rise when known masses of magnesium metal and magnesium oxide, respectively, are added to hydrochloric acid. Reaction (c) as written is an endothermic reaction. Since it is easier to perform the reverse (exothermic) reaction, the data you collect will be of opposite sign to that needed for the Hess's law calculation for reaction (d). By application of Hess's law, the enthalpy of formation of magnesium oxide can be calculated by applying equation (d).

PROCEDURE:

Note: Handle the Styrofoam cups gently. They will be used by other lab sections!
If your instructor demonstrates the combustion of Magnesium reaction, do NOT look directly at the burning Mg.

A. Determination of the Heat Capacity of the Calorimeter

1. Rinse the graduated cylinder with water and then rinse with a small amount of 1.0 M NaOH (coat the sides by turning the graduated cylinder). Discard the rinses. With the graduated cylinder, place 50.0 mL of 1.0 M NaOH into the calorimeter. Measure the temperature (in °C) of the NaOH solution using the thermometer provided. Record this value in the Data Section. Rinse the thermometer end after obtaining the temperature.
2. Rinse the graduated cylinder with water and then rinse with 1.0 M HCl. Discard the rinses. Measure 50.0 mL of 1.0 M HCl into the graduated cylinder. Measure the temperature of the HCl solution in the graduated cylinder. Record this value in the Data Section. The initial temperature, T_i , will be defined as the average temperature of the two solutions. Record this average temperature in the Data Section.
3. Note the time (time = zero). Then add the HCl solution quickly to the NaOH solution in the calorimeter, swirl the solution then add the stir bar, and replace the lid on the calorimeter. Add the thermometer making sure it does not touch the stir bar. You can use a clamp to hold the thermometer at the proper height (in the solution but not touching the stir bar or sides of the calorimeter). Start the stir motor (on low) to gently mix the solution. Immediately begin collecting and recording temperature readings at 30-second intervals for 7 minutes. Keep the lid on the calorimeter.
4. When data collection is completed, rinse the calorimeter and the thermometer with distilled water and dry as completely as possible.

B. Determination of the Enthalpy of Formation of Magnesium Oxide

1. Reaction of Magnesium and Hydrochloric Acid

- a. Using a clean graduated cylinder, add 100.0 mL of 1.0 M HCl to the empty calorimeter.
- b. Determine the mass of a sample of magnesium ribbon (about 0.15 g) on the analytical balance, then wrap it with a piece of copper wire. The copper will not react in the solution; its purpose is to prevent the magnesium from floating to the surface during the reaction. Do not wrap the magnesium too tightly with the copper or it will not react with the HCl solution. Do not wrap the magnesium too loosely since it may escape the copper “cage” and float.
- c. Record the initial temperature (T_i) of the 1.0 M HCl in the calorimeter.
- d. Note the time (time = zero). Then add the magnesium/copper bundle to the calorimeter. The stir bar may interfere with the Mg/Cu bundle so do not add it for this run. Replace the thermometer and lid, and gently swirl the solution. Record the temperature at one-minute intervals until a definite linear decrease in temperature is noted. Keep swirling the solution. About 7 or 8 points are necessary on the linear portion of the curve to make an extrapolation so make sure to collect enough data *after* the temperature starts decreasing.
- e. When data collection is completed, rinse the calorimeter and thermometer with distilled water and dry as completely as possible. Place the piece of copper in the container labeled “copper waste.”

2. Reaction of Magnesium Oxide and Hydrochloric Acid

- a. Place 100.0 mL of 1.0 M HCl into a clean graduated cylinder.
- b. On a top-loading balance, transfer approximately 0.7 to 0.8 g of MgO to a clean weighing boat (no need to record this mass). Next, determine the mass of the MgO and the weighing boat on the analytical balance and record the data. Transfer the MgO to the dry calorimeter.
- c. On the analytical balance, record the mass of the “empty” weighing boat *after the transfer* and calculate the mass of MgO actually transferred to the calorimeter.
- d. Record the initial temperature (T_i) of the 1.0 M HCl solution in the graduated cylinder.
- e. Note the time (time = zero). Then add the 100.0 mL of 1.0 M HCl to the calorimeter containing the MgO. Record the temperature at one-minute intervals in the same manner described above. A stir bar can be used for this run. In this reaction all the MgO should react since HCl is used in excess. *However, if the solid MgO is allowed to sit on the bottom or sides of the cup it will not dissolve and hence it will not react. Make sure the solution is mixing constantly but gently.*

(Before discarding this solution, check to see that all of the MgO has reacted. If solid MgO remains, the results from this portion of the experiment are not accurate. If any solid is present, this portion of the experiment must be repeated.)

f. When data collection is completed, rinse the calorimeter and thermometer with distilled water and dry as completely as possible.

Clean up:

1. All solutions are dilute aqueous solutions and may be poured down the drain.
2. Wash all glassware. Rinse your calorimeter well and invert it on a paper towel to dry.
3. Return all equipment to their original location.

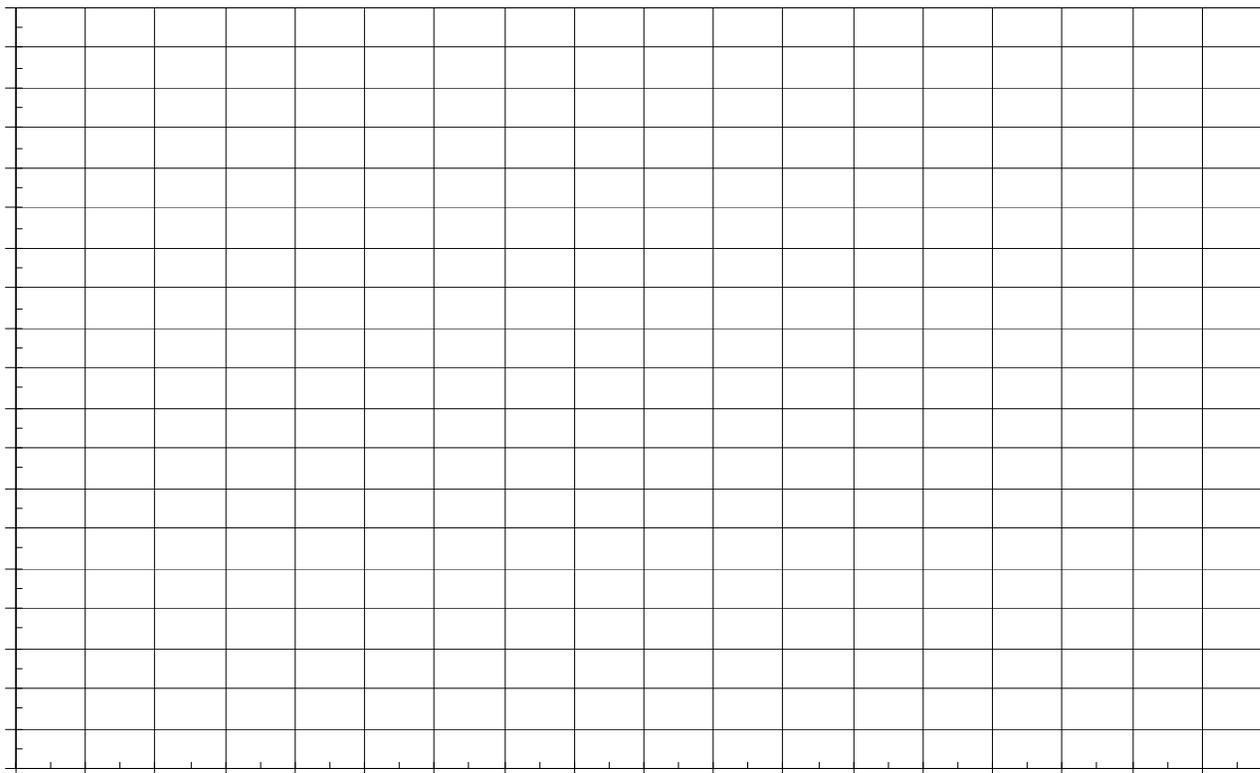
In-Lab Data Analysis

Part A. Determination of the Heat Capacity of the Calorimeter

1. On the graph below, construct a temperature vs. time plot for the data obtained in Part A. Label the axes. By extrapolation of the linear portion of the graph, determine the final temperature, T_f . Label T_i and T_f on your graph and below. Show your graph to your instructor.

$$\Delta T = T_f - T_i$$

$T_i =$ _____ $T_f =$ _____ $\Delta T =$ _____



2. The acid/base neutralization reaction in Part A was:



a. Write the net ionic equation for this reaction.

What are the spectator ions? _____

b. Using the volume and molarity of the HCl (or NaOH) solution used in Part A and the balanced reaction, determine the number of moles of water produced, n . Show all work and include units.

$n =$ _____

3. Calculate the heat capacity, C , of the calorimeter and the solvent using equation (4). Show your value to your instructor. **Include the units.**

$C =$ _____
(with units)

If you don't finish this data analysis section before the end of lab today, complete it before next week's lab.

Name _____

Section _____

Partner _____

Date _____

DATA SECTION
Experiment 12A

Part A. Determination of the Heat Capacity of the Calorimeter

Initial temperature of the NaOH solution: _____

Initial temperature of the HCl solution: _____

Average of the two temperatures: _____ = T_i

Time (minutes)	Temperature ($^{\circ}\text{C}$)
0.0	= T_i
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
4.0	
4.5	
5.0	
5.5	
6.0	
6.5	
7.0	

Part B. Determination of the Enthalpy of Formation of Magnesium Oxide

1. Reaction of Magnesium and Hydrochloric Acid

mass of Mg metal _____

number of moles of Mg _____

2. Reaction of Magnesium Oxide and Hydrochloric Acid

mass of MgO sample and weighing boat _____

mass of weighing boat after transfer _____

mass of MgO _____

number of moles of MgO _____

Time (minutes)	1. Mg + HCl reaction	2. MgO + HCl reaction
	Temperature (°C)	Temperature (°C)
0.0	= T _i	= T _i
1.0		
2.0		
3.0		
4.0		
5.0		
6.0		
7.0		
8.0		
9.0		
10.0		
11.0		
12.0		

DATA TREATMENT
Experiment 12A

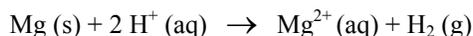
Part B. Determination of the Enthalpy of Formation of Magnesium Oxide

(B.1) Using a spreadsheet program, generate temperature vs. time graphs with the data collected for the reactions of:
1. Mg with HCl
and 2. MgO with HCl.

Perform a linear regression on the linear portions of the graphs and determine the *extrapolated* value of T_f for each reaction. Include your properly-formatted graphs with your lab report.

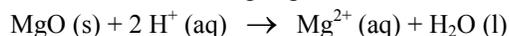
	<u>1. Mg reaction</u>	<u>2. MgO reaction</u>
Extrapolated value of final temperature, T_f	_____	_____
Temperature change, ΔT	_____	_____
Moles of reactant, n	_____	_____

(B.2) Using equation (5) and your calorimeter constant C from Part A, calculate ΔH_b for the reaction involving Mg with HCl. Report your value in units of kJ/mole.



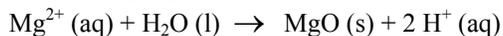
$$\Delta H_b = \frac{\quad}{\quad} \text{(with units)}$$

(B.3) Similarly, calculate ΔH for the reaction involving MgO and HCl.



$$\Delta H = \frac{\quad}{\quad}$$

(B.4) What is ΔH_c for the reaction involving Mg^{2+} with H_2O ? How does this reaction compare to the one in B.3?



$$\Delta H_c = \frac{\quad}{\quad}$$

Name _____

Section _____

Date _____

PRE-LAB QUESTIONS
Experiment 12A

1. Plot the following set of temperature vs. time data using a spreadsheet program, with time on the x-axis and temperature on the y-axis. Extrapolate the linear portion* of the graph and determine T_f of the reaction for which the data have been recorded. (Refer to the Excel directions in [Appendix O](#).) Include the graph with your Pre-lab.

Time (minutes)	Temperature (°C)
0.0	23.3
1.0	27.8
2.0	28.4
3.0	28.5
4.0	28.5
5.0	28.4
6.0	28.3
7.0	28.3

 $T_i =$ _____ $T_f =$ _____ $\Delta T =$ _____

* The linear portion will include the maximum temperature and all data points *after* it.

Appendix O = <http://www.chemistry.usna.edu/manual/AppendixO.pdf>

2. Review the following websites:

<http://www.fas.org/man/dod-101/sys/dumb/luu2.htm>

http://www.blazetech.com/Products_Services/Fires_and_Explosions/Magnesium_Fire/magnesium_fire.html

a. List 2 military applications for the reaction studied in this experiment. $\text{Mg (s)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{MgO (s)}$

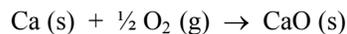
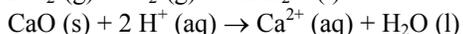
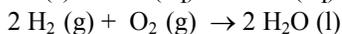
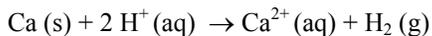
i.

ii.

b. True or False: Use water to put out a Magnesium fire. (Hint: watch the video on the website)

c. In our experiment, why can't we determine ΔH_f for $\text{Mg (s)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{MgO (s)}$ by direct measurement?

3. Use Hess's Law to determine the ΔH_{rxn} for:



$$\Delta H = 1925.9 \text{ kJ/mol}$$

$$\Delta H = -571.68 \text{ kJ/mole}$$

$$\Delta H = 2275.2 \text{ kJ/mole}$$

$\Delta H_{\text{rxn}} =$ _____