Experiment 12A

FV-8/30/04

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.

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

$$Mg\ (s) + \tfrac{1}{2}\ O_2\ (g) \rightarrow MgO\ (s)$$

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:

Chemical reactions are associated with the absorption of thermal energy (endothermic reactions) or the evolution of thermal energy (exothermic reactions). The magnitude of the energy change is determined by the particular reaction as well as the amount of product(s) formed.

The energy change associated with a chemical reaction carried out at constant pressure is called the enthalpy of reaction (also heat of reaction) and is given the symbol ΔH. ΔH is often expressed in units of kJ/mole, where the 'mole' refers to the amount of a specific reactant or product. In general, the reaction must be specified.

Magnesium burns in air to produce magnesium oxide. Your instructor may show you this reaction by burning a piece of magnesium metal in the hood. 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 as discussed below.

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.

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

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

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:

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

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).

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

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:

$$HCl\ (aq) + NaOH\ (aq) \rightarrow H_2O\ (l) + NaCl\ (aq) \qquad \Delta H = -57.20\ kJ/mol$$

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 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 the linear portion of the curve 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.

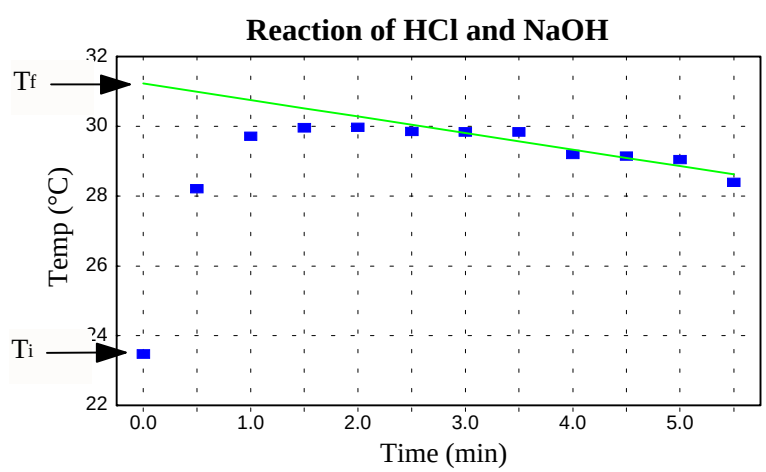

Figure 1. Determining temperature change from calorimetry data

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:

(a) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\Delta H_f^o (H_2O) = -285.84$ kJ/mole

(b) $Mg(s) + 2 H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$ ΔH_b

(c) $Mg^{2+}(aq) + H_2O(l) \rightarrow MgO(s) + 2 H^+(aq)$ ΔH_c

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

(d) $Mg(s) + \frac{1}{2} O_2(g) \rightarrow MgO(s)$ $\Delta H_f (MgO) = \Delta H_f^o (H_2O) + \Delta H_b + \Delta H_c$

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 ΔH_f (MgO).

Reaction (a) represents the formation of liquid water from its constituent elements. The enthalpy change for this reaction, symbolized $\Delta H_f^o (H_2O)$ above, is the standard heat of formation of liquid water 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!

A. Determination of the Heat Capacity of the Calorimeter

1. Rinse the graduated cylinder with water and then rinse with 1.0 M NaOH. Discard the rinses. Using 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.

✍ Answer Question #1 on page E12A-10.

3. Note the time (time = zero). Then add the HCl solution quickly to the NaOH solution in the calorimeter, mix well, and replace the lid on the calorimeter with the thermometer in place. Immediately begin collecting and recording temperature readings at 30-second intervals for 7 minutes. Swirl the calorimeter while collecting the data and keep the lid on the calorimeter.

4. When data collection is completed, rinse the calorimeter 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. Allow the calorimeter and the solution to reach thermal equilibrium.

✍ Answer Question #2 on page E12A-10.

Record your hand graph results from Part A here: T_f = _____ ΔT = _____

   b. Determine the mass of a sample of magnesium (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.

   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. Replace the thermometer and lid, swirl the reaction mixture, and record the temperature at one-minute intervals until a definite linear decrease in temperature is noted. About 7 or 8 points are necessary on the linear portion of the curve to make an extrapolation.

e. When data collection is completed, rinse the calorimeter with distilled water and dry as completely as possible. Place the piece of copper in the container labeled "copper waste."

✍ Answer Question #3 on page E12A-10.

2. Reaction of Magnesium Oxide and Hydrochloric Acid

a. Place 100.0 mL of 1.0 M HCl into a clean graduated cylinder. Allow the solution to reach thermal equilibrium.

b. On a top-loading balance, transfer approximately 0.7 to 0.8 g of MgO to a weighing boat. 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. Record the mass of the "empty" weighing boat after the transfer and calculate the mass of MgO 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. 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 it dissolves by constantly and gently swirling the solution during the reaction process.*

(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 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.

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 (°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)	**Mg + HCl reaction**	**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

For all calculations, include the proper number of significant figures and the appropriate units. Show your work for full credit.

Part A. Determination of the Heat Capacity of the Calorimeter

(A.1) For the data from Part A, construct a temperature vs. time graph using a spreadsheet program. Include this graph with your lab report. The graph should look similar to the hand graph you constructed in lab. Using the data from ONLY the linear portion of the graph, perform a linear regression. From the regression output, determine the extrapolated value of the final temperature, T_f, and determine ΔT. (Refer to the Excel instructions in Appendix O.)

T_f = _____ ΔT = _____

(A.2) For the Part A data, compare the values of T_f from your two graphs (hand graph and Excel graph). These values should be similar. Explain any discrepancies.

(A.3) The acid/base neutralization reaction in Part A was:

$$HCl\ (aq) + NaOH\ (aq) \rightarrow H_2O\ (l) + NaCl\ (aq) \qquad \Delta H = -57.20\ kJ/mol$$

a. Write the net ionic equation for this reaction.

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

n = _____

(A.4) Calculate the heat capacity, C, of the calorimeter and the solvent using equation (4).

C = _____

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 Mg with HCl and 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 graphs with your lab report.

	Mg reaction	MgO reaction
Extrapolated value of final temperature, T_f	_____	_____
Temperature change, ΔT	_____	_____
Moles of reactant, n	_____	_____

(B.2) Using equation (5), calculate ΔH_b for the reaction involving Mg with HCl.

(b) $Mg\ (s) + 2\ H^+\ (aq) \rightarrow Mg^{2+}\ (aq) + H_2\ (g)$

$\Delta H_b =$ _____

(B.3) Using equation (5), calculate ΔH for the reaction involving MgO and HCl.

$MgO\ (s) + 2\ H^+\ (aq) \rightarrow Mg^{2+}\ (aq) + H_2O\ (l)$

$\Delta H =$ _____

(B.4) What is ΔH_c for reaction (c)?

(c) $Mg^{2+}\ (aq) + H_2O\ (l) \rightarrow MgO\ (s) + 2\ H^+\ (aq)$

$\Delta H_c =$ _____

(B.5) By applying Hess's Law, calculate the enthalpy of formation of MgO, ΔH_f (MgO).

$Mg\ (s) + \frac{1}{2}\ O_2\ (g) \rightarrow MgO\ (s)$

ΔH_f (MgO) = _____

(B.6) The accepted value of ΔH_f for the formation of MgO is -601.83 kJ/mole. Calculate the percent deviation of your result from this value.

% deviation = _____

Optional: To check your results, enter them into the "Data Input and Feedback" section of MOLS.

Name _____ Section _____

Date _____

✍ IN-LAB QUESTIONS ✍
Experiment 12A

(Turn in this page and the graph from #2 before you leave lab.)

1. Why is it important to thoroughly rinse the graduated cylinder between measuring the sodium hydroxide and hydrochloric acid solutions?

2. Using the graph paper provided, construct a temperature vs. time graph for the data obtained in Part A. By extrapolation of the linear portion of the graph, determine the final temperature, T_f.
   Show your graph to your instructor. Include the graph with this sheet.

$$\Delta T = T_f - T_i$$

T_i = _____ T_f = _____ ΔT = _____

Record your T_f and ΔT values on page E12A-4 also.

3. If your Mg solid doesn't completely dissolve during the reaction, would this lead to problems (in your enthalpy calculations later)? Explain.

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_f = _____

ΔT = _____

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. $Mg\ (s) + \frac{1}{2} O_2\ (g) \rightarrow MgO\ (s)$

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 $Mg\ (s) + \frac{1}{2} O_2\ (g) \rightarrow MgO\ (s)$ by <u>direct</u> measurement?

3. Use Hess's Law to determine ΔH_f for CaO: $Ca\ (s) + \frac{1}{2} O_2\ (g) \rightarrow CaO\ (s)$

$Ca\ (s) + 2\ H^+\ (aq) \rightarrow Ca^{2+}\ (aq) + H_2\ (g)$ $\Delta H = 1925.9$ kJ/mol

$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$ $\Delta H = -571.68$ kJ/mole

$CaO\ (s) + 2\ H^+\ (aq) \rightarrow Ca^{2+}\ (aq) + H_2O\ (l)$ $\Delta H = 2275.2$ kJ/mole

$\Delta H_f\ (CaO)$ = _____