Experiment 12A

CALORIMETRY AND HESS'S LAW: FINDING ΔH FOR THE COMBUSTION OF MAGNESIUM

MATERIALS: 12 oz. Styrofoam cup with lid, thermometer, 50-mL and 100-mL graduated cylinders, weighing boat,

1.0 M HCl, 1.0 M NaOH, magnesium ribbon, magnesium oxide, copper wire.

PURPOSE: The purpose of this experiment is to determine the enthalpy change for the combustion of magnesium:

$$Mg\ (s)\ +\ \tfrac{1}{2}\,O_2\ (g)\ \rightarrow\ MgO\ (s) \qquad \Delta H_{rxn} = \Delta H_{comb}$$
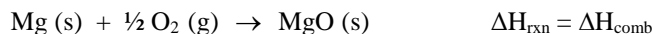
by determining the ΔH values for reactions which can be combined together according to Hess' Law, yielding the ΔH for the desired reaction.

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 using a reaction with known ΔH.
3. Calculate the enthalpy change 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 difficult, so 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 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 Styrofoam cup), a thermometer, and a lid (which is loose fitting to allow the pressure to remain constant. 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 that is absorbed by the calorimeter and solvent is calculated from the equation:

$$q_{cal} = C \cdot \Delta T \tag{1}$$

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:

$$q_{rxn} = n \cdot \Delta H \tag{2}$$

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).

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

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

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

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

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

      The main experimental problem in any calorimetric measurement 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), because (1) reactions do not occur instantaneously, and (2) calorimeters are not perfectly insulating, but actually allow some heat energy to slowly enter or escape from the calorimeter over time. This occurs both during the reaction and after its completion. Figure 1 illustrates the situation, and suggests a solution.

      If an exothermic reaction occurs in a hypothetical calorimeter that is perfectly insulated, all of the heat produced by the reaction will remain in the calorimeter, resulting in a constant final temperature. This would yield the same ΔT whether or not the reaction is instantaneous. Now consider a hypothetical exothermic reaction that occurs instantaneously, but in a realistic calorimeter that is not perfectly insulated. In this

Figure 1

case, the temperature of the calorimeter would diminish over time due to the gradual escape of heat energy to the surroundings. The "final" temperature to be used in determining ΔT in this case is actually the maximum temperature reached immediately after reaction occurs, since this temperature change is due exclusively to the heat produced in the reaction, and no escaping of heat to the surroundings has occurred yet.

      For real calorimeter experiments, reactions neither occur instantaneously nor are calorimeters perfectly insulated. Thus, during an exothermic reaction the temperature of the calorimeter increases initially, but never has a chance to reach the correct maximum "final" temperature since heat is escaping to the surroundings even while the reaction is proceeding toward completion. A correction for this heat exchange is made by an *extrapolation* process using the 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 <u>linear</u> <u>portion</u> 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 <u>Appendix O</u> for specific instructions for extrapolation using Microsoft Excel.

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

      Before measuring the enthalpy change of an unknown 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 <u>known</u> reaction is carried out in the calorimeter. For this experiment, the reaction:

$$HCl\ (aq) + NaOH\ (aq) \rightarrow H_2O\ (l) + NaCl\ (aq) \qquad \Delta H = -55.83\ kJ/mol$$

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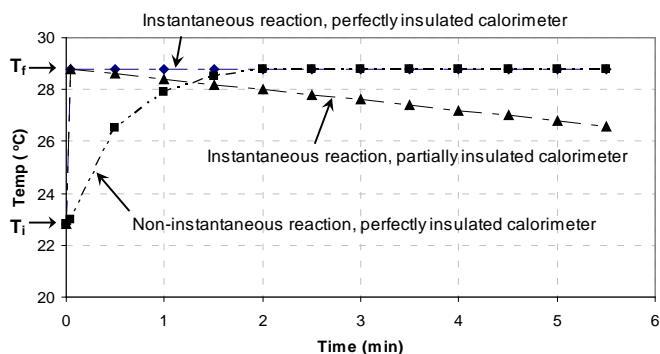
product formed, the heat capacity (C) can be calculated using equation (4). With the value of C known, the calorimeter can be used to determine the ΔH for other reactions by carrying out the reaction in the same calorimeter, measuring ΔT and using equation (5).
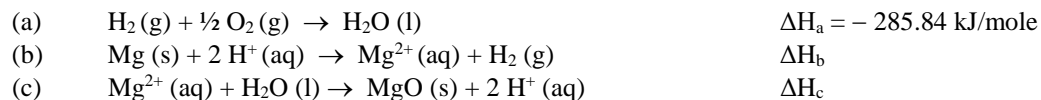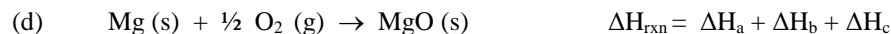
B. Determination of the Enthalpy of Combustion of Mg Using Hess's Law

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

(a) $H_2 (g) + \frac{1}{2} O_2 (g) \rightarrow H_2O (l)$ $\Delta H_a = - 285.84$ 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) $Mg (s) + \frac{1}{2} O_2 (g) \rightarrow MgO (s)$ $\Delta H_{rxn} = \Delta H_a + \Delta H_b + \Delta H_c$

which represents the combustion of Mg(s).

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 ΔH_f^o (H_2O)) 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). When data from your analysis is correctly combined with that for the known reaction (a), the enthalpy of combustion of magnesium metal can be obtained.

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 <u>NOT</u> look directly at the burning Mg.

A. Determination of the Heat Capacity of the Calorimeter

1. Ensure that the Styrofoam cup is clean and dry inside, and that it has a properly fitting cap.
2. Rinse the 50-mL 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 rinsed graduated cylinder, place 50.0 mL of 1.0 M NaOH into the calorimeter. Measure the temperature (in °C) of the NaOH solution and record this value in the Data Section. Rinse and dry the thermometer end after obtaining the temperature.
3. Rinse the100-mL 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. Working quickly, note the time (time = 0 s.) when the HCl solution is added to the calorimeter containing the NaOH solution. Replace the lid with the thermometer in place, and gently swirl the assembly to mix. **The thermometer must be supported in some way to avoid puncturing the cup and to prevent the cup from tipping over.** (You can use a clamp to hold the thermometer at the proper height (in the solution but not touching the sides of the calorimeter). Immediately begin collecting and recording temperature readings at 30-second intervals for 7 minutes. Continue to swirl the calorimeter while collecting data and keep the lid on the calorimeter.
4. When data collection is completed, rinse the calorimeter, and thermometer with distilled water and dry as completely as possible.

B. Determination of the Enthalpy of Combustion of Magnesium

<u>Reaction of Magnesium Metal and Hydrochloric Acid</u>

1. Using the graduated cylinder, add 100.0 mL of 1.0 M HCl to the empty calorimeter. Wait for a few minutes to allow the set-up to reach thermal equilibrium.
2. While waiting, determine the mass of a sample of magnesium ribbon (about 0.15 g) on the <u>analytical</u> balance, and 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 or it will not react quickly enough with the HCl solution. Do not wrap the magnesium too loosely since it may escape the copper "cage" and float.
3. Record the initial temperature (T_i) of the 1.0 M HCl in the calorimeter.
4. Working quickly, note the time (time = 0 s.) when the magnesium/copper bundle is added to the HCl solution. Replace the lid with the thermometer in place, and begin swirling to mix. Be sure to support the thermometer. Immediately begin collecting and recording temperature readings at 1-minute intervals until a definite linear decrease in temperature is noted. Continue swirling and collecting data and record about 7 or 8 points <u>*after* the temperature starts decreasing</u>. These provide the linear part of the curve, and are the most important points for the extrapolation procedure.
5. 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."

<u>Reaction of Magnesium Oxide and Hydrochloric Acid</u>

1. Place 100.0 mL of 1.0 M HCl into a clean graduated cylinder.
2. On a <u>top-loading</u> 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 <u>analytical </u>balance and record the data. Transfer the MgO to the dry calorimeter.
3. On the <u>analytical</u> balance, record the mass of the "empty" weighing boat *after the transfer* and calculate the mass of MgO actually transferred to the calorimeter.
4. Record the initial temperature (T_i) of the 1.0 M HCl solution in the graduated cylinder.

5.   Note the time (time = zero) and add the 100.0 mL of 1.0 M HCl to the calorimeter containing the MgO. Begin swirling and record the temperature at one-minute intervals in the same manner as described above, being sure to collect 7-8 points *after* the temperature maximum. 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 mixed constantly but gently.*
(NOTE: 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.)

6.   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.
4.   Clean up your work area.

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 Combustion of Magnesium

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 <u>after</u> 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

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

Part A. Determination of the Heat Capacity of the Calorimeter

(A.1)   Using a spreadsheet program, construct a temperature vs. time graph with the data collected for the reaction between HCl and NaOH solutions. Obtain the trendline for the <u>linear</u> portion of the graph (this begins at the point of the maximum temperature and includes all <u>later</u> points). (Refer to Appendix O in the lab manual for help in using Excel to accomplish this.) Use the trendline equation to determine the *extrapolated* value of T_f for the reaction. Include your properly-formatted graphs with your lab report.

Trendline equation: _____ T_f _____

(A.2)   Using the extrapolated T_f and your experimentally determined initial temperature T_i, calculate the change in temperature ΔT for the reaction.

ΔT _____

(A.3)   Using the volume and molarity of the HCl (or NaOH) solution, determine the number of moles reacted, n, in the acid-base reaction of Part A. Show all work and include units.

n _____

(A.4)   Given the following information and the actual amount of reactant used in the experiment, calculate the heat, q, (in Joules) produced by the reaction.

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l) \qquad \Delta H^\circ = -55.83 \text{ kJ}$$
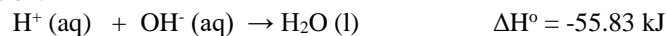
q _____

(A.5)   Use Eq. 4 to calculate the total heat capacity of the calorimeter, C, in J/°C.

C _____

Part B. Determination of the Enthalpy of Combustion of Magnesium

(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. Obtain trendlines for the <u>linear</u> portions of the graphs and determine the *extrapolated* value of T_f for <u>each</u> reaction. Include your properly-formatted graphs with your lab report.

	1. Mg reaction	2. MgO reaction
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.
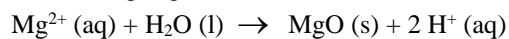
$$Mg \text{ (s)} + 2 H^+ \text{ (aq)} \rightarrow Mg^{2+} \text{ (aq)} + H_2 \text{ (g)}$$

$\Delta H_b = $ _____
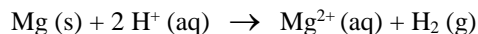
(B.3)   Similarly, calculate ΔH for the reaction involving MgO and HCl.

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

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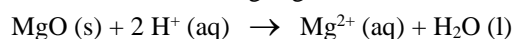
(B.4)   What is ΔH_c for the reaction involving Mg^{2+} with H_2O? How does this reaction compare to the one in (B.3)?

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

$\Delta H_c = $ _____

(B.5)   By applying Hess's Law, calculate the enthalpy of combustion of Mg, ΔH_{comb} Show your work.

$$Mg \text{ (s)} + \tfrac{1}{2} O_2 \text{ (g)} \rightarrow MgO \text{ (s)} \qquad \Delta H_{comb} = ?$$

Given previously: $H_2 \text{ (g)} + \tfrac{1}{2} O_2 \text{ (g)} \rightarrow H_2O \text{ (l)}$ $\Delta H_a = -285.84$ kJ/mole
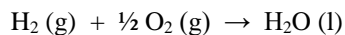
$\Delta H_{comb} = $ _____

Is the combustion of magnesium an exothermic or endothermic reaction? _____

(B.6)   The accepted value of ΔH for the combustion of Mg is –601.83 kJ/mole. Calculate the percent error of your result from the accepted value.
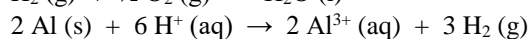
% error _____

E12A-9

Post-Lab Questions

1. Determine $\Delta H°$ for $2\ Al\ (s)\ +\ 3/2\ O_2\ (g)\ \rightarrow\ Al_2O_3\ (s)$

   given

       $H_2\ (g)\ +\ \frac{1}{2}\ O_2\ (g)\ \rightarrow\ H_2O\ (l)$ $\Delta H° = -286\ kJ/mol$

       $2\ Al\ (s)\ +\ 6\ H^+\ (aq)\ \rightarrow\ 2\ Al^{3+}\ (aq)\ +\ 3\ H_2\ (g)$ $\Delta H° = -1050\ kJ/mol$
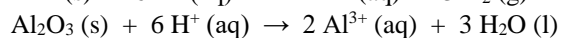
       $Al_2O_3\ (s)\ +\ 6\ H^+\ (aq)\ \rightarrow\ 2\ Al^{3+}\ (aq)\ +\ 3\ H_2O\ (l)$ $\Delta H° = -238\ kJ/mol$

2. Assume a coffee-cup calorimeter had a heat capacity (C) of 420 J/°C. If 1.00 g of Al_2O_3 completely reacted with HCl (H^+) in the calorimeter, calculate the temperature change, ΔT. Hint: one of the reactions and ΔH values from question #1 may be helpful. Watch your units!   MW (Al_2O_3) = 101.96 g/mol

3. If the value of the heat capacity (C) calculated in Part A of the experiment were too high, what effect would this have on your value for ΔH_b, the enthalpy change for the reaction between magnesium metal and hydrochloric acid? Be specific. Would your answer be too high, or too low, and why?

4. Suppose that you used a metal container, rather than a Styrofoam cup, as the calorimeter. How might this affect the temperature-time curve? If the mass of the container and solvent is the same in both cases, will the heat capacity values be the same for both calorimeters? Explain your answers.

5. Sketch the temperature vs. time graph that you would expect for an endothermic reaction carried out in a calorimeter similar to the one used in the experiment (assume the reaction is not instantaneous and that the calorimeter is not perfectly insulated).

Name _____   Section _____

Date _____

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PRE-LAB QUESTIONS
Experiment 12A

</div>

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 = _____

ΔT = _____

* The linear portion will include the maximum temperature and all data points *after* it.
Appendix O = http://www.usna.edu/ChemDept/_files/documents/manual/Apdxo.pdf

2.   Review the following websites:

https://www.youtube.com/watch?v=GYNd2yOdtdk
https://www.youtube.com/watch?v=TOpsB5n9DZ8
https://en.wikipedia.org/wiki/Flameless_ration_heater

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

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

   given: $Ca\ (s) + 2\ H^+\ (aq)\ \rightarrow Ca^{2+}\ (aq) + H_2\ (g)$ $\Delta H = 1925.9$ 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

ΔH_{rxn} = _____