Experiment 12F

FV 9/30/05

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

MATERIALS: Styrofoam coffee cup and lid, thermometer, magnetic stirrer, magnetic stir bar, 50-mL and 100-mL graduated cylinders, magnesium ribbon, magnesium oxide, 1.00 M HCl, 1.00 M NaOH, copper wire.

PURPOSE: The purpose of this experiment is to determine the ΔH^o for the combustion of magnesium by determining the ΔH^o's for reactions which can be combined together according to Hess' Law, yielding the ΔH^o 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^o.
3. Determine a set of reactions which, after applying Hess' Law, yield the ΔH^o for the desired reaction.
4. Devise procedures to address experimental challenges associated with the reactions.
5. Use a spreadsheet program for data manipulation, graphing, and regression analysis.

PRE-LAB: Complete the pre-lab questions on page E12F-9 **before** lab.

DISCUSSION:

Calorimetry is a technique for measuring the heat produced or consumed by a chemical reaction (q_{rxn}). If the heat of reaction is measured in a constant-pressure calorimeter (e.g., a coffee-cup calorimeter), then:

$$q_{rxn} = q_p = \Delta H$$

(The subscript "p" emphasizes that the heat of reaction was measured at constant pressure.)

In a calorimetry experiment, a reaction is performed inside a calorimeter and the resulting temperature change ($\Delta T = T_{final} - T_{initial}$) of the calorimeter is measured. The heat produced by the reaction (at constant pressure) is calculated as:

$$q_{rxn} = -C \cdot \Delta T$$

where C is the total heat capacity of the calorimeter and its contents, and ΔT is the temperature **change** of the calorimeter. The negative sign reflects the fact that an exothermic reaction (negative ΔH) results in a positive ΔT (temperature increase).

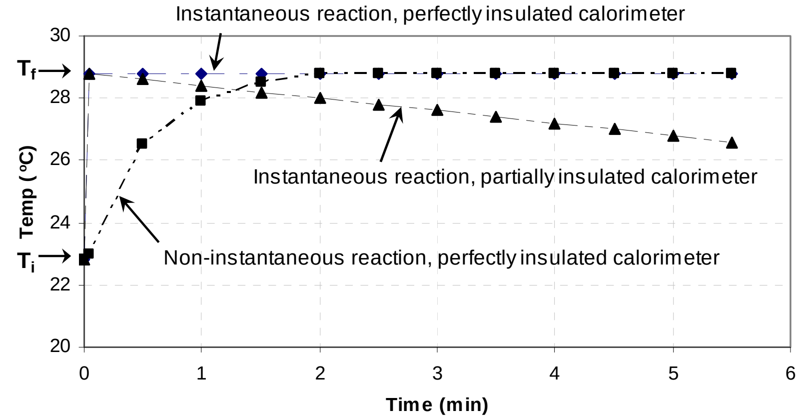
Total heat capacity (C) is the amount of heat required to raise the temperature by 1^oC (or 1K). In a calorimetry experiment, one measures the change in temperature of the calorimeter and its contents. (In this experiment, the calorimeter consists of a Styrofoam cup and its lid. The calorimeter will contain a dilute solution, a magnetic stir bar, and the end of a thermometer.) **Specific heat capacity (s)** is the amount of heat required to raise the temperature of **one gram** of material by 1^oC. **Molar heat capacity (C_m)** is the amount of heat required to raise the temperature of **one mole of a pure substance** by 1^oC. Typical units for C, s, and C_m are $J/^oC$, $J/g\text{-}^oC$, and $J/mol\text{-}^oC$, respectively. Thus:

$$C = m \cdot s = n \cdot C_m$$ **where m is mass and n is number of moles of substance.**

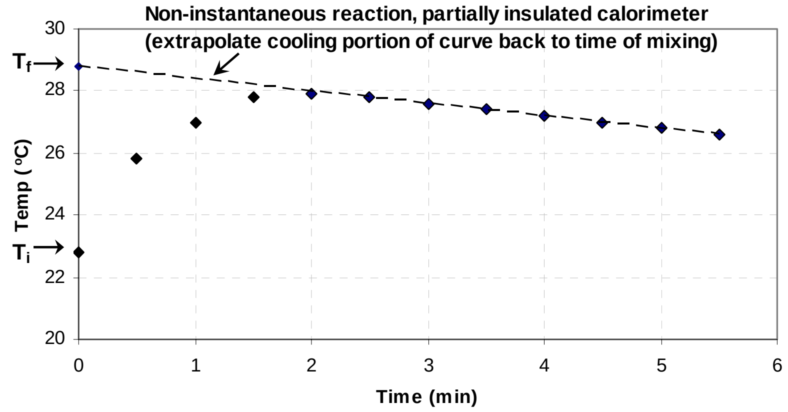
In this experiment, the **total heat capacity** (C) of the calorimeter and its contents will be measured using a reaction with a known ΔH.

The correct determination of ΔT for a reaction requires careful consideration of two key issues: (1) reactions do not occur instantaneously, and (2) calorimeters are not perfectly insulated from their surroundings, thus allowing heat energy to slowly enter or escape from the calorimeter over time.

Consider an exothermic reaction which occurs in a hypothetical calorimeter which is perfectly insulated. In this case, whether the reaction occurs instantaneously or not, all of the heat produced by the reaction will remain in the calorimeter, resulting in the same final temperature, and hence the same ΔT. Now consider a hypothetical exothermic reaction which occurs instantaneously, but in a realistic calorimeter which is not perfectly insulated. In this 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. These three hypothetical cases are all depicted on the following temperature vs. time graph:



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. The best way to account for these experimental difficulties, thereby obtaining a very good estimate of the correct "final" temperature, is to linearly extrapolate the gradual cooling portion of the temperature vs. time graph back to the initial time of mixing. This is the temperature that the calorimeter would have reached if all the heat energy from the reaction had remained absorbed by the calorimeter. This approach to obtaining the correct "final" temperature is depicted on the following temperature vs. time graph, and can easily be accomplished using a spreadsheet (see Appendix O of the Plebe Chemistry Lab Manual):



PROCEDURE:

Part A: How to determine ΔH^o for the combustion of one mole of magnesium

1. Observe the combustion reaction of magnesium metal, as demonstrated by your instructor. The objective of this experiment is to determine the ΔH^o for this reaction. (The superscript "o" indicates that all of the reactants and products are in their standard states.) Make any notes needed for later use.

✍ **Answer in-lab questions #1 and #2 on page 7.**

2. Since the direct measurement of ΔH^o for the combustion of magnesium is difficult, an alternate set of reactions must be found that add to yield the desired reaction. If the ΔH^o's for these alternate reactions can be measured, then by applying Hess' Law, you can calculate ΔH^o for the desired reaction. While there are many sets of reactions that could accomplish this objective, we will focus on a particular set of three reactions. One of them will **not** be experimentally determined during this study, but is given as follows:

$$H_2(g) + \tfrac{1}{2}\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H^o = -285.83 \text{ kJ}$$

The other two reactions must obviously involve magnesium and magnesium oxide. Many metals and metal oxides react with strong acids. Determine as best you can, using actual experimental tests in the lab, the reactions that each of these materials undergoes with hydrochloric acid. Carefully note any interesting observations of these reactions.

✍ **Answer in-lab questions #3, #4, and #5 on pages 7 and 8.**

3. It now remains to determine the ΔH^o for the two reactions involving magnesium and magnesium oxide with hydrochloric acid. Following the direction of your instructor, each set of students will be assigned to study one of the two reactions, with a specific target calorimeter temperature change. Class data will then be combined for later analysis and final determination of the ΔH^o's for the two reactions.

Part B: Measuring the total heat capacity of the calorimeter and its contents

1. Calorimetry requires that the heat capacity of the calorimeter and its contents be known. In this experiment, the calorimeter will consist of a Styrofoam cup and lid. It will contain a stir bar, thermometer, and a dilute solution. You will need to measure how much the temperature of the calorimeter and its contents changes when they absorb a **known** amount of heat. To produce a known amount of heat, you will perform the following acid-base neutralization reaction, for which ΔH^o is well known:

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

2. Place the magnetic stir bar into a clean, dry Styrofoam cup.

3. Rinse a clean graduated cylinder with a few milliliters of 1.00 M HCl and transfer 50.0 mL of 1.00 M HCl into the cup.

4. Place the cup on the magnetic stirrer and begin stirring gently. (Why gently?)

5. After rinsing the graduated cylinder with distilled water and with a few milliliters of 1.00 M NaOH, obtain a 50.0 mL sample of 1.00 M NaOH.

6. Record the molarity and volume of each solution used.

7. **Before mixing**, measure the temperature of the two solutions. (Rinse and dry the thermometer between readings). Record the average of the two temperatures. This is the initial temperature (T_i).

8. Working quickly, note the time (time = 0 s) when the NaOH solution is added to the Styrofoam cup, then put on the lid, and place the thermometer into the solution. **(The thermometer must be supported in some way to prevent the cup from tipping over.)**

9. Record the time and temperature every 15 - 30 seconds for a total of 8 minutes. The time intervals can be increased as the rate of temperature change decreases.

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

Important: For this and all subsequent experiments, use a total solution volume of 100.0 mL.

Part C: Measuring ΔH^o for the reaction of Mg or MgO with HCl

Obtain your assigned reaction and target ΔT from your instructor.

→ *For students assigned to study the Mg/acid reaction:*

1. In part A, you probably observed that the magnesium metal floated on top of the acid solution as it reacted with it. (Think about why this is a problem.)

✍ **Answer in-lab question #6 on page 8.**

With available materials, devise a method that would successfully address the “floating” magnesium problem. **Think about how to prevent small pieces of magnesium from floating to the surface during the reaction.**

2. Do a trial calorimeter experiment with a small amount of magnesium (no more than 3 inches of the ribbon). Use this result to estimate the mass of magnesium metal required for achieving your assigned target temperature change.

3. Using this estimate, carry out the calorimeter experiment for your target ΔT. **Record your time and temperature data and the mass of Mg used.**

→ *For students assigned to study the MgO/acid reaction:*

1. Do a trial calorimeter experiment with a small amount of magnesium oxide (no more than 0.3 g). Use this result to estimate the mass of magnesium oxide required for achieving your assigned target temperature change.

2. Using this estimate, carry out the calorimeter experiment for your target ΔT. **Record your time and temperature data and the mass of MgO used.**

Cleanup:

1. All solutions can be disposed down the sink with plenty of water.
2. Rinse your calorimeter and lid, and leave it to dry for the next lab section.
3. Return all equipment to their original locations.
4. Clean up your work area.

DATA ANALYSIS:

Part B: Measuring the total heat capacity of the calorimeter and its contents

1. Construct a plot of temperature versus time with Excel and determine the highest temperature (T_f) that would have been achieved if the calorimeter was perfectly insulated (see DISCUSSION section). Use this final temperature to calculate the temperature change ($\Delta T = T_f - T_i$) of the calorimeter. (Refer to Appendix O in the lab manual for help in determining T_f using Excel.)

2. Using the following information and the amounts of reactants used in the experiment, calculate the heat (in Joules) produced by the reaction.

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

3. Calculate the total heat capacity of the calorimeter (C) in J/^{o}C.

Part C: Measuring ΔH^o for the reaction of Mg or MgO with HCl

1. Calculate the number of moles of Mg or MgO that were consumed in the reaction that you studied.

2. Determine the temperature change ($\Delta T = T_f - T_i$) for the reaction you studied by constructing a temperature versus time plot on the graph paper provided. (Your instructor will tell you whether you must reproduce this graph in Excel.)

3. Using the total heat capacity of your calorimeter (C) and the temperature change, calculate the heat produced by the reaction that you studied ($q_{rxn} = \Delta H^o$).

4. Report the number of moles of Mg or MgO and your calculated ΔH^o (q_{rxn}) to the class.

5. Create an Excel spreadsheet that lists the results from the entire class (moles of reactant and ΔH^o for **each** of the two reactions studied.)

6. Use Excel to graph the class data for both reactions (two graphs) and use the graphs to determine the average value for ΔH^o **per mole** of magnesium, and the average value for ΔH^o **per mole** of magnesium oxide. (Think about which data you should plot on the y-axis.)

7. Combine these results and the ΔH^o for the reaction below to obtain ΔH^o for the combustion of magnesium.

$$H_2(g) + \tfrac{1}{2}\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H^o = -285.83 \text{ kJ}$$

QUESTIONS FOR CONSIDERATION:

1. Using available thermodynamic tables of $\Delta H^o{}_f$ (standard enthalpy of formation), determine the ΔH^o values for the magnesium/acid and magnesium oxide/acid reactions and compare with your experimentally determined values. Explain any differences. $\Delta H_f°$ (Mg^{2+}) = - 462 kJ/mol

2. Is the combustion reaction for magnesium the same as the "formation" reaction for magnesium oxide? Does this mean that the ΔH^o obtained is the same as the $\Delta H^o{}_f$ for magnesium oxide? Compare your experimental value with that found in the table of thermodynamic properties in your textbook. Determine the percent error.

3. 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).

4. Could the same procedures be applied for determining the ΔH^o for the combustion of aluminum metal as were used in this experiment? Show how the analogous reactions would combine together, applying Hess' Law, to yield the ΔH^o for the combustion reaction.

5. Using thermodynamic tables and your calorimeter heat capacity, predict the ΔT if 1.00 g of aluminum oxide completely reacted with hydrochloric acid. $\Delta H_f°$ (Al^{3+}) = - 525 kJ/mol

6. If the material absorbing the heat produced by reaction were limited to just the water, what would be the expected heat capacity of your calorimeter? How does the experimentally determined heat capacity compare?

7. In Parts B and C, we assumed that the heat of reaction was equal to the **standard** enthalpy change. For both Part B and Part C, discuss whether or not this was a good assumption.

Name ______________________________ Section ___________

✍ IN-LAB QUESTIONS ✍

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Complete these questions during lab.

1. Write the balanced chemical equation for combustion of **one mole** of magnesium metal. (The coefficient in front of Mg should be 1, but other coefficients may be fractional coefficients. We are doing this because we want to determine ΔH^o **per mole** of magnesium.)

2. Why would it be difficult to study the combustion of magnesium directly using a simple water-filled calorimeter?

3. Write the balanced molecular, complete ionic, and net ionic equations for the reaction of magnesium metal with hydrochloric acid. (Hint: the Activity Series table may help you determine what the products are in this reaction.)

Molecular:

Complete ionic:

Net ionic:

4. Write the balanced molecular, complete ionic, and net ionic equations for the reaction of **solid** magnesium oxide with hydrochloric acid. (Hint: Magnesium oxide is a base!)

Molecular:

Complete ionic:

Net ionic:

5. Combine the two deduced reactions (net ionic equations) and the given reaction so that the 3 reactions add to give the desired reaction (combustion of one mole of magnesium).

   The given reaction is: $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

6. Based on the Activity Series, identify two different metals that could be used as weights to keep the magnesium metal submerged in the hydrochloric acid solution which would not react with the acid. Explain your answer.

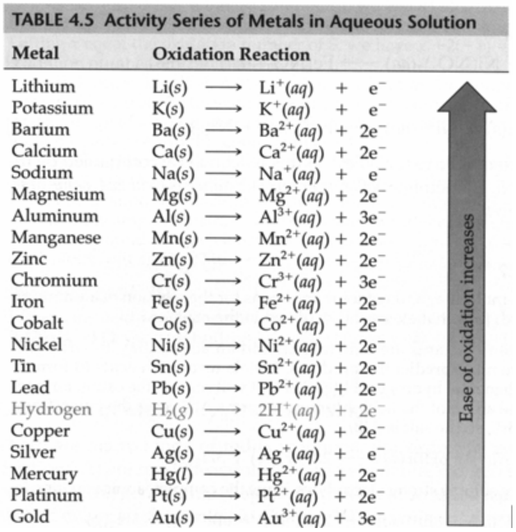

TABLE 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^+(aq) + e^-$
Potassium	$K(s) \longrightarrow K^+(aq) + e^-$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^-$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$
Sodium	$Na(s) \longrightarrow Na^+(aq) + e^-$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^-$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
Hydrogen	$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^-$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^-$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$

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Date ________________________

PRE-LAB QUESTIONS
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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 your properly formatted 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
http://science.howstuffworks.com/mre.htm

a. List 2 military applications for the reaction studied in this experiment. $Mg\ (s) + \frac{1}{2}\ O_2\ (g) \longrightarrow MgO\ (s)$

i.

ii.

b. True or False: Water should be used to put out a Magnesium fire. (Hint: watch the video on the website.)

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
$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$ $\Delta H = -\ 571.68$ kJ
$CaO\ (s) + 2\ H^+ (aq) \rightarrow Ca^{2+} (aq) + H_2O\ (l)$ $\Delta H = 2275.2$ kJ

ΔH_f (CaO) = ____________________