

Reading assignment: Chang, Chemistry 9th edition, pp. 239-245.

Goals

We will become familiar with the principles of calorimetry in order to determine the heats of reaction for endothermic and exothermic reactions.

Equipment and Materials

LabPro interface, Logger Pro software, temperature probe, 100 mL graduated cylinder, insulated bottle with cork, 1.5M citric acid solution, 10 g sodium hydrogen carbonate (sodium bicarbonate), 1M hydrochloric acid solution, 12 cm strip (0.1 g) of magnesium metal, 1 g magnesium oxide.

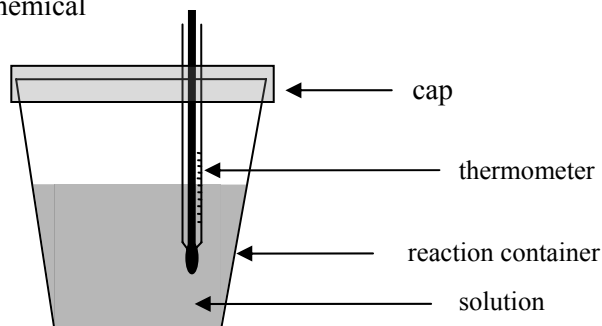
Be sure to bring a USB flash drive to the laboratory for saving data.

Discussion

Chemical reactions are often accompanied by the release or absorption of heat. For example, when hydrogen gas is combined with oxygen gas and heated the reaction produces an enormous amount of heat. Reactions that produce (release) heat are said to be exothermic. Reactions that absorb heat are said to be endothermic.

The heat released in a chemical reaction is often determined by measuring the temperature change of the material surrounding the chemical reactants and products. This works because the amount of heat associated with a reaction is equal to the amount of heat that is either transferred to or from its surroundings. The study of heat associated with chemical reactions is called thermochemistry. The measure of temperature changes associated with chemical reactions is called calorimetry.

To the right is a diagram of a simple calorimeter, a device in which the heat of a reaction is measured. The calorimeter can be as simple as a styrofoam cup and a thermometer. In a calorimeter the reactants are placed into the container and allowed to react. The reactants and the products of a chemical reaction, are called the system. The materials surrounding the system are called the surroundings. As the reaction proceeds, the temperature of the liquid in which the reaction is occurring changes because heat is transferred between the system and the surroundings.



The first law of thermodynamics can be stated as:

$$\Delta E = q + w$$

where ΔE is the change in internal energy for a system, q is the heat transferred during a process, and w is the work done on or by the system and:

$w = -\Delta(PV)$ where P is an external pressure applied to the system and V is the volume of the of the system.

At constant pressure, we generally use the change in enthalpy (ΔH) as opposed to ΔE where:

$$\Delta H = \Delta E + \Delta(PV)$$

At constant pressure:

$$\Delta H = \Delta E + \Delta(PV) = q + w + \Delta(PV) = q_p - P\Delta V + P\Delta V = q_p$$

We can measure the change in enthalpy (ΔH) for a reaction by measuring the heat (q) transferred during the process. We use the system as the reference and use the following sign convention:

Heat is absorbed by the system $\Delta H > 0$ endothermic

Heat is released by the system $\Delta H < 0$ exothermic

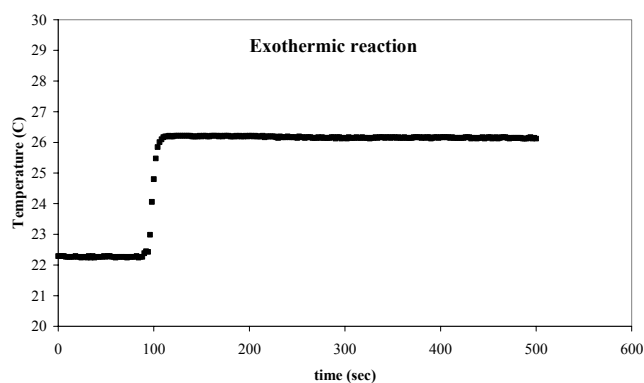
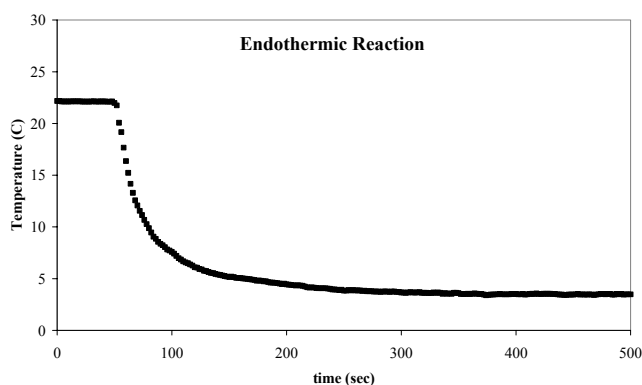
If the reaction is exothermic then the temperature of the solvent (surroundings) will increase. If the reaction is endothermic then the temperature of the solvent (surroundings) will decrease. The change in temperature of the solvent can then be used to determine the amount of heat transferred:

$$\Delta H = -ms\Delta T$$

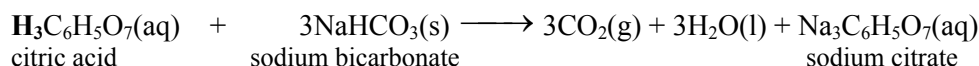
where ΔH is the change in enthalpy for the reaction (heat of reaction), m is the mass of the solution in which the reaction is occurring, s is a constant called the specific heat capacity, and ΔT is the change in temperature of the solution as the reaction takes place. The specific heat capacity depends on the material used. Values of s are given below for several materials.

Below are two temperature plots for chemical reactions. The first is an example of an endothermic reaction. The temperature decreases with time because heat is absorbed from the surroundings (which includes the thermometer), resulting in a lower temperature. The second figure shows an example of an exothermic reaction. Here, the temperature of the surroundings increases with time as heat is released to the surroundings (including the thermometer).

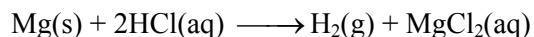
Material	$s \left(\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right)$
alcohol (ethanol)	2.45
copper	0.39
gold	0.13
graphite	0.71
iron	0.45
lead	0.13
silver	0.24
water (l)	4.18



In this experiment we will measure the amount of heat associated with three chemical reactions. The first system we will study is the reaction between citric acid and sodium hydrogen carbonate (sodium bicarbonate). Citric acid possesses three acidic protons and reacts with three sodium bicarbonate molecules. This reaction is endothermic ($\Delta H > 0$):

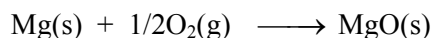


The second system we will study is the reaction of magnesium metal with hydrochloric acid. This reaction is exothermic ($\Delta H < 0$)



Combustion Reactions

For some reactions the measure the amount of heat released or absorbed is performed in a constant volume calorimeter. One such example is magnesium reacting with oxygen gas to form magnesium oxide:



This is an example of a combustion reaction. Combustion reactions are typically studied in constant volume calorimeters, devices we will not use in this experiment. Another example of an experiment typically performed in constant volume calorimeters is the combustion of foods. The calorie content of foods is really a measure of energy content. Calories are units of energy. The conversion of joules to calories is: $1 \text{ cal} = 4.184 \text{ J}$. Calories reported in foods are actually kilocalories (kCal).

Sample Calculation

A banana has a caloric content of around 150 Calories. How much energy is this in the units of joules?

Solution

Food calories are kilocalories: $150 \text{ Cal} = 150 \text{ kcal} = 1.5 \times 10^5 \text{ cal}$

Calories can be converted to joules using the conversion $1 \text{ cal} = 4.184 \text{ J}$

$$1.5 \times 10^5 \text{ cal} \left(\frac{4.184 \text{ J}}{1 \text{ cal}} \right) = 6.3 \times 10^5 \text{ J} = 0.63 \text{ MJ where MJ are megajoules} (10^6 \text{ J})$$

Hess's Law

Hess's law is an application of the fact that enthalpy is a state function. State functions are thermodynamic quantities that are path-independent. This means that the history of the system is unimportant. Hess's law is an application of the first law of thermodynamics: Energy is neither created nor destroyed in chemical processes. Application of the first law allows us to determine the heat of a reaction by combining other chemical equations for which we know the values of the heats of reaction. The reaction of magnesium with oxygen gas can be generated by combining:

- (1) $\text{MgO(s)} + 2\text{HCl(aq)} \longrightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{O(l)}$
- (2) $\text{Mg(s)} + 2\text{HCl(aq)} \longrightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{(g)}$
- (3) $\text{H}_2\text{(g)} + 1/2\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)} \quad \Delta H = -285.8 \text{ kJ}$

The enthalpy change for reaction 1 will be measured in Part 2 of this experiment. The enthalpy change for reaction 2 will be performed in Part 3 of this experiment. The enthalpy change for reaction 3 is given. By combining the three enthalpy changes we can calculate the enthalpy change for the combustion of magnesium, even though we did not measure it directly.

Procedure

SAFETY PRECAUTIONS

Obtain and wear eye protection. The cap of the calorimeter should not be held down during the reactions. Gases will build up and cause pressure to rise.

Work in pairs.

Part 1: Citric Acid and Sodium Bicarbonate

1. Using a 100 mL graduated cylinder obtain about 40 mL of citric acid solution and measure the volume to the nearest 0.1 mL. Record the volume in the Data Sheet. Pour this solution into the calorimeter and place the temperature probe into the solution.
2. Start the Logger Pro application. Open the folder **Chemistry with Computers**. Then open the file **Endo-Exothermic**. Using the **Experiment** menu select **Data Collection**. Set the experiment length to 500 seconds. Set the sample rate to 0.5 samples/second. Oversampling should not be selected.
3. Double-click on the graph to select Graph Options. Set the time scale (x-axis) to 0 sec to 500 sec. Set the temperature scale (y-axis) to 0°C to 30°C. Enter a title for the graph.
4. Measure about 10 g of sodium bicarbonate to the nearest 0.1 mg on a weighing boat and record the mass in the Data Sheet.
5. Begin collecting data. The data should appear as a curve in the graph window. After you have at least thirty seconds of data displayed on the graph quickly add the sodium bicarbonate solid to the citric acid solution in the calorimeter. Quickly place the temperature probe back into the solution.
6. The cork should not be pushed in tightly over the calorimeter opening. Begin gently swirling the calorimeter for the length of the experiment.
7. The instrument should stop taking data automatically after 500 seconds. Waste can be disposed of in the sink. Rinse and dry the calorimeter using deionized water.
8. Perform the analysis of the graph (described on pages 6-7) before moving to Part 2.
9. Print the graph in landscape format.

Part 2: Hydrochloric Acid and Magnesium

1. Using a 100 mL graduated cylinder obtain about 75 mL of hydrochloric acid solution and measure the volume to the nearest 0.1 mL. Record the volume in the Data Sheet. Pour this solution into the calorimeter and place the temperature probe into the solution.
2. Start the Logger Pro application. Open the folder **Chemistry with Computers**. Then open the file **Endo-Exothermic**. Using the **Experiment** menu select **Data Collection**. Set the experiment length to 500 seconds. Set the sample rate to 0.5 samples/second. Oversampling should not be selected.
3. Double-click on the graph to select Graph Options. Set the time scale (x-axis) to 0 sec to 500 sec. Set the temperature scale (y-axis) to 0°C to 60°C. Enter a title for the graph.
4. Obtain a 12 cm long sample of magnesium metal. Record the mass to the nearest 0.1 mg in the data sheet. Fold the magnesium metal into a ribbon so that it is fully submerged when it is dropped into the hydrochloric acid solution.
5. Begin collecting data. The data should appear as a curve in the graph window. After you have at least thirty seconds of data displayed on the graph quickly add the magnesium ribbon to the hydrochloric acid solution in the calorimeter. Quickly place the temperature probe back into the solution.

6. The cork should not be pushed in tightly over the calorimeter opening. Begin gently swirling the calorimeter for the length of the experiment.
7. The instrument should stop taking data automatically after 500 seconds. Waste can be disposed of in the sink. Rinse and dry the calorimeter using deionized water.
8. Perform the analysis of the graph (described on pages 6-7) before moving to the Part 3.
9. Print the graph in landscape format.

Part 3: Hydrochloric Acid and Magnesium Oxide

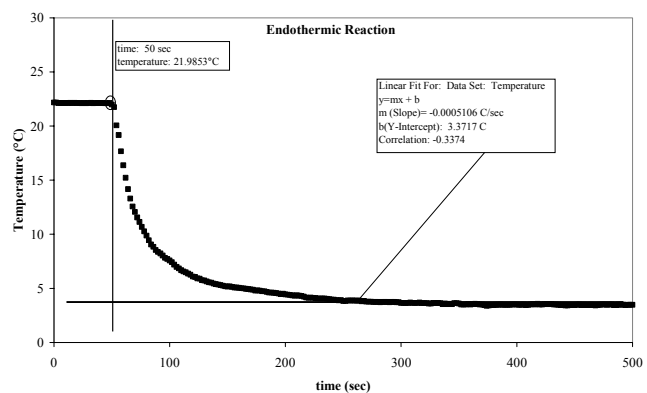
1. Using a 100 mL graduated cylinder obtain about 100 mL of hydrochloric acid solution and measure the volume to the nearest 0.1 mL. Record the volume in the Data Sheet. Pour this solution into the calorimeter and place the temperature probe into the solution.
2. Start the Logger Pro application. Open the folder **Chemistry with Computers**. Then open the file **Endo-Exothermic**. Using the **Experiment** menu select **Data Collection**. Set the experiment length to 500 seconds. Set the sample rate to 0.5 samples/second. Oversampling should not be selected.
3. Double-click on the graph to select Graph Options. Set the time scale (x-axis) to 0 sec to 500 sec. Set the temperature scale (y-axis) to 0°C to 60°C. Enter a title for the graph.
4. Measure about 1 g of magnesium oxide to the nearest 0.1 mg on a weighing boat and record the mass in the data sheet.
5. Begin collecting data. The data should appear as a curve in the graph window. After you have at least thirty seconds of data displayed on the chart quickly add the magnesium oxide solid to the hydrochloric acid solution in the calorimeter. Quickly place the temperature probe back into the solution.
6. The cork should not be pushed in tightly over the calorimeter opening. Begin gently swirling the calorimeter for the length of the experiment.
7. The instrument should stop taking data automatically after 500 seconds. Waste can be disposed of in the sink. Rinse and dry the calorimeter using distilled or deionized water.
8. Perform the data analysis described on pages 6-7.
9. Print the graph in landscape format.

Part 1: Citric Acid + Sodium Hydrogen Carbonate

The time-dependent temperature curve is used to find ΔT ($T_{\text{final}} - T_{\text{initial}}$). The initial temperature is the temperature just before the second reactant is added to the calorimeter. The final temperature is approximately (but not exactly) the minimum temperature for the curve. The final temperature is more difficult to determine than the initial because as the reaction is taking place heat is being transferred through the walls of the calorimeter. This means we need to perform a more sophisticated analysis of the data to determine T_{final} .

Data analysis is performed by using the functions in the **Analysis** menu. Consider the figure to the right when reading the explanation that follows.

1. To determine T_{initial} highlight the graph of the data and then select the **Examine** function from the **Analyze** menu. Move the cursor to the point on the graph right before the temperature just starts to decrease. This should be room temperature. The dialogue box on the screen should display temperature and time. Record the temperature and time at this point.



2. To determine T_{final} we need to find what the temperature would be at the end of the experiment if there were no heat transfer out of the calorimeter.

First highlight the flat part of the temperature curve on the graph near the end of the experiment. Select **linear fit** from the **Analyze** menu and a line of best fit should appear on the graph with the slope and y-intercept for the linear fit. To calculate T_{final} use the following equation:

$$y = mx + b$$

$$T_{\text{final}} = (\text{slope})(t_{\text{initial}}) + y\text{-intercept}$$

where t_{initial} is the time that NaHCO_3 was added to the citric acid. The slope and the y-intercept are found from the line of best fit on the graph.

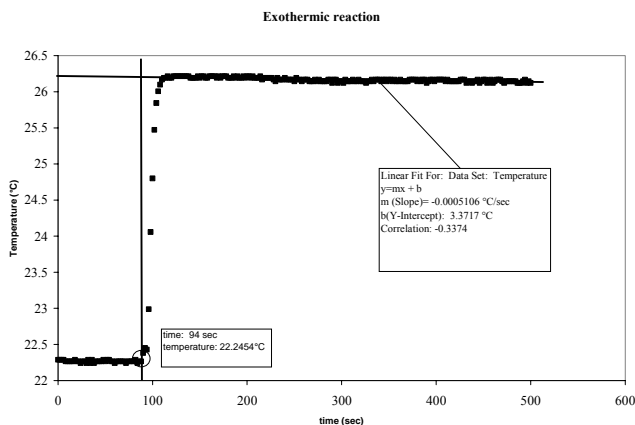
3. ΔT can now be calculated from $T_{\text{final}} - T_{\text{initial}}$.

4. The graph should be titled and the axes should be labeled with units.

5. Print a copy of the graph (not the data) for the report.

Part 2: Hydrochloric Acid + Magnesium

1. To determine T_{initial} highlight the graph and then select the **Examine** function from the **Analyze** menu. Move the cursor to the point on the graph right before the temperature just starts to increase. This should be room temperature. The dialogue box on the screen should display



temperature and time. Record the temperature and time at this point.

2. To determine T_{final} we need to find what the temperature would be at the end of the experiment if there were no heat transfer out of the calorimeter.

First highlight the flat part of the temperature curve on the graph near the end of the experiment. Select **linear fit** from the **Analyze** menu and a line of best fit should appear on the graph with the slope and y-intercept for the linear fit. To calculate T_{final} use the following equation:

$$y = mx + b$$

$$T_{\text{final}} = (\text{slope})(t_{\text{initial}}) + \text{y-intercept}$$

where t_{initial} is the time that magnesium was added to the hydrochloric acid. The slope and the y-intercept are found from the line of best fit on the graph.

3. ΔT can now be calculated from $T_{\text{final}} - T_{\text{initial}}$.

4. The graph should be titled and the axes should be labeled with units.

5. Print a copy of the graph (not the data) for the report.

Part 3: Hydrochloric Acid + Magnesium Oxide

The analysis of this reaction is performed using the same method as used in Part 2.

Heat of formation values for selected materials

Material	ΔH_f° (kJ/mol)
H ₂ O(l)	-285.9
H ₂ O(g)	-241.8
MgCl ₂ (s)	-641.8
MgCl ₂ (aq)	-801.3
HCl(g)	-92.5
HCl(aq)	-167.2

Questions

Answer the following questions and include them in your report.

1. Show the Hess's law calculations, including the manipulation of chemical equations, used to determine the enthalpy change for Part 3.
2. Consider the percent error values you obtained for Parts 2 and 3. In a few sentences describe the most important factors in the experimental error.
3. Why is the experiment performed in a thermos, as opposed to in a beaker?
4. What does it mean to say that the enthalpy of formation is at standard state?
5. What does the term adiabatic mean? Was this experiment performed under adiabatic conditions?
6. Calculate the standard heat of combustion for the following molecules:
 - a. ethanol
 - b. methanol
 - c. hydrogen gas

Based on the values you obtained which material gives off the most energy per gram? Which would make the best fuel and why?

7. Turn in a typed one-page discussion of your results. What were your results? How do these results compare with the result you would expect? If there are significant discrepancies between your results and the expected results, what are the sources of those discrepancies?

Observations and Notes
Experiment 8: Thermochemistry

Date _____

Part 1: Citric Acid + Sodium Hydrogen Carbonate

Heat capacity of solution (J/g°C) 4.68

Mass of NaHCO₃ (g) _____

Volume of citric acid (mL) _____

Molarity of citric acid (mol/L) _____

Final temperature (T₂) _____

Initial temperature (T₁) _____

Temperature change ($\Delta T = T_2 - T_1$) _____

Part 2: Hydrochloric Acid + Magnesium

Heat capacity of solution (J/g°C) 4.68

Mass of magnesium (g) _____

Volume of HCl (mL) _____

Final temperature (T₂) _____

Initial temperature (T₁) _____

Temperature change ($\Delta T = T_2 - T_1$) _____

Part 3: Hydrochloric Acid + Magnesium Oxide

Heat capacity of solution (J/g°C) 4.68

Mass of magnesium oxide (g) _____

Volume of HCl (mL) _____

Final temperature (T₂) _____

Initial temperature (T₁) _____

Temperature change ($\Delta T = T_2 - T_1$) _____

Calculations Sheet
Experiment 8: Thermochemistry

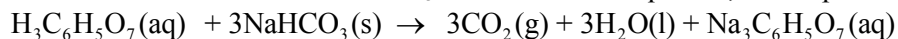
Part 1: Citric Acid + Sodium Hydrogen Carbonate

The strategy with this set of calculations is to determine the amount of heat transferred per one mole of the limiting reagent in the experiment. The limiting reagent in Part 1 is sodium hydrogen carbonate. To determine the amount of heat transferred in the reaction we use $\Delta H = -ms\Delta T$. Once this value has been calculated then the units are converted from Joules to kilojoules.

Volume of citric acid solution (mL)	_____
Density of citric acid solution (g/mL)	_____ 1.02 _____
Mass of citric acid solution (g) (d=m/V)	_____
Specific heat capacity of citric acid solution (J/g°C)	_____ 4.68 _____
Change in temperature for reaction (°C)	_____
ΔH (J) ($-ms\Delta T$)	_____
Mass NaHCO ₃ (g)	_____
Moles NaHCO ₃ (mol)*	_____
ΔH per mole of NaHCO ₃ (J/mol) [use $\frac{\Delta H}{\text{moles NaHCO}_3}$]	_____
ΔH per 3 moles of NaHCO ₃ (J/mol)**	_____
ΔH per 3 moles of NaHCO ₃ in kJ/mol (1 kJ = 1000 J)	_____ kJ/mol

*Use the mass and molar mass of NaHCO₃

**There are three moles of NaHCO₃ in the balanced equation, so ΔH per mol NaHCO₃ is multiplied by 3.



Calculations Sheet
Experiment 8: Thermochemistry

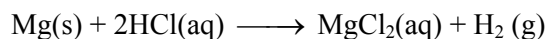
Part 2: Hydrochloric Acid + Magnesium

The strategy for these calculations are similar to those in Part 1. In Part 2, magnesium is the limiting reagent.

Volume of hydrochloric acid solution (mL)	_____
Density of hydrochloric acid solution	_____ 1.02 g/mL
Mass of hydrochloric acid solution (g) (d=m/V)	_____
Specific heat capacity of hydrochloric acid solution	_____ 4.68 J/g°C
Change in temperature for reaction (°C)	_____
ΔH (-ms ΔT)	_____ J
Mass Mg (g)	_____
Moles Mg (mol)*	_____
ΔH per mole of Mg (J/mol) $\left(\frac{\Delta H}{\text{moles Mg}} \right)$ *	_____
ΔH per mole of Mg in kJ/mol (1 kJ = 1000 J)	_____ kJ/mol

* Use the mass and atomic mass of Mg

**The amount of heat we measured is, according to the equation below, per 1 mol of Mg.



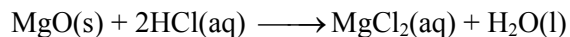
Part 3: Hydrochloric Acid + Magnesium Oxide

In Part 3 magnesium oxide is the limiting reagent.

Volume of hydrochloric acid solution (mL)	_____
Density of hydrochloric acid solution	_____ 1.02 g/mL
Mass of hydrochloric acid solution (grams)	_____
Specific heat capacity of hydrochloric acid solution	_____ 4.68 J/g°C
Change in temperature for reaction (°C)	_____
ΔH ($-ms\Delta T$)	_____ J
Mass MgO (grams)	_____
Moles MgO (mol)*	_____
ΔH per mole of MgO (J/mol) $\left(\frac{\Delta H}{\text{moles MgO}} \right)**$	_____
ΔH per 1 mole Mg in kJ/mol (1 kJ = 1000 J)	_____ kJ/mol

* Use the mass and molar mass of MgO

**The amount of heat we measured is, according to the equation below, per 1 mole of MgO:



Part 1: Citric Acid + Sodium Hydrogen CarbonateExperimental enthalpy change (ΔH) _____ kJ/mol

Is this reaction endothermic or exothermic? _____

Part 2: Magnesium + Hydrochloric AcidExperimental enthalpy change (ΔH) _____ kJ/molHandbook value for enthalpy change (ΔH) _____ kJ/mol*Percent error for enthalpy change (ΔH) _____

Is this reaction endothermic or exothermic? _____

Part 3: Magnesium Oxide + Hydrochloric AcidExperimental enthalpy change (ΔH) _____ kJ/molHandbook value for enthalpy change (ΔH) _____ kJ/mol*Percent error for enthalpy change (ΔH) _____

Is this reaction endothermic or exothermic? _____

* The handbook value for the enthalpy change for this reaction can be found from the heats of formation tables in any general chemistry textbook (including Chemistry Matters and Its Changes, 4th edition, Brady and Senese, Appendix C, p. A18-A21). There is also a table of selected values on page 65 of this manual.

Hess's Law(1) $\text{MgO(s)} + 2\text{HCl(aq)} \longrightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{O(l)}$ _____ kJ/mol(2) $\text{Mg(s)} + 2\text{HCl(aq)} \longrightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{(g)}$ _____ kJ/mol(3) $\text{H}_2\text{(g)} + 1/2\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)}$ $\Delta H = -285.8$ kJ/mol(4) $\text{Mg(s)} + 1/2\text{O}_2\text{(g)} \longrightarrow \text{MgO(s)}$ _____ kJ/mol**Handbook value for enthalpy change (ΔH) _____ kJ/molPercent error for enthalpy change (ΔH) _____

** Combine equations 1-3 so that when added together the result is equation 4.

