

Reading assignment: Chang, Chemistry 10th edition, pp. 249-258.

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, 1.5 M citric acid solution, 10-g sodium hydrogen carbonate (sodium bicarbonate), 1.0 M hydrochloric acid solution, 12 cm strip (0.1 g) of magnesium metal, 1 g magnesium oxide.

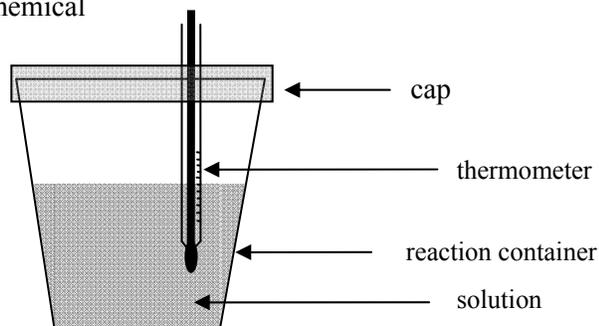
Be sure to bring a USB flash drive to the laboratory for saving data.

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. 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

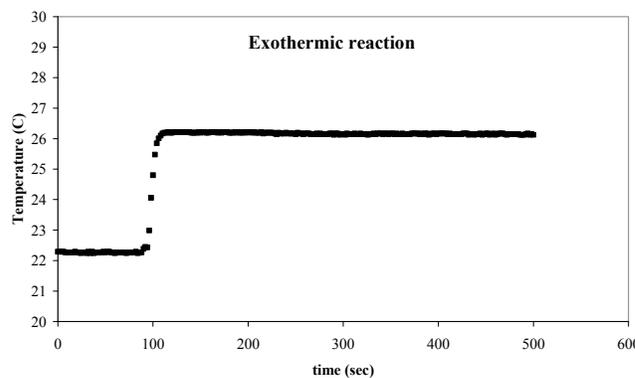
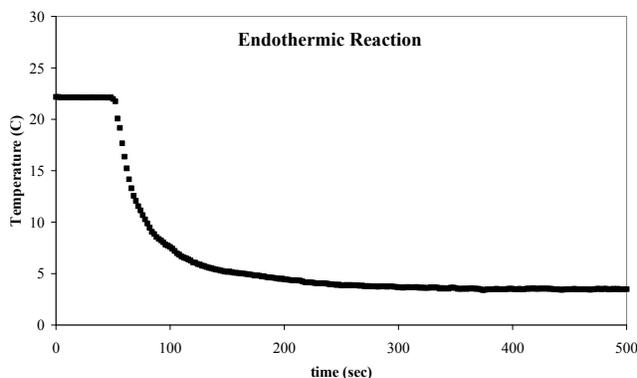
If the reaction is exothermic then the temperature of the solvent (surroundings) will increase. If the reaction is endothermic then the temperature of the solvent (surroundings) will decrease. The change in temperature of the solvent can then be used to determine the amount of heat transferred:

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

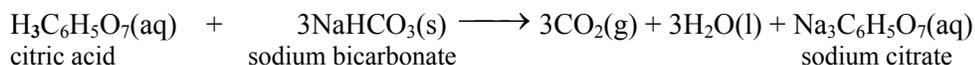
where ΔH is the change in enthalpy for the reaction (heat of reaction), m is the mass of the solution in which the reaction is occurring, s is a constant called the specific heat capacity, and ΔT is the change in temperature of the solution as the reaction takes place. The specific heat capacity depends 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).

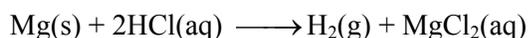
Material	$s \left(\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right)$
alcohol (ethanol)	2.45
copper	0.39
gold	0.13
graphite	0.71
iron	0.45
lead	0.13
silver	0.24
water (l)	4.18



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 ($\Delta H > 0$):

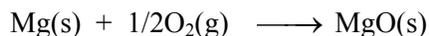


The second system we will study is the reaction of magnesium metal with hydrochloric acid. This reaction is exothermic ($\Delta H < 0$)



Combustion Reactions

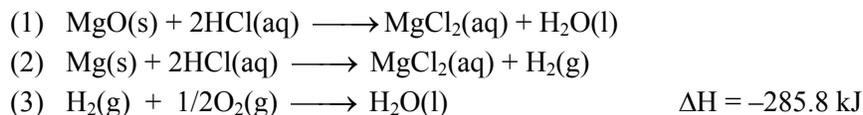
For some reactions the measure the amount of heat released or absorbed is performed in a constant volume calorimeter. One such example is magnesium reacting with oxygen gas to form magnesium oxide:



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).

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:



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. Determine the change in temperature of the reaction before moving on 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. Determine the change in temperature of the reaction as described on page 6 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. Determine the change in temperature of the reaction as described in page 6.
9. Print the graph in landscape format.

Part 1: Citric Acid + Sodium Hydrogen Carbonate

The temperature-time 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.

Part 2: Hydrochloric Acid + Magnesium

The temperature-time 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 maximum temperature for the curve.

Part 3: Hydrochloric Acid + Magnesium Oxide

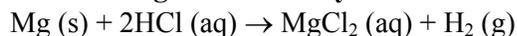
The analysis of this reaction is performed using the same method as used in Part 2.

We can determine how close our experiment is to the accepted literature values by performing percent error calculations.

Handbook heat of formation values for selected materials

Material	$\Delta H^{\circ}_f(\text{kJ}\cdot\text{mol}^{-1})$	Material	$\Delta H^{\circ}_f(\text{kJ}\cdot\text{mol}^{-1})$
H ₂ O(l)	-285.9	HCl(aq)	-167.2
H ₂ O(g)	-241.8	HCl(g)	-92.5
MgCl ₂ (s)	-641.8	MgCl ₂ (aq)	-801.3
MgO (s)	-601.2		

Part 2: Magnesium and hydrochloric acid

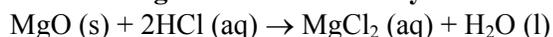


The literature value is found by summing the heats of formation for the products and reactants and taking the difference:

$$\Delta H^{\circ}_{\text{reaction}} = \text{Sum} (\Delta H^{\circ}_f, \text{products}) - \text{Sum} (\Delta H^{\circ}_f, \text{reactants})$$

By definition, heats of formation for elements in their standard states are equal to zero. So for hydrogen and magnesium the values are zero. Heats of formation for hydrochloric acid and magnesium chloride is shown in the table above. Note that each table value refers to the amount of heat per 1 mole of material.

Part 3: Magnesium oxide and hydrochloric acid



The literature value is found in the same way as in Part 2. In this case, there are no elements. So we need to use four values from the table.

$$\% \text{ error} = \frac{|\text{literature value} - \text{experimental value}|}{\text{literature value}} \times 100$$

Hess's Law: Finding the heat of formation of magnesium oxide

The heat of formation of magnesium oxide can be found in the table on this page. It can also be found by combining equations 1-3 on page 12 and adding the heats of reaction for those equations. Note that one of the equations must be reversed. Be sure to use your experimental values for equations 1 and 2 in this calculation.

Observations and Notes
Thermochemistry

Date _____

Part 1: Citric Acid + Sodium Hydrogen Carbonate

Heat capacity of solution	<u>4.68</u>	<u>J·g⁻¹°C⁻¹</u>
Mass of NaHCO ₃ (g)	_____	<u>g</u>
Volume of citric acid (mL)	_____	<u>mL</u>
Molarity of citric acid (mol/L)	_____	<u>mol·L⁻¹</u>
Final temperature	_____	<u>°C</u>
Initial temperature	_____	<u>°C</u>
Temperature change	_____	<u>°C</u>

Part 2: Hydrochloric Acid + Magnesium

Heat capacity of solution	<u>4.68</u>	<u>J·g⁻¹°C⁻¹</u>
Mass of magnesium	_____	<u>g</u>
Volume of HCl	_____	<u>mL</u>
Final temperature	_____	<u>°C</u>
Initial temperature	_____	<u>°C</u>
Temperature change	_____	<u>°C</u>

Part 3: Hydrochloric Acid + Magnesium Oxide

Heat capacity of solution (J/g°C)	<u>4.68</u>	<u>J·g⁻¹°C⁻¹</u>
Mass of magnesium oxide	_____	<u>g</u>
Volume of HCl	_____	<u>mL</u>
Final temperature	_____	<u>°C</u>
Initial temperature	_____	<u>°C</u>
Temperature change	_____	<u>°C</u>

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

*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.



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

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

* 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 Carbonate

Experimental enthalpy change _____ kJ·mol⁻¹

Is this reaction endothermic or exothermic? _____

Part 2: Magnesium + Hydrochloric Acid

Experimental enthalpy change (from page 10) _____ kJ·mol⁻¹

Handbook value for enthalpy change (see page 6) _____ kJ·mol⁻¹

Percent error for enthalpy change (see page 6) _____

Is this reaction endothermic or exothermic? _____

Part 3: Magnesium Oxide + Hydrochloric Acid

Experimental enthalpy change (from page 11) _____ kJ·mol⁻¹

Literature value for enthalpy change (see page 6) _____ kJ·mol⁻¹

Percent error for enthalpy change (see page 6) _____

Is this reaction endothermic or exothermic? _____

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⁻¹

(2) $\text{Mg(s)} + 2\text{HCl(aq)} \longrightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{(g)}$ _____ kJ·mol⁻¹

(3) $\text{H}_2\text{(g)} + 1/2\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)}$ _____ -285.8 kJ·mol⁻¹

(4) $\text{Mg(s)} + 1/2\text{O}_2\text{(g)} \longrightarrow \text{MgO(s)}$ (see page 6) _____ kJ·mol⁻¹

Literature value for enthalpy change (see page 6) _____ kJ·mol⁻¹

Percent error for enthalpy change (see page 6) _____