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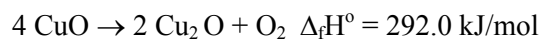
PRE-LABORATORY ASSIGNMENT EXPERIMENT 6

1. Is the sign of $\Delta_r H$ for an exothermic reaction positive or negative? Why?

2. When 4.21 grams of potassium hydroxide are added to 250 mL of water, the temperature rises by 4.14 °C. Assume that the density and specific heat of the dilute aqueous solution are the same as those of H_2O and calculate the molar heat of solution of potassium hydroxide.

3. Calculate the standard heat of formation of copper(I) oxide using the following data:

$$CuO \rightarrow Cu + \tfrac{1}{2} O_2 \quad \Delta_f H° = 157.3 \text{ kJ/mol}$$

$$4 CuO \rightarrow 2 Cu_2 O + O_2 \quad \Delta_f H° = 292.0 \text{ kJ/mol}$$

EXPERIMENT 6 THERMOCHEMISTRY

Introduction

Thermochemistry is the study of the relationship between chemical reactions and energy changes. Thermochemistry has many practical applications. For example, using thermochemistry:

(1) mining engineers can calculate how much fuel will be needed to prepare metals from their ores,
(2) structural engineers can determine how much heat will be evolved by cement as it sets, and
(3) the number of Calories in an edible compound can be determined.

The experimental measurement of the heat change that results from a chemical or physical process is known as *calorimetry.* Calorimetry is of interest to chemists because one of the fundamental characteristics of a chemical reaction is the evolution or absorption of heat. This heat change is the result of the breakage or formation of chemical bonds during the chemical reaction. Breaking a chemical bond requires energy; thus, it is an endothermic process. Forming a chemical bond releases energy; thus, it is an exothermic process. For example, coal is burned in oxygen (combusted) to produce carbon dioxide and heat in the following exothermic reaction:

$$coal + O_2 \rightarrow CO_2 + heat$$
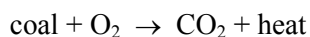
In this example, heat is released because the products release more energy in forming bonds than is absorbed by the reactants in breaking bonds.

A calorimeter is an apparatus that is used to measure heat flow. It consists of an insulated container (you will use a Styrofoam cup in this experiment) fitted with a thermometer. The aqueous solution to be studied is placed inside the insulated container and the temperature change of the solution is monitored as the reaction proceeds. The calorimeter and its contents can be thought of as an isolated system, insulated from its surroundings, from which or into which no heat can be transferred.

Refer to the sections on calorimetry and enthalpy in your textbook for additional information and sample problems.

Heat of Solution

When ionic solids dissolve in a solvent, the solid is first surrounded by solvent molecules and an attraction between the solute ions and solvent molecules forms. This attraction allows the solvent molecules to pull the individual solute ions away from the solid and, as a result, the solid breaks apart. Eventually, each individual solute ion becomes completely surrounded by solvent molecules and a solution forms. This process is called *solvation,* and, in the case where water is the solvent, *hydration.* Solvation/hydration can be either exothermic or endothermic. The enthalpic quantity associated with solvation/hydration is the *molar heat of solution* which is defined as the quantity of heat evolved or absorbed when one mole of a solid solute is solvated/hydrated.

A commercial application of an endothermic heat of solution is the instant cold packs used in athletics to treat sprains. In these cold packs, water and salt are initially separated and then mixed by squeezing the pack to break the separation device. Heat is absorbed in the endothermic hydration process, so the pack quickly becomes extremely cold. Hot packs, which take advantage of the exothermic heat of solution, work in an analogous manner, releasing heat when the contents are mixed.

In the experimental measurement of the heat of solution of a substance, a known mass of solute is added to a known volume of water in a calorimeter. The temperature of the water is measured before mixing and as a function of time after mixing. These data are plotted to find the change in temperature, ΔT, and then the heat

absorbed or generated in the reaction ($q_{reaction}$) and the molar heat of solution *(Δ_rH)* are calculated. In part A-(1) and A-(2) of this experiment, you will determine the molar heats of solution of two ionic solutes, sodium hydroxide (NaOH) and potassium nitrate (KNO_3).
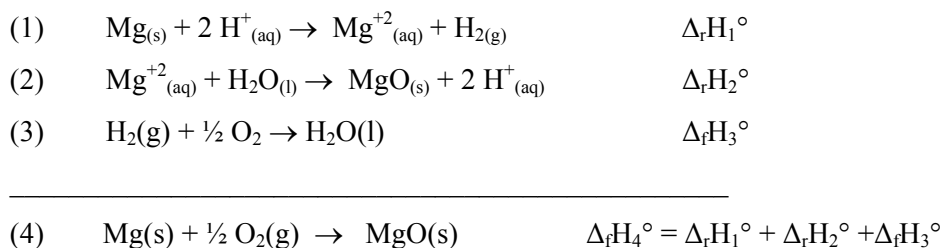
Heat of Neutralization

An acid (an H^+ donor) reacts with a base (an OH^- donor) to form water in a neutralization reaction represented by the following net ionic equation:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$
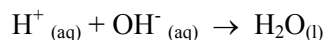
The heat of reaction associated with a neutralization reaction is referred to as the *heat of neutralization.* In parts A-(3) and A-(4) of this experiment, you will react hydrochloric acid (HCl) with sodium hydroxide (NaOH) and measure the heat of neutralization. The heat of neutralization is dependent on the number of moles of H^+ and OH^- present, not the particular acid or base used. The nature of the spectator ions, sodium and chloride in this case, is not important.

Hess 's Law – Part B

        In part B of this experiment, we will be finding the enthalpy of formation for MgO(s) using an indirect method. According to Hess's Law, if two or more reactions can be added to give a net reaction, $\Delta H°$ for the net reaction is simply the sum of the $\Delta H°$'s for the reactions which are added. Consider the following three reactions:

(1) $Mg_{(s)} + 2\ H^+_{(aq)} \rightarrow Mg^{+2}_{(aq)} + H_{2(g)}$ $\Delta_rH_1°$

(2) $Mg^{+2}_{(aq)} + H_2O_{(l)} \rightarrow MgO_{(s)} + 2\ H^+_{(aq)}$ $\Delta_rH_2°$

(3) $H_2(g) + ½\ O_2 \rightarrow H_2O(l)$ $\Delta_fH_3°$

_____

(4) $Mg(s) + ½\ O_2(g) \rightarrow MgO(s)$ $\Delta_fH_4° = \Delta_rH_1° + \Delta_rH_2° + \Delta_fH_3°$

Notice that when the three reactions are added, they form the formation reaction for MgO. Analogously, when we add the enthalpies for the three reactions, they give the enthalpy change associated with the formation reaction.
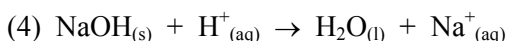
Objectives

        In this experiment, you will (1) measure the heat of solution of sodium hydroxide, (2) measure the heat of solution of potassium nitrate, (3) measure the heat of neutralization for an acid-base reaction, (4) measure the heat of reaction for the reaction of solid sodium hydroxide with aqueous hydrochloric acid, (5) compare your experimental results with calculated values, and (6) utilize Hess's Law to determine the enthalpy of reaction for a reaction you will not actually perform, the formation of MgO(s).

Experimental Procedure
Part A.

      Measurements will be made using a calorimeter consisting of a Styrofoam cup and cover, thermometer, and magnetic stir bar. For stability, the Styrofoam cup should be placed in a beaker. The solutions should be stirred with a magnetic stir bar and a magnetic stirrer. **You will work with a partner for this experiment.**

      The balanced net ionic equations for the four reactions in part A are:

(1) $KNO_{3(s)} \rightarrow K^+_{(aq)} + NO_3^-{}_{(aq)}$

(2) $NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

(3) $OH^-_{(aq)} + H^+_{(aq)} \rightarrow H_2O_{(l)}$

(4) $NaOH_{(s)} + H^+_{(aq)} \rightarrow H_2O_{(l)} + Na^+_{(aq)}$
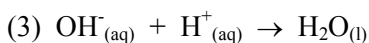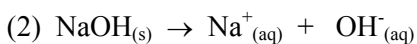
1.   *Heat of Solution of KNO₃.* Weigh approximately 5 g of potassium nitrate (KNO_3) on an analytical balance and record the mass to the nearest 0.001 g. Place 50.0 mL of distilled water in your calorimeter using a graduated cylinder. Record the volume of water to the nearest 0.1 mL. Using your thermometer, record the temperature of the water at 30-second intervals for three minutes. Add the solid KNO_3 to the water and stir rapidly with a magnetic stirrer as your partner takes temperature readings every 10 seconds. Continue taking temperature readings for at least five readings after the direction of the temperature change reverses. When done, wash and dry the calorimeter.

2.   *Heat of Solution of NaOH.* Weigh about 2 g (12 pellets) of sodium hydroxide (NaOH) on an analytical balance and record the mass to the nearest 0.001 g. Do this weighing as quickly as possible since the NaOH will slowly absorb water. Also, be sure to use a weighing boat and **<u>do not touch the NaOH pellets with your fingers!</u>** Place 50.0 mL of distilled water in your the calorimeter using a graduated cylinder. Record the volume of the water to the nearest 0.1 mL. Proceed as in part (1) above. Remember to take five readings after the direction of the temperature change reverses and to wash and dry the calorimeter when you are finished.

3.   *Heat of Neutralization.* Place 50.0 mL (record the volume to the nearest 0.1 mL) of 1.0 M HCl in your calorimeter and record the temperature at 30-second intervals for three minutes. Pour 50.0 mL (record the volume to the nearest 0.1 mL) of 1.0 M NaOH into the HCl solution in the calorimeter and stir rapidly with a magnetic stirrer as the temperature is recorded at 10-second intervals. Again, take at least five readings after the direction of the temperature change reverses and clean and dry the calorimeter after use.

4.   *Heat of Reaction.* Weigh another 2 g sample of NaOH as in step two above. Place 50.0 mL (record the volume to the nearest 0.1 mL) of 1.0 M HCl in your calorimeter and record the temperature at 30-second intervals for three minutes. Add the solid NaOH to the HCl solution in the calorimeter and stir rapidly with a magnetic stirrer as your partner takes temperature readings at 10-second intervals after mixing. Again, take at least five readings after the direction of the temperature change reverses and clean and dry the calorimeter after use.

Experimental Procedure
Part B. Enthalpy of Reaction and Verification of Hess's Law

(**Again work in partners.**)

The calorimeter and the thermometer setup will be the same as that used in Part A. Rinse the inner cup of your calorimeter thoroughly with distilled water and dry. Assemble your calorimeter, being certain that there is no water in the space between the two cups.

(a) Weigh a sample containing 0.45 - 0.55 g of 20-mesh granulated magnesium. Load the calorimeter with 100 mL of 1.0 M HCl, and measure the temperature until it stabilizes. Record this reading as your initial temperature. Then add the Mg. Stir vigorously as the metal dissolves, and record the temperature every 30 seconds. Continue taking temperature readings for at least five readings after the direction of the temperature change reverses.

(b) When the reaction has reached completion, cautiously add small amounts of sodium bicarbonate to neutralize the remaining HCl. When no fizzing is observed after an addition, you may safely dispose of the neutralized solution by washing it down the drain. When done, wash and dry the calorimeter.

(c) Calculate the mass of MgO that would contain the same number of moles of Mg as you used in part (a). Weigh enough MgO to be within 5% of this value. Clean and dry the calorimeter as before, and load once again with 100 mL of 1.0 M HCl. Proceed as in part (a), but note that it may take longer for the MgO(s) to dissolve than it did for the Mg(s). Vigorous stirring is essential. Neutralize your solution as in part (b) before disposing of it.

Graphical Treatment of Data

In this experiment, it is not valid to make the assumption that no heat is exchanged between the contents of the calorimeter and the room. This heat transfer may be corrected for using graphical techniques if data are collected over a period of time. For this reason, at least five measurements were made after the direction of the temperature change reversed. You will plot graphs of the four data sets in order to correct for the heat exchanged. Figure 1 shows a set of data taken for the determination of a heat of solution. The time of mixing was at 190 seconds and data were recorded for 330 seconds.

In order to determine the temperature change, ΔT, which would have occurred if the mixing was instantaneous, it is assumed that the loss of heat to the room is constant and linear. This is a reasonably valid assumption if the temperature of the calorimeter contents is not vastly different from room temperature. This assumption then allows the extrapolation back to the instant the reagents were mixed, 190 seconds in this example.

To determine ΔT as in Figure 2, use the following extrapolation procedure:

1.   Draw a vertical line, which passes through the time corresponding to the time of mixing. In this example, the line was drawn at *190* seconds.

2.   Draw best-fit straight lines through the approximately linear before mixing and after mixing data points which intersect the vertical line drawn in step one.

3.   Read the initial temperature (T_i) and final temperature (T_f) from the points of intersection of the vertical line and the two best-fit straight lines. In this example, T_i is 23.2 $^{\circ}$C and T_f is 29.4 $^{\circ}$C. The difference between these two temperatures ($T_f - T_i$) is the temperature change, ΔT. In this case, ΔT *is* 6.2 $^{\circ}$C (29.4 $^{\circ}$C - 23.2 $^{\circ}$C). See Figures 1 and 2 below.
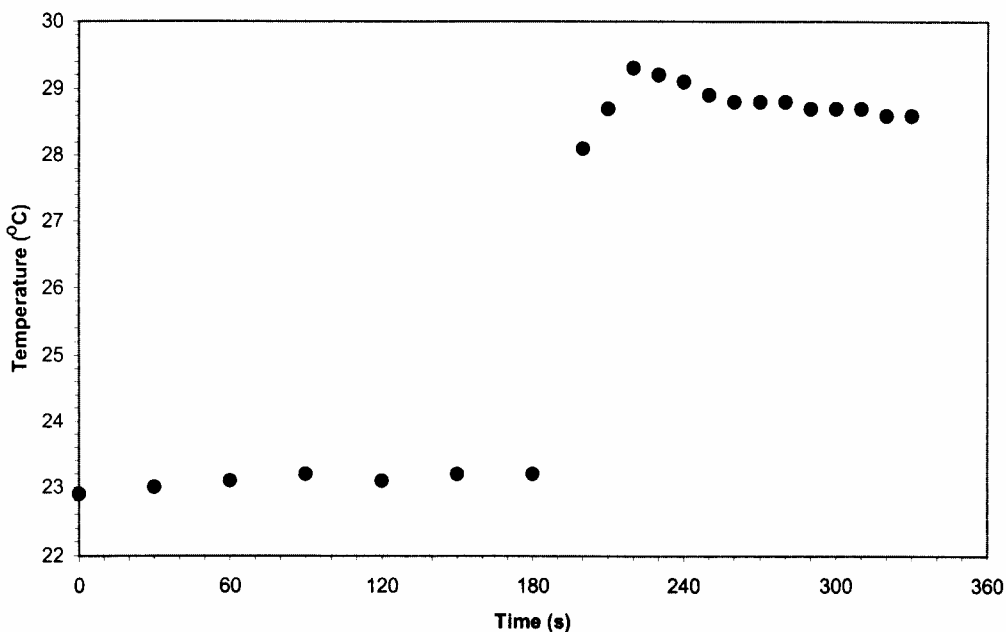

Figure 1. Plotted temperature-time data for an exothermic process.
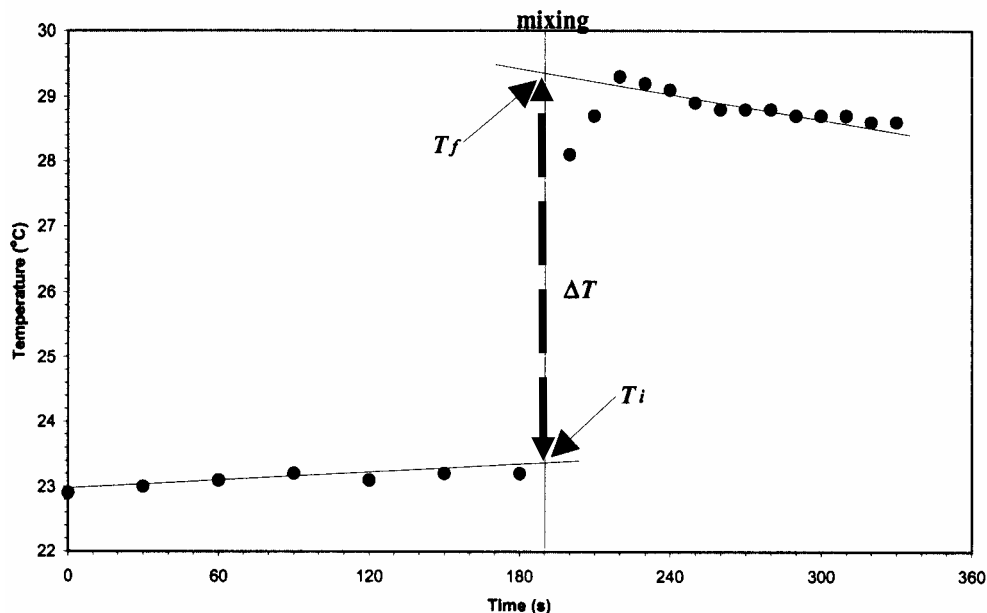Note that the plot for an endothermic process will show a drop in temperature between T_i and T_f.

Figure 2. Extrapolation of temperature-time data in Figure 1 to find the temperature change, ΔT.

Calculations

First, plot, <u>using Excel</u>, a graph of temperature versus time for each of your four data sets. For each data set, determine T_i, T_f, and ΔT from the temperature versus time graph using the extrapolation procedure (by hand) given above. Calculate $q_{solution}$ and then reverse the sign on $q_{solution}$ to obtain $q_{reaction}$. Lastly, convert $q_{reaction}$ to the molar change in enthalpy, ΔH. A sample calculation is provided below.

Sample Calculation for Heat of Solution

Given: 5.20 g of sodium carbonate (Na_2CO_3) is dissolved in 75.0 mL of distilled water in a calorimeter. The temperature of the water before the addition of the Na_2CO_3 was 26.0 °C. The temperature after mixing was 29.9 °C.

1. Mass of solution

   Calculate the mass of the water, m_w, in the calorimeter using the density of water, 1.00 g/mL.

   m_w = (volume of water) (density of water)
       = (75.0 mL) (1.00 g/mL)
       = 75.0 g
   The total mass of solution equals the mass of the water (m_w) plus the mass of solute (m_s).
   $m_T = m_w + m_s = 75.0 \text{ g} + 5.20 \text{ g} = 80.2 \text{g}$

2. $q_{solution}$ *(J)*

   Calculate the heat gained by the solution, $q_{solution}$. Use the specific heat of water, 4.184 J/g·°C, for C_w.

Note, you must find the ΔT by graphing your data and determining the initial and final temperatures as described in the section on the graphical treatment of the data.

$$q_{solution} \quad = m_T C_w \Delta T$$
$$= (80.2 \text{ g}) \, (4.184 \text{ J/g·°C}) \, (29.0 \text{ °C} - 26.0 \text{ °C})$$
$$= (80.2 \text{ g}) \, (4.184 \text{ J/g·°C}) \, (3.9 \text{ °C})$$
$$= 1300 \text{ J}$$

3. $q_{reaction}$ (J)

Reverse the sign on $q_{solution}$ to obtain the heat given off in the solvation process, $q_{reaction}$.

$$q_{reaction} = -q_{solution}$$
$$= -1300 \text{ J}$$

4. ΔH Experimental

Remember that the enthalpy change associated with this process, ΔH, is a molar quantity expressed in kJ/mol. Therefore, the mass of Na_2CO_3 solvated must be converted to moles using the molecular weight of Na_2CO_3.

$$\text{moles of } Na_2CO_3 \; = \; \frac{\text{grams of } Na_2CO_3 \text{ used}}{\text{molecular weight of } Na_2CO_3}$$

$$= \; \frac{5.20 \text{ g } Na_2CO_3}{106 \text{ g } Na_2CO_3/\text{mol } Na_2CO_3}$$

$$= \; 0.0491 \text{ mol } Na_2CO_3$$

Note that if the solute is a liquid, as in step A-(3) of the experiment, the moles of solute can be found by multiplying the volume in liters by the molarity:

moles of solute = (volume of solute [L]) (molarity of solute [mol/L])

Then, divide q_{sol} by the moles of Na_2CO_3 to give ΔH in J/mol.

$$\Delta_{sol}H = \frac{q_{reaction}}{\text{mol } Na_2CO_3}$$

$$= \; \frac{(-1300 \text{ J})}{(0.0491 \text{ mol } Na_2CO_3)}$$

$$= \; -26000 \text{ J/mol}$$

Finally, convert joules to kilojoules to give ΔH in the proper units.

$$\Delta_{sol}H = (-26000 \text{ J/mol}) \, (1 \text{ kJ} / 1000 \text{ J})$$
$$= -26 \text{ kJ/mol}$$

The negative sign on $\Delta_{sol}H$ indicates that the solvation of Na_2CO_3 is exothermic.

Comparison of Experimental Results with Literature Values

You will also compare your experimental results with literature values. To do this:

5.   a. Write a balanced net ionic equation for the reaction.

      b. Use the heats of formation in Table 1 to calculate the actual value of ΔH. Note that you do not need to do this for part A-(4). Recall that:

$\Delta_r H$ = (sum of ΔH_f of products) - (sum of ΔH_f of reactants)

Table 1. Heats of Formation*

Compound	ΔH_f (kJ/mol)
KNO_3 (s)	-492.7
$NaOH$ (s)	-426.7
H_2O (l)	-285.9
H^+ (aq)	0.0
OH^- (aq)	-229.9
KNO_3 (aq)	-457.8
$NaOH$ (aq)	-469.6

* R.C. Weast, ed., *Handbook of Chemistry and Physics,* 61st Ed., C.R.C. Press, Inc., 1980, pp. D67-D78 (converted from kcal/mol)

6.   Percent Error

Calculate a percent error by comparing your experimental value with the calculated result. Remember that errors of 10 % or more are not unreasonable.

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

Part A Data   (*DO NOT* TURN IN THIS PAGE)

Solution 1

Time	Temp (°C)	Time	Temp (°C)
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____
____	____	____	____

Solution 2	**Time**	**Temp (°C)**	**Time**	**Temp (°C)**
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____
	____	____	____	____

Part A Data   (*DO NOT* TURN IN THIS PAGE)

Solution 3	Time	Temp (°C)	Time	Temp (°C)
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____

Solution 4	Time	Temp (°C)	Time	Temp (°C)
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____

Data and Results: **Name:** _____

Part A *(Turn this and the following pages in)*   **Section:_____**

Reaction 1: Heat of Solution KNO₃

Mass KNO₃ _____   **Moles KNO₃_____**   **Solution volume_____**

Mass of solution (g)   _____   **Initial T (°C) _____ Final T (°C)_____**

Δ_r**T_____ (careful of your sign)**

q solution (J) _____   **q reaction (J) _____**

Δ_r**H experimental_____** Δ_r**H literature_____**

Percent Error_____

Data and Results: **Name: _____**

Part A   **Section:_____**

Reaction 2: Heat of Solution NaOH

Mass NaOH _____   **Moles NaOH _____**   **Solution volume_____**

Mass of Solution (g) _____   **Initial T (°C) _____ Final T (°C)_____**

Δ_rT_____ (careful of your sign)

q solution (J) _____   **q reaction (J) _____**

Δ_rH experimental_____   **Δ_rH literature_____**

Percent Error_____

Data and Results: **Name: _____**

Part A   **Section:_____**

Reaction 3: Heat of Neutralization

mL NaOH _____   **Moles NaOH _____**   **Solution volume (mL) _____**

Mass of Solution (g)   _____   **Initial T (°C) _____ Final T (°C)_____**

Δ_r**T_____ (careful of your sign)**

q solution (J) _____   **q reaction (J) _____**

Δ_r**H experimental_____** Δ_r**H literature_____**

Percent Error_____

Data and Results: **Name:** _____

Part A   **Section:**_____

Reaction 4: Heat of Reaction NaOH + HCl

Mass NaOH _____   **Moles NaOH** _____   **Solution volume**_____

Mass of Solution (g) _____   **Initial T (°C)** _____ **Final T (°C)**_____

Δ_r**T**_____ **(careful of your sign)**

q solution (J) _____   **q reaction (J)** _____

Δ_r**H experimental**_____

Part B Data   (*DO NOT* TURN IN THIS PAGE)

Mg Reaction Data

Time	Temp (°C)	Time	Temp (°C)
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

MgO Reaction Data

Time	Temp (°C)	Time	Temp (°C)
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

Data and Results: Name: _____

Part B *(Turn this page in)*   Section:_____

	Mg	MgO
Mass of sample and weighing paper	_____ g	_____ g
Mass of weighing paper	_____ g	_____ g
Mass of sample	_____ g	_____ g
Moles of sample	_____ mol	_____ mol
Volume of solution	_____ mL	_____ mL
Initial temperature (T_i)	_____ °C	_____ °C
Final temperature (T_f)	_____ °C	_____ °C
$\Delta_r T$ reaction (watch sign)	_____ °C	_____ °C
mass of solution	_____ g	_____ g
q solution	_____ J	_____ J
q reaction	_____ J	_____ J
$\Delta_r H$ reaction	_____ kJ/mol	_____ kJ/mol

Hess's Law Calculation: Refer to reactions in introduction.

$\Delta_r H°_1$ _____

$\Delta_r H°_2$ _____

$\Delta_r H°_3 = -285.9$ kJ/mol   (heat of formation of water)

Combine the appropriate heats of reaction and use Hess's law to find $\Delta H°_f(MgO)$.

SHOW YOUR WORK HERE:

Literature value for $\Delta_f H°$ MgO (CRC handbook)   _____

Percent Error from literature   _____