Enthalpy of Formation of Magnesium Oxide

LEARNING OBJETIVES

The objectives of this laboratory are to:
1. Determine the enthalpy of reaction for two experimental reactions.
2. Apply Hess's Law to determine $\Delta H_f°$ for MgO.

BACKGROUND

In this laboratory, we will introduce one of the most often used techniques in thermochemistry, calorimetry. Although we often think of calorimetry in terms of finding the number of calories in a certain amount of food, calorimetry is valuable to the chemist in measuring basic thermodynamic data. Along with learning calorimetry techniques, you will use the data you collect, along with heats of formation and Hess's Law, to determine $\Delta H_f°$ for MgO.

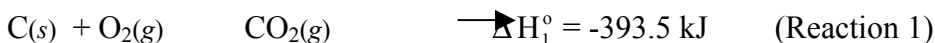**Enthalpy and Hess's Law**

The enthalpy change, $\Delta H°_{rxn}$, of a chemical reaction is called the heat of reaction and represents the amount of heat gained or lost by the reaction system as the reaction proceeds from reactants to products. The heat formation, $\Delta H_f°$, is defined as the $\Delta H°_{rxn}$ when one mole of a compound is formed from its elements in their standard states. Enthalpy is a state function; the enthalpy change of a reaction is independent of its path and depends only on the initial and final states of the reactants and products. This principle, applied to enthalpy, is known as Hess's Law. *Hess's Law states the enthalpy change of a reaction is the same whether it occurs in one step or in many steps.*

For example, the enthalpy change for the reaction between carbon and oxygen to form carbon monoxide:

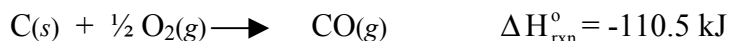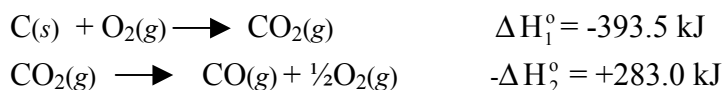$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H°_{rxn} = ?$$

cannot be directly measured since carbon dioxide is also a product of this reaction (there is no way to run this reaction to ONLY give CO.) However, to obtain the desired heat of reaction, we can react carbon (rxn.1) and carbon monoxide (rxn. 2) in large excesses of oxygen to form carbon dioxide and measure the enthalpies of these reactions:

$$C(s) + O_2(g) \qquad CO_2(g) \qquad \Delta H_1° = -393.5 \text{ kJ} \qquad \text{(Reaction 1)}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \qquad CO_2(g) \qquad \Delta H_2° = -283.0 \text{ kJ} \qquad \text{(Reaction 2)}$$

According to Hess's Law, we can combine the above two reactions in a manner that will give the desired reaction. Note that if we reverse reaction 2 and add it to reaction 1, we

will obtain the desired reaction (see below). Since we reversed reaction 2, we must also change the sign on ΔH_2^o. Summing the resultant reactions yields the desired reaction and summing the resultant ΔH's yields the desired ΔH_{rxn}^o. The same chemical species on opposite sides of the arrow can be canceled. Mark which species below cancel out.
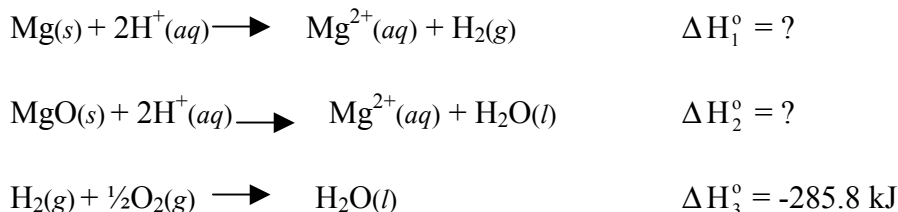
$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H_1^o = \text{-393.5 kJ}$$
$$CO_2(g) \longrightarrow CO(g) + \tfrac{1}{2}O_2(g) \qquad\qquad \text{-}\Delta H_2^o = \text{+283.0 kJ}$$

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad\qquad \Delta H_{rxn}^o = \text{-110.5 kJ}$$

Heat of Reaction

In this laboratory, you will apply Hess's Law in determining ΔH_{rxn}^o for the following reaction:

$$Mg(s) + \tfrac{1}{2}O_2(g) \longrightarrow MgO(s) \qquad\qquad \Delta H_{rxn}^o = ?$$
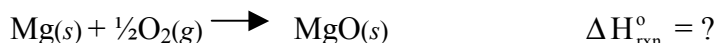
This reaction is extremely exothermic and therefore very difficult to accurately measure calorimetrically. However, we can apply Hess' law to find the heat of formation for MgO by combining a series of reactions that are much safer and more suitable for a calorimetry experiment. For example, these three reactions may be used:

$$Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g) \qquad\qquad \Delta H_1^o = ?$$

$$MgO(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l) \qquad\qquad \Delta H_2^o = ?$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad\qquad \Delta H_3^o = \text{-285.8 kJ}$$

Using the techniques presented in the CO example above, you can combine these equations to find ΔH_{rxn}^o for MgO (see the prelab):

$$Mg(s) + \tfrac{1}{2}O_2(g) \longrightarrow MgO(s) \qquad\qquad \Delta H_{rxn}^o = ?$$
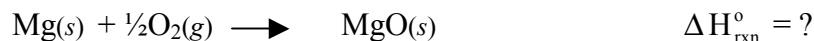
Correctly figuring out how to add the equations together to get the reaction shouldn't pose a problem; however, before we can obtain the value of ΔH_{rxn}^o, we need to **experimentally** determine the values of ΔH_1^o or ΔH_2^o values using calorimetry

Calorimetry

Almost any type of container can be used as a calorimeter, but to collect good data we must account for all heat absorbed or evolved by the chemical process. Therefore, we want a container that traps the heat in a location where it can be measured rather than spreading the heat around. In this experiment you will use Styrofoam cups, since they are excellent at trapping heat (an insulator).

The important thing to remember when conducting thermochemistry experiments is you *must account for all heat gained or lost* during a reaction. For example, if an exothermic reaction occurs in a well-insulated calorimeter, the heat can be transferred two places: (1) the reaction mixture, which can be measured as a temperature rise, and (2) the walls of the calorimeter. In this experiment we will assume the cup is a perfect insulator and as such, no heat is <u>not</u> transferred between the calorimeter and the surroundings. Therefore, the following statement and equation applies:

heat from rxn = heat absorbed by calorimeter + heat absorbed by rxn. mixture

$$-q_{rxn} = q_{cal} + q_{liq}$$
(where q is heat)

NOTE: This equation DOES NOT necessarily mean that the reaction in the calorimeter is exothermic. The (-) sign indicates that the heat lost by the chemical reaction must be exactly equal to the total heat gained and vice-versa.

Now let's examine each of the terms in the equation.

Heat from Reaction (q_{rxn}): In our system, q_{rxn} is equivalent to $n\Delta H°_{rxn}$, where n is the number of moles of the limiting reactant and $H°_{rxn}$ is the <u>molar enthalpy</u> of the reaction for the limiting reactant

$$NaOH(aq) + HCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O(l) \qquad \Delta H°_{rxn} = -57.7 \text{ kJ}$$
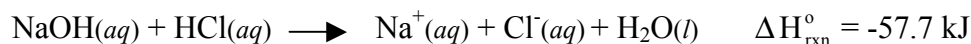
Heat Absorbed by the Calorimeter (q_{cal}): For our calorimeter, the heat simply changes the temperature of the calorimeter. We can replace q_{cal} by $C_{cal}\Delta T$, where C_{cal} is the heat capacity of the calorimeter and ΔT is the temperature change. Note the heat capacity is the amount of heat required to raise the temperature of a substance by 1°C. The units of heat capacity are usually J/°C. Thus we need the heat capacity of the calorimeter, C_{cal}, which is specific for each calorimeter. You will find C_{cal} for your calorimeter by performing a reaction for which ΔH_{rxn} is known. It should be noted C_{cal} cannot be negative, unless it is very warm in the room.

Heat Absorbed by Reaction Mixture (q_{liq}): This term is equal to $(m)(s)(\Delta T)$. The mass of the solution is represented *m* and is equal to the total volume of the solution times the density of solution. We simplify by using density equal to 1.00 g/mL since all the

solutions are dilute aqueous solutions. Specific heat is represented by s and is the heat capacity divided by mass. Specific heats allow the heat absorbing capabilities of different substances to be compared. Although for pure water the specific heat is 4.184 J/(g°C), when ions or molecules are dissolved in it the specific heat changes. For the NaOH and HCl reaction, the specific heat of the solution, s, is equal to 4.025 J/(g°C) while for the Mg and MgO reactions with HCl, s equals 3.862 J/(g°C). Using these terms we obtain:

$$-n\Delta H^{\circ}_{rxn} = C_{cal}\Delta T + (m)(s)(\Delta T)$$

where:

n	= number of moles of product found from limiting reagent
ΔH°_{rxn}	= heat evolved by the reaction
C_{cal}	= calorimeter constant (specific for your calorimeter)
ΔT	= temperature change resulting form the reaction
m	= mass of the solution
s	= specific heat of the solution

Note we used q = $(m)(s)(\Delta T)$ for the liquid in the calorimeter because we know its exact composition. For the calorimeter itself, however, a heat capacity, C_{cal}, was used because the exact calorimeter composition, shape, and size may vary form calorimeter to calorimeter.

Determining the Calorimeter Constant

Every calorimeter is different, not only due to its composition, but also it's size and shape. These factors determine the calorimeter's ability to absorb heat.   As a result, every calorimeter will have a different $C_{cal.}$ Therefore we must determine the unique value of C_{cal} before we can use it in the calorimetry equation and find the values of ΔH°_1 and ΔH°_2.

Now let's apply this concept to your experiment. First the calorimeter must be "calibrated" to find C_{cal}. This calibration is accomplished by producing a known quantity of heat from a reaction and measuring ΔT.   The following reaction will be used to determine C_{cal}.

$$NaOH(aq) + HCl(aq) \longrightarrow Na^{+}(aq) + Cl^{-}(aq) + H_2O(l) \qquad \Delta H^{\circ}_{rxn} = \text{-57.7 kJ}$$
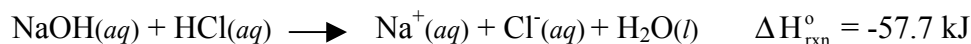
Since $\Delta H°_{rxn}$, the specific heat, and the quantities of the NaOH and HCl are known (assuming all volumes are additive), the only unknown in the equation is C_{cal}, which you can now calculate. Once the value of C_{cal} is known, you can use it in the calorimetry equation to determine your two unknown $\Delta H_f°$ values.

Measuring the Temperature Change

You will need to find ΔT, the temperature change for the reaction mixture and the calorimeter. However, you will not be able to simply measure the maximum temperature because the temperature may never actually reach the theoretical maximum. This irregular behavior is due to the calorimeter's inability to absorb heat as quickly as extrapolate to the maximum temperature for each of your experiments.

During this experiment the Windows Temperature program will measure and record the temperature at given time intervals. It will automatically plot this data on a graph like the one shown in **Figure 1**. Notice the temperature vs. time plot is irregular until is stabilizes on a slowly decreasing temperature line. Ideally, you want the maximum temperature that would be produced if the reaction happened instantaneously at the time of mixing (time = 0), not some time later when the reaction mixture and the calorimeter have cooled slightly due to leaks in our "adiabatic" system. The proper method to obtain ΔT is depicted in **Figure 1**.

Figure 1. Temperature Extrapolation.

The rate of cooling is used to extrapolate back to what the maximum temperature should have been. This is the intersection of the extrapolation line with the y-axis (time = 0, or when the reactants were originally mixed). The difference between the extrapolated maximum, T_f, and the initial temperature, T_i, is ΔT.

SAFETY PROCEDURES

1. Avoid skin contact with hydrochloric acid or sodium hydroxide solution.
2. Swirl (do not shake) calorimeters gently to avoid spilling the contents.
3. Handle thermometers, which are used to calibrate the thermometers, carefully to avoid breaking.
4. If you spill any chemicals on the lab benches, clean it up IMMEDIATELY with a damp sponge.

EXPERIMENTAL PROCEDURES

Getting Started

1. **Obtain stock solutions:** (One partner should do this while the other partner is weighing the solid chemicals.) Use two clean beakers to get stock solutions of 1.0M HCl (100 mL) and 1M NaOH (50 mL) from the side shelf. Record the exact molarity of HCl and NaOH as labeled on the containers. WARNING! HCl is corrosive, clean up spills immediately.

2. **Weigh Mg solid:** The top-loading balances are delicate instruments. Do not spill any chemicals on the balance. If you do spill chemicals, clean them up immediately. To weigh a chemical, place a clean, small piece of paper on the top of the balance. Press the TARE button to ZERO the balance. Add the solid slowly onto the paper until the proper mass has been weighed. Weigh 0.20g to 0.30g of the Mg turnings to the nearest milligram on the top-loading balance. Record the exact mass of Mg used on your lab data sheet.

3. **Weigh the MgO solid:** Following the directions in step 2 above weigh 0.50g to 0.60g of MgO solid. Record the exact mass of MgO used on your data sheet.

Determining the Calorimeter Constant

1. Using a 50-mL graduated cylinder, measure 50 mL of your 1.00 M HCl solution. Pour the HCl into the Styrofoam calorimeter. Insert the *calibrated* temperature probe into the calorimeter cups. The temperature probe's tip must be in the HCl solution, but *not touching the bottom of the cup*.

2. Now rinse the graduated cylinder successively with tap water, deionized water, and 5.0 mL of 1.0 M NaOH solution. Measure 50 mL of your 1.0 M NaOH solution into the graduated cylinder.

3.	With the temperature probe in the HCl solution, the plastic cover on the cup, use your Windows temperature program to begin measuring and recording the temperature of the HCl solution for at least one minute. This will establish $T_{initial}$. Since the NaOH in the graduated cylinder has been sitting in the room for the same length of time as the HCl, we will assume its $T_{initial}$ is the same.

4.	Gently lift the lid off of the calorimeter and pour in the NaOH. ***Do NOT stop the program at this time. You will lose important data!*** Immediately replace the lid and gently swirl the calorimeter while your program is taking data. Observe the temperature until a maximum is reached, then ***continue taking data for <u>one or two more minutes</u> to obtain plenty of data points for the extrapolation of T_{final}.***

5.	You now have the data you need to calculate the calorimeter constant, C_{cal}. Remember, the total mass of the solution is the sum of mass of the HCl and NaOH solutions. This mass can be determined by subtracting the weight of the calorimeter from the total weight of calorimeter/solution assembly.

Heat of Reaction of Mg and HCl

1.	Clean and dry your calorimeter. Using a graduated cylinder, add 50 mL of 1.0 M HCl solution and 50 mL of deionized water. As before, use your Windows temperature program to measure and record the temperature of this resulting solution for at least one minute to establish $T_{initial}$.

2.	Gently lift the lid off the calorimeter and put in the Mg turnings. Immediately replace the lid and gently swirl the calorimeter while your program is taking data. Observe the temperature until a maximum is reached, then continue taking data for one or two more minutes to obtain plenty of data points for the extrapolation of T_{final}.

3.	You now have the data you need to determine ΔH for Mg/HCl reaction. Remember, the total mass of the solution is the sum of the mass of the HCl solution, the water, and the Mg.

Heat of Reaction of MgO and HCl

1. Clean and dry your calorimeter. Using a graduated cylinder add 50 mL of 1 M HCl solution and 50 mL of deionized water. As before, use the Windows temperature program to measure and record the temperature of this resulting solution for at least one minute to establish $T_{initial}$.

2. Gently lift the lid off the calorimeter and pour in the MgO solid. Immediately replace the lid and gently swirl the calorimeter while your program is taking data. Observe the temperature until a maximum is reached, then continue taking data for one or two more minutes to obtain plenty of data points for the extrapolation of T_{final}.

3. You now have the data you need to determine $\Delta H°_{rxn}$ for the Mg/HCl reaction. Remember the total mass of the solution is the sum of the mass of the HCl solution, the water, and the MgO.

Name_____

Lab Partner's Name_____

Class_____Section_____

Lab Instructor_____

Date_____

Experiment #16

ENTHALPY OF FORMATION OF MAGNESIUMN OXIDE

Data Sheet

Determining the Colorimeter Constant:

Exact concentration of HCl solution   _____

Amount of HCl solution used   _____

Exact concentration of NaOH   _____

Initial Temperature (from graph)   _____

Final Temperature (from extrapolation)   _____

Heat of Reaction (Mg + HCl):

Amount of HCl solution used   _____

Mass of Magnesium   _____

Initial Temperature   _____

Final Temperature   _____

Heat of Reaction (MgO + HCl):

Amount of HCl solution used   _____

Mass of Magnesium Oxide   _____

Initial Temperature   _____

Final Temperature   _____

Calculations

I.   Calorimeter constant determination

II.   Determination $\Delta H°_{rxn}$ for Mg + HCl

III. **Determination of ΔH°$_{rxn}$ for MgO + HCl**

IV. **Determination of ΔH°$_f$ for MgO**

V. **Percent Error Calculation from literature value.**