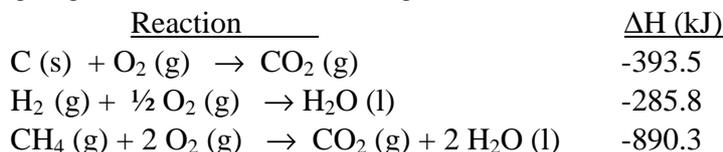# Enthalpy of Formation of Magnesium Oxide

PRELAB:

**Reading:** Chapter 5, Brown, LeMay, and Bursten.

1. What is the change in enthalpy for the formation of methane, CH_4, from solid carbon (as graphite) and hydrogen gas? Refer to the following reactions:

Reaction	ΔH (kJ)
$C\ (s)\ +\ O_2\ (g)\ \rightarrow\ CO_2\ (g)$	-393.5
$H_2\ (g)\ +\ \frac{1}{2}\ O_2\ (g)\ \rightarrow H_2O\ (l)$	-285.8
$CH_4\ (g)\ +\ 2\ O_2\ (g)\ \rightarrow\ CO_2\ (g)\ +\ 2\ H_2O\ (l)$	-890.3

2. If the ionization of 1.00 g $Mg_{(s)}$ in excess acid solution (Eq. 3) evolves 19.3 kJ of heat, what is the standard enthalpy of formation for $Mg^{2+}_{(aq)}$ expressed in kJ/mol?

Introduction:

The goal of this exercise is to measure the enthalpies of formation of $Mg^{2+}_{(aq)}$ and $MgO_{(s)}$. The enthalpy of formation of $Mg^{2+}_{(aq)}$ can be determined from the enthalpy of dissolution of 1 mol of Mg metal in a very large amount of very dilute acid (eq 1).
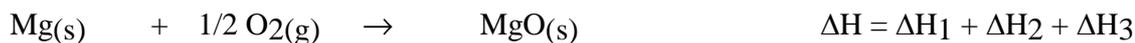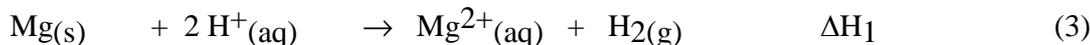
$$Mg_{(s)}\ +\ 2\ H^+_{(aq)}\ \rightarrow\ Mg^{2+}_{(aq)}\ +\ H_{2(g)} \qquad \Delta H = \Delta H^\circ_{f\,(Mg^{2+},aq)} \qquad (1)$$
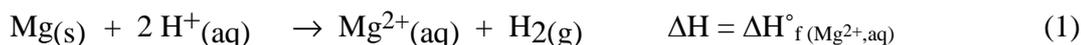
The ΔH for this reaction is the ΔH°_f for Mg^{2+}, because the ΔH°_f for $Mg_{(s)}$, $H^+_{(aq)}$, and $H_{2(g)}$ are zero by definition. The only species in equation 1 with a nonzero ΔH°_f is $Mg^{2+}_{(aq)}$, so that its enthalpy of formation is simply the enthalpy of this reaction. The enthalpy of formation of MgO is more difficult to measure directly.

$$Mg_{(s)}\ +\ 1/2\ O_{2(g)}\ \rightarrow MgO_{(s)} \qquad \Delta H = \Delta H^\circ_{f\,(MgO)} \qquad (2)$$

It is more convenient to use the first law of thermodynamics in the form of Hess's law to simplify the measurement of $\Delta H^\circ_{f\,(MgO)}$. If a chemical reaction can be broken up into the sum of two or more other reactions, the sum of the enthalpies of these reactions will be the enthalpy of the desired reaction.

Consider the following reaction equations:

$$Mg_{(s)}\ +\ 2\ H^+_{(aq)}\ \rightarrow\ Mg^{2+}_{(aq)}\ +\ H_{2(g)} \qquad \Delta H_1 \qquad (3)$$

$$Mg^{2+}_{(aq)}\ +\ H_2O_{(1)}\ \rightarrow\ MgO_{(s)}\ +\ 2\ H^+_{(aq)} \qquad \Delta H_2 \qquad (4)$$

$$H_{2(g)}\ +\ 1/2\ O_{2(g)}\ \rightarrow\ H_2O_{(1)} \qquad \Delta H_3 \qquad (5)$$

$$\overline{Mg_{(s)}\ +\ 1/2\ O_{2(g)}\ \rightarrow\ MgO_{(s)} \qquad\qquad \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3}$$

The sum of these three equations is the desired equation; thus $\Delta H^\circ_{f\,(MgO)} = \Delta H_1 + \Delta H_2 + \Delta H_3$. ΔH_1 is simply the enthalpy of reaction of a mole of Mg metal in excess acid; ΔH_2 is the negative of the enthalpy of reaction of MgO in excess acid; and ΔH_3 is the molar enthalpy of formation of water (a known constant of –285.8 kJ/mol).

The heat effect for a chemical reaction run at constant pressure (such as those run on the bench top in open vessels) is the enthalpy change, $q_{rxn} = \Delta H$. The heat evolved for a chemical reaction can be determined by running the reaction in a calorimeter and measuring the temperature change.

$$q_{cal} = C_{sys} \Delta T \qquad (6)$$

where C_{sys} is the heat capacity of the system. The heat capacity of the system is sum of the heat capacity of the solution in the calorimeter, C_{soln}, and the heat capacity of the calorimeter, C_{cp}.

$$C_{sys} = C_{soln} + C_{cp} \qquad (7)$$

The heat capacity of the calorimeter includes the Styrofoam cups and the thermometer. The heat capacity of the solution is given by the specific heat of the solution, C_s, multiplied by the mass of the solution:

$$C_{soln} = C_s * \text{mass of the solution} \qquad (8)$$

The specific heat of 0.4 M HCl, which is the average molarity of the acid used during today's reaction, is 4.07 J g^{-1} $^{\circ}$C^{-1} and its density is 1.01 g/cm^3. The heat capacity of the calorimeter must be measured in a separate experiment. The heat effect for the chemical reaction is then

$$\Delta H = q_{rxn} = -q_{cal} \qquad (9)$$

since if the calorimeter gains energy (positive ΔT) the chemical reaction must loose an equal amount of energy. Another way of saying this is that exothermic reactions have a negative ΔH and heat up their surroundings (positive ΔT).

Heat Capacity of the Calorimeter:

The idea behind the determination of the heat capacity of the calorimeter is to run a process where the heat effects can be easily calculated. If we pour 50.0 mL of hot water into 50 mL of cold water in a perfectly insulating container, the heat lost by the hot water will be equal to the heat gained by the cold water, $q_{hot} = - q_{cold}$, since energy is conserved in all processes. However, if the Styrofoam cup and thermometer for the cold water absorb a little of the heat then $q_{hot} = -(q_{cold} + q_{cp})$, where q_{cp} is the heat absorbed by the calorimeter. Solving for q_{cp} gives:

$$q_{cp} = -q_{hot} - q_{cold} \qquad (10)$$

Note that q_{hot} is a negative number, since energy is lost from the hot water; therefore, $-q_{hot}$ in equation 10 is a positive number. The heat capacity of the calorimeter is then given by dividing by the change in temperature for the process:

$$C_{cp} = q_{cp}/\Delta T \qquad (11)$$

The result simply measures the amount of heat required to raise the temperature of the styrofoam cups and the thermometer by 1.0 $^{\circ}$C.

PROCEDURE:[1]

Heat Capacity of Calorimeter: Determine the heat capacity of the calorimeter by the following procedure. Prepare two calorimeters, each similar to the one illustrated in Figure 1. Compare the readings of two thermometers by immersing them together in water at room temperature for one minute and reading the temperature to the nearest 0.10 $^{\circ}$C. Be careful to avoid parallax in your readings. Always use the same thermometer in the calorimeter with the cold water and apply this correction to all readings of the thermometer in the hot water to ensure that the readings of both thermometers will always correspond.
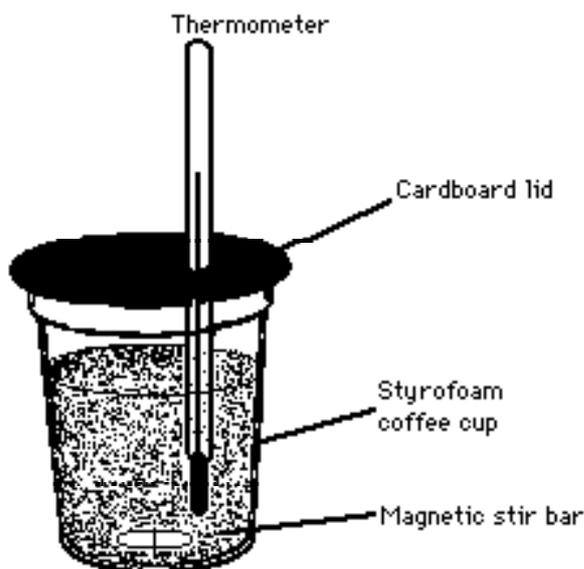

Figure 1. Styrofoam Cup Calorimeter. Use two nested cups.

To find the heat that is lost to the calorimeter, place 50.0 mL of tap water at room temperature in one calorimeter and 50.0 mL of hot tap water that is about 20-25 $^{\circ}$C above room temperature in the other calorimeter. With the lids and thermometers in place, take careful temperature readings ($\pm$ 0.10 $^{\circ}$C) of each calorimeter after one minute has elapsed. Then, <u>pour the warmer water</u> quickly and as completely as possible <u>into the other</u> calorimeter, and take a reading of the combined water after another minute has elapsed using the thermometer from the cooler water calorimeter.

Calculate the heat lost by the warm water and the heat gained by the cold water (mass H_2O * ΔT * specific heat.). You can assume that the density of water is 1.0 g/mL, and the specific heat of water is 4.184 J/g $^{\circ}$C. The result simply measures the amount of heat required to raise the temperature of the styrofoam cups and the thermometer by 1.0 $^{\circ}$C.

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[1] Excerpts taken from: *Chemical Principles in the Laboratory*, Second Edition, by Lester R. Morss and Robert S. Boikess and *Laboratory Studies in General Chemistry*, by Julian L. Roberts, Jr., and James B. Ifft

The following is an example of how the **heat capacity of the calorimeter** is determined.

Temperature of 50 mL of hot water:	37.9 °C
Temperature of 50 mL of cold water:	20.9 °C
Temperature after mixing warm with cold water:	29.1 °C
Heat lost by hot water: $-(50.0 \text{ g} * -8.8 \text{ °C} * 4.184 \text{ J/g °C}) =$	-1841 J
Heat gained by cold water: $(50.0 \text{ g} * 8.2 \text{ °C} * 4.184 \text{ J/g °C}) =$	<u>1715 J</u>
Heat lost to calorimeter: $q_{cp} + q_{hot} + q_{cold} = 0$ or $q_{cp} = -(q_{hot} + q_{cold})$	126 J
heat capacity of the calorimeter = <u>(heat lost to calorimeter)</u> =	15. J/°C

$$\text{(T }_{H2O} \text{ mixed - T }_{H2O} \text{ cold)}$$

REPEAT this work again. Calculate the heat capacity of the calorimeter for trial two. Average your values for trial 1 and 2 for heat capacity of the calorimeter.

Reaction #1 (eq 3): Use an analytical balance to weigh out 0.480 ± 0.020 g of granular magnesium metal into a pre-weighed vial. Assemble a calorimeter as shown in Figure 1 on top of a magnetic stir plate. Check the demonstration set-up in the lab before you begin. Fill your calorimeter with 100 mL of 0.5 M HCl and start stirring. Measure the temperature in 30-second intervals for two minutes. Add the Mg and continue to measure the temperature over 30-second intervals until the temperature passes a plateau <u>and</u> subsequently begins to drop (as shown in Figure 3).
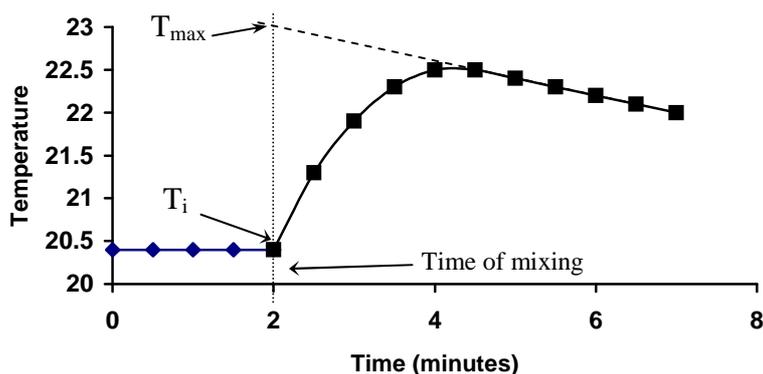

Figure 3.   Graphical method of calculating corrected temperature rise: $(T_{max} - T_i)$.

Reaction #2 (the reverse of eq 4): Weigh a clean weighing bottle. To this bottle add approximately as many moles ($\pm$ 2%) of MgO as you weighed of Mg for reaction #1. The MW of MgO = 40.30 g/mol. Record the mass accurately. Using a clean calorimeter with 100 mL of 0.5 M HCl, perform the same measurements as for Mg (reaction #1). Make sure all the MgO falls into the acid in the calorimeter. You can then account for any MgO stuck to the weighing bottle by reweighing the bottle, thus determining the mass of MgO that actually reacted. Stir the reaction mixture vigorously to ensure all the MgO reacts and that the temperature is accurately recorded. Continue recording values until the temperature passes a plateau and then **decreases** for <u>at least 4</u> consecutive readings.

DATA ANALYSIS:

- Make graphs for your two reactions referring to Figure 3. You only need to plot the data points in the linear portion of the curve after mixing. The data points in the region where the temperature is increasing rapidly are not necessary. Set the time of mixing to 0 minutes, so that the y-intercept will be equal to T_{max}. Use a linear trendline (linear regression) to find the y-intercept. Determine the corrected temperature rise for each reaction.

- The heat capacity of the solution in this experiment is approximately the heat capacity of 0.4 M HCl, which is the average molarity during the reaction. Use the specific heat $(4.07 \, J \, g^{-1} \, {}^{\circ}C^{-1})$ of 0.4 M HCl solution and its density $(1.01 \, g/cm^3)$ to calculate the heat evolved. Substituting Eq 8 into Eq. 7 and Eq. 7 into Eq. 6 gives:

$$q_{cal} = (C_s * (\text{mass of solution}) + C_{cp})*(T_{max} - T_i)$$

Then use Eq. 9 to calculate the change in enthalpy for the reaction, ΔH.

- For each reaction, calculate the ΔH per mole of Mg or MgO. The molar enthalpy of reaction of Mg with acid, Eq. 3, is approximately $\Delta H^{\circ}_{f(Mg^{2+},aq)}$[1]. Is the reaction exothermic or endothermic? Be sure to indicate the correct sign for $\Delta H^{\circ}_{f(Mg^{2+},aq)}$.

- The molar enthalpy of reaction of MgO with acid is the reverse of equation 4. Use the correct sign for the molar enthalpy of reaction of MgO and change the sign to yield ΔH_2.

- Calculate $\Delta H^{\circ}_{f(MgO)}$ by summing the enthalpies for equations 3 through 5, keeping the correct sign in each case.

BEFORE LEAVING, *please* put your data into the GRADING SPREADSHEET.

What should be in your laboratory notebook:
Include all observations, temperatures, masses and calculations. All equations and calculations associated with your Hess's law analysis. Error analysis should include a comparison of your calculated value of $\Delta H^{\circ}_{f(MgO)}$ to a literature value. Calculate your percent relative experimental error and % accuracy. As always, cite your literature source used to complete your work.

What should be attached to your discussion now but put into your laboratory notebook later?
  Excel data tables and any graphs that you made.
  Supplemental Report Sheet

What should be in your Discussion:
Address your objective, report your final results and % accuracy. For any value presented
    provide the significance. Be sure to use proper significant figures. Discuss the
accuracy of your $\Delta H^{\circ}_{f(MgO)}$ and present sources of error that *directly explain* whether your value is larger or smaller than the literature value.

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[1] The molar enthalpy is not exactly $\Delta H^{\circ}_{f(Mg^{2+},aq)}$ because your experiment was not carried out at infinite dilution.

Supplemental Report Sheet

Heat Capacity of the Calorimeter (make sure to include units)

Entry	Trial 1	Trial 2
Extrapolated temperature of 50 mL of hot water:	_____	_____
Extrapolated temperature of 50 mL of cold water:	_____	_____
Extrapolated temperature after mixing warm with cold water:	_____	_____
Heat lost by hot water:	_____	_____
Heat gained by cold water:	_____	_____
Heat lost to calorimeter:	_____	_____
Heat capacity of the calorimeter	_____	_____
Average heat capacity of the calorimeter	_____	

Reactions:

Reactant	Mass (g)	ΔT (°C)	q_{cal} (J)	ΔH (kJ)	ΔH (kJ/mol)	kJ/mol
Mg						$\Delta H_1=$
MgO						$\Delta H_2=$

$\Delta H^{\circ}_{f\ (MgO)}$ _____ kJ/mol