Using Calorimetry to Determine the Enthalpy of Formation of Magnesium Oxide

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).

$$Mg\ (s) + 2H^{+}\ (aq) \rightarrow Mg^{2+}\ (aq) + H_2\ (g) \qquad \Delta H = \Delta H^{\circ}_{f}\ (Mg^{2+}, aq) \qquad (1)$$

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, shown in eq 2, 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 **Hess's law** to simplify the measurement of ΔH°_{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:

$$\begin{array}{llllll}
Mg\ (s) & + 2\ H^{+}\ (aq) & \rightarrow Mg^{2+}\ (aq) & + H_2\ (g) & \Delta H_1 & (3) \\
Mg^{2+}\ (aq) & + H_2O\ (l) & \rightarrow MgO\ (s) & + 2\ H^{+}\ (aq) & \Delta H_2 & (4) \\
H_2\ (g) & + 1/2\ O_2\ (g) & \rightarrow H_2O\ (l) & & \Delta H_3 & (5) \\
\hline
Mg\ (s) & + 1/2\ O_2\ (g) & \rightarrow MgO\ (s) & & \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 &
\end{array}$$

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 (in kJ/mol) times the amount (mol) of reaction, $q_{rxn} = n(\Delta H)$. The heat evolved for a chemical reaction can be determined by running the reaction in a calorimeter and measuring the temperature change.

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

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

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

The heat capacity of the calorimeter includes the styrofoam cups, the stir bar, the thermometer, and anything else present that is not part of the solution. The heat capacity of the solution is given by the specific heat of the solution, C_s, multiplied by the mass of the solution:

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

Note: mass of solution = mass of measured liquids and dissolved solids

Note that for this experiment, we will estimate the specific heat of the solution (C_s) as equal to the average molarity of the acid present during the experiment (see the procedure section, below, for specific values), and you will determine the heat capacity of your calorimeter (C_{cal}) experimentally. Once C_s and C_{cal} are known, then the heat released/absorbed by the system (calorimeter + solution) can be related to a chemical reaction by:

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

The above relationship reinforces that if the system (calorimeter + solution) gains energy (positive ΔT), then the chemical reaction must lose (give off) 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:

You will first determine the heat capacity of your calorimeter. To do this, you will 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, stir bar, and thermometer, etc. that are in contact with the cold water absorb a little of the heat, then
$q_{hot} = -(q_{cold} + q_{cal})$, where q_{cal} is the heat absorbed by the calorimeter. Solving for q_{cal} gives:

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

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:

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

The result simply measures the amount of heat required to raise the temperature of the calorimeter (styrofoam cups, stir bar, thermometer, etc.) by 1.0 ˚C.

<u>Procedure:</u>

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. Remember to put an empty weigh paper and stir bar in the cold calorimeter. 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 °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.

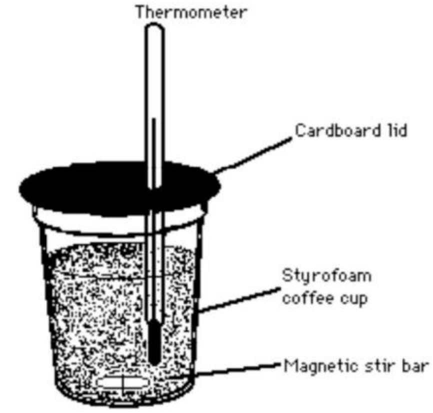

Figure 1. Styrofoam Cup Calorimeter. Use two nested cups and two cardboard covers.

To find the heat that is lost to the calorimeter, place 100.0 cm^3 of room temperature water in one calorimeter and 100.0 cm^3 of hot water that is about 20-25 ˚C above room temperature in the othercalorimeter. With the lids and thermometers in place, take careful temperature readings of each calorimeter after approximately one minute has elapsed. Then, pour the hot water quickly and as completely as possible into the other calorimeter. Make sure you are stirring with the stirring magnet. Record the maximum temperature upon mixing (after about another 15-30 seconds 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 × specific heat × ΔT). You can assume that the density of water is 1.0 g cm^{-3}, and the specific heat of water is 4.184 J g^{-1} $^\circ C^{-1}$. The result simply measures the amount of heat required to raise the temperature of the entire calorimeter setup (shown in Figure 1) by 1.0 ˚C.

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

Temperature of 100 mL of hot water:		37.9 ˚C
Temperature of 100 mL of cold water:		20.9 ˚C
Temperature after mixing warm with cold water:		29.2 ˚C
Heat lost by hot water:	(100.0 g × 4.184 J g^{-1} $^\circ C^{-1}$ × -8.7 ˚C) =	–3640 J
Heat gained by cold water:	(100.0 g × 4.184 J g^{-1} $^\circ C^{-1}$ × 8.3 ˚C) =	3473 J
Heat lost to calorimeter (q_{cal}):	$-q_{hot} - q_{cold}$ =	167 J
heat capacity of the calorimeter (C_{cal}) =	$\frac{\text{(heat lost to calorimeter)}}{(T_{H2O}\text{ mixed} - T_{H2O}\text{ cold})}$ =	20. J/˚C

REPEAT this experiment, calculate the heat capacity of the calorimeter, and then average your two values.

Reaction #1 (eq 3): Use an analytical balance to weigh out 0.4800 ± 0.0200 g of granular magnesium metal into a tared weighing paper. 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 cm^3 of 0.500 mol dm^{-3} HCl and start stirring. Measure the temperature in 30- second intervals for two minutes. Add the Mg *with weighing paper* and continue to measure the temperature over 30-second intervals until the temperature passes a plateau and subsequently begins to drop (as shown in Figure 3). Make sure to take at least four temperature measurements past the plateau point (highest temperature reading), and also make sure each of those successive temperature measurements is lower in temperature than the previous reading.

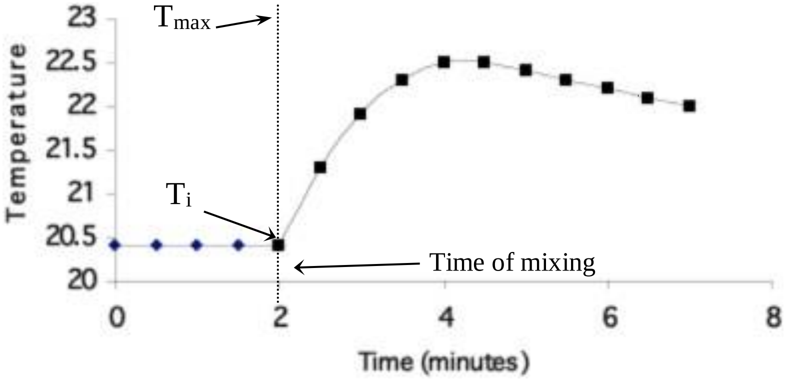

Figure 3. Graphical method of calculating corrected temperature rise: (T_{max}–T_i).

Reaction #2 (the reverse of eq 4): Tare a clean weighing paper. To this add approximately as many moles (±2%) of MgO as you weighed of Mg for reaction #1. The MW of MgO = 40.30 g mol^{-1}. Record the mass accurately to four decimal places. Cleaning the calorimeter from Reaction 1 above, add 100 cm^3 of 0.500 mol dm^{-3} HCl, and perform the same measurements as for Mg (reaction #1). Be sure to use the *same* calorimeter for reactions 1 and 2. Make sure all the MgO falls into the acid in the calorimeter. Stir the reaction mixture vigorously to ensure all the

MgO reacts and that the temperature is accurately recorded. Make sure to take at least four temperature measurements past the plateau point (highest temperature reading), and also make sure each of those successive temperature measurements is lower in temperature than the previous reading.

Data

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

Entry	**Trial 1**	**Trial 2**
Starting temperature of 100 cm^3 of hot water:	________	________
Starting temperature of 100 cm^3 of cold water:	________	________
Maximum temperature after mixing hot and cold water:	________	________
Heat lost by hot water: (q_{hot})	________	________
Heat gained by cold water: (q_{cold})	________	________
Heat lost to calorimeter: (q_{cal})*	________	________
Heat capacity of the calorimeter*	________	________
Average heat capacity of the calorimeter (C_{cal})	____________	

Reactions conducted:

Reaction	Mass solid (g)	Mass solid + solution (g)*	$T_{max} - T_i$ (°C)*	q_{rxn} (J)*	ΔH_{rxn} (kJ/mol)*
Mg					ΔH_1=
MgO					ΔH_2=
					ΔH_3=

Determination of the enthalpy of formation for MgO:

ΔH°_f (MgO)*__________________kJ/mol

Literature value for ΔH°_f (MgO)__________________kJ/mol

% Accuracy*: __________________

***Show example calculation in your lab report**

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 (see video on adding trendlines to a subset of your data). Determine the corrected temperature rise for each reaction.

- The specific heat capacity of the solution in this experiment is approximately $4.07 \text{ J g}^{-1} \text{ °C}^{-1}$ and its density (1.01 g/cm^3)[1], which is required to calculate the heat evolved. Substituting Eq 8 into Eq. 7 and Eq. 7 into Eq. 6 gives:

$$q_{rxn} = -q_{sys} = -[mC_s\Delta T + C_{cal}\Delta T] = -(C_s \times (\text{mass of reacted solids and solution}) + C_{cal}) \times (T_{max} - T_i)$$

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 $\Delta H^\circ_f(Mg^{2+}, aq)$[2]. 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.

- Calculate the percent error and percent accuracy of your experimental and literature $\Delta H^\circ_f(MgO)$ values.

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[1] These values are the specific heat and density of 0.4 M HCl, which is estimated to be the average molarity of the acid used during the reaction.

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