The standard enthalpy of formation of a compound, $\Delta H^o_f$, is the heat change accompanying the formation of one mole of compound from the elements at standard state. The standard state of a substance is the most stable physical form of the compound at one atmosphere pressure and 25°C. Elements in their standard states are assigned a $\Delta H^o_f$ value of zero. The overall heat change is:

$$\Delta H_{\text{rxn}}^o = \Sigma \Delta H^o_f \text{(Products)} - \Sigma \Delta H^o_f \text{(Reactants)}$$

The $\Delta H_f$ of a compound can be determined by synthesizing one mole of the compound and measuring the heat change by calorimetry. If the energy of the system increases at the expense of the surroundings, the reaction is **endothermic**. If energy flows from the system to the surroundings, the reaction is **exothermic**. We will work with magnesium oxide, MgO, in this experiment. The $\Delta H^o_f$ of MgO is the heat produced when one mole of Mg combines with one-half mole of $O_2$ at standard conditions:

**Overall Equation**  
Mg(s) + ½ $O_2$(g) $\rightarrow$ MgO(s)

When it is impossible or inconvenient to perform a single-step synthesis of one mole of a compound, chemists can still calculate the $\Delta H^o$ of a reaction by using stoichiometry and Hess’s Law. We can produce any quantity of desired compound, then relate the measured heat change, $q$, to the quantity produced and find heat change per mole. Also, Hess’s Law states that when a reaction is performed in a series of steps, rather than directly, the sum of the heat changes for each step equals the overall heat change for the reaction.

We will apply Hess’s Law to determine the enthalpy of formation of MgO by performing a series of reactions, measuring their heat change, then summing the reactions and heats to find the $\Delta H_f$ for MgO.

**Equation 1**  
Mg(s) + 2 $H^+$(aq) $\rightarrow$ Mg$^{2+}$(aq) + $H_2$(g)  
$\Delta H_1$

**Equation 2**  
Mg$^{2+}$(aq) + $H_2$O(l) $\rightarrow$ MgO(s) + 2 $H^+$(aq)  
$\Delta H_2$

**Equation 3**  
$H_2$(g) + ½$O_2$(g) $\rightarrow$ $H_2$O(l)  
$\Delta H_3$

**Overall Equation**  
Mg(s) + ½ $O_2$(g) $\rightarrow$ MgO(s)  
$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3$

By adding Equations 1, 2, and 3, the Overall Equation is obtained. Summation of their enthalpies gives the enthalpy of formation for MgO.

We will not perform the reaction described in Equation 3 since hydrogen gas is explosively flammable. You will use the accepted value for the enthalpy change of this reaction, $-285.8$ kJ/mol.

For convenience we perform the reverse of Equation 3 by mixing solid MgO with dilute aqueous acid. This reaction is rapid and exothermic while the reverse is not spontaneous at standard conditions. The reverse of Equation 3 has identical $\Delta H$ but opposite sign.
Also, we will not be working at standard conditions, so we cannot find $\Delta H^\circ$. Normal laboratory conditions are close to standard conditions, however, and allow a close approximation.

Finally, every calorimeter absorbs some of the heat released in the reaction. The heat required to raise the temperature of the calorimeter by 1°C is the calorimeter constant, $C_{cal}$. We must determine $C_{cal}$ for a particular calorimeter (a Thermos bottle), then use the same calorimeter for the rest of the experiment.

**PROCEDURE**

Wear your **safety glasses** while doing this experiment.

**Step 1** Determination of the Calorimeter Constant.

Check out a calorimeter and record its code number.

Measure out 50.0 mL of cold water, pour it into the calorimeter and allow it to remain for three minutes to reach thermal equilibrium with the calorimeter. Read and record the temperature of the cold water ($T_c$) to the nearest 0.1°C.

Heat another sample of water to approximately 60°C then remove the flame. Pour 50.0 mL of hot water into a graduated cylinder, read and record its temperature ($T_h$) then IMMEDIATELY pour the hot water into the calorimeter. Stopper the calorimeter to prevent heat loss, swirl to mix for approximately one minute then read the temperature of the mixture of hot and cold waters ($T_{hc}$).

Repeat the procedure for at least 3 trials.

**Calculation of the calorimeter constant**

The general formula for heat absorbed or released by a substance is:

$$q = c \cdot m \cdot \Delta T$$

where $q$ is the heat, $c$ is the specific heat of the substance in J · g$^{-1} · ^\circ\text{C}^{-1}$, $m$ is the mass of the substance and $\Delta T$ is the temperature change, $\Delta T = T_{\text{final}} - T_{\text{initial}}$. Since this experiment is performed under constant pressure conditions, $q$ can also be expressed as $\Delta H$.

The heat lost by the hot water equals the heat gained by the cold water plus the heat gained by the calorimeter (Law of Conservation of Energy):

$$0 = \Delta H_{\text{hot water}} + \Delta H_{\text{cold water}} + \Delta H_{\text{calorimeter}}$$

or

$$0 = (c \cdot m \cdot \Delta T)_{\text{hot water}} + (c \cdot m \cdot \Delta T)_{\text{cold water}} + (C_{cal})(\Delta T_{cal})$$

Since the only unknown is $C_{cal}$ we can calculate the heat capacity of the calorimeter. No mass is needed to find the heat absorbed by the calorimeter since its mass is constant throughout the experiment. The $\Delta T$ for the cold water and the calorimeter are equal since they were originally in contact.
Step 2  Determination of $\Delta H_1$

Carry out this step **AWAY FROM ANY FLAME!**

Dry the calorimeter. BE CAREFUL; the lining is **fragile**. Measure out 60.0 mL of 1.00 M HCl and pour it into the calorimeter. Let the calorimeter stand to equilibrate while weighing the magnesium metal.

Weigh a clean vial on the top-loading balance. Place 0.55-0.60 g of magnesium metal into the vial and weigh, recording the total mass.

Record the temperature of the HCl solution in the calorimeter then carefully but quickly pour the Mg metal into the acid solution. **IMMEDIATELY** cover the opening but **LEAVE THE STOPPER LOOSE** to allow the hydrogen gas to escape. Gently swirl the calorimeter, taking care not to spill any of the solution. Record the **maximum** temperature reached by the solution. **DO NOT USE THE THERMOMETER AS A STIRRER**; it must remain immersed in the solution. Empty and dry the calorimeter.

Repeat the procedure.

Calculation of $\Delta H_1$

Assume that all the heat released by the reaction was absorbed by the HCl solution and by the calorimeter. Also assume that the density and specific heat of the dilute aqueous 1.00 M HCl solution are the same as that of pure water: density equals 1.00 g/mL and specific heat equals 4.184 J · g$^{-1}$ · °C$^{-1}$.

We will first calculate the heat, $q_1$, in kJ for the amount of Mg used in the experiment. Then we calculate $\Delta H_1$ for one mole of Mg. Note that $q$ and $\Delta H_1$ will be negative since the reaction is exothermic.

$$0 = q_1 + q_{HCl} + q_{calorimeter} \quad \text{or} \quad q_1 = -(c \cdot m \cdot \Delta T)_{HCl} + (C_{cal})(\Delta T_{cal})$$

Then,

$$\Delta H_1 = \frac{q_1}{g \cdot Mg} \times \frac{24.31 g \cdot Mg}{1 \text{ mol} \cdot Mg}$$

Step 3  Determination of $\Delta H_2$

Measure 60.0 mL of 1.00 M HCl solution into the dry calorimeter.

Place about 0.95 g of MgO in a clean vial and record the mass.

Record the temperature of the HCl solution in the calorimeter. Pour the weighed MgO into the calorimeter, taking care to empty all the sample quickly into the solution. Immediately stopper the calorimeter tightly (no gas is evolved in this reaction) and gently swirl the mixture. Record the **maximum** temperature reached by the mixture.

Weigh the vial with any residue. Find the total mass of MgO used in the experiment by difference. Repeat the procedure.
Calculation of $\Delta H_2$

Calculate $q$ for the second experiment in the same manner as for the first experiment. Then, remember that the reaction whose enthalpy we want is THE REVERSE of the reaction performed in the laboratory. Finally, convert $q_2$ to $\Delta H_2$ by calculating the amount of heat for one mole of MgO, using a calculation similar to step 2.

Calculation of $\Delta H_f$ for magnesium oxide

For your calculated values of $\Delta H_1$ and $\Delta H_2$, find the mean value and range for each. Use the experimental values for $\Delta H_1$ and $\Delta H_2$ and the given value for $\Delta H_3$ to calculate the enthalpy of formation of MgO. Include an expression of the uncertainty in your answer equal to $\pm$ one-half of the difference of the values.
Chemistry 101  Experiment 7 - ENTHALPY OF REACTION USING HESS’S LAW

Section________________ Name____________________________

Pre-laboratory Assignment

1. How much heat is absorbed by a 550. g sample of water as it warms from 22.5°C to 47.1°C?

2. Calculate \(\Delta H^\circ\) for the reaction: \(\text{GeO}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{GeO}_2(s)\) by combining the enthalpies of these two known equations, using Hess’s Law.

\[
\text{Ge}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{GeO}(s) \quad \Delta H^\circ = -255 \text{ kJ}
\]
\[
\text{GeO}_2(s) \rightarrow \text{Ge}(s) + \text{O}_2(g) \quad \Delta H^\circ = +535 \text{ kJ}
\]

3. In determining \(\Delta H_1\), the thermometer registers an increase in temperature for the solution in the calorimeter. What change occurs to the chemical potential energy of the Mg(s) and the HCl(aq) in the experiment?
Chemistry 101  Experiment 7 - ENTHALPY OF REACTION USING HESS’S LAW

Report Sheet

I. Determination of the Calorimeter Constant

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Calculation of ( C_{cal} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_c ) (cold water)</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( T_h ) (hot water)</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( T_{hc} ) (mixture)</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( \Delta T_c = \Delta T_{cal} )</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( \Delta T_h )</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( C_{cal} )</td>
<td>_____</td>
<td>_____</td>
<td>_____</td>
</tr>
</tbody>
</table>

Mean value for calorimeter constant ____________ (show units)

Show one complete sample calculation of \( C_{cal} \) above.

II. Determination of \( \Delta H_1 \)

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Calculation of ( \Delta H_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of Mg + vial</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>Weight of vial</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>Weight of Mg</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>Mass of HCl solution</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( T_i ) (initial T of HCl)</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( T_f ) (final T of HCl)</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( \Delta T_{HCl} = T_f - T_i )</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( q_1 ) (heat released by rxn)</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>Moles of Mg used</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>( \Delta H_1 ), kJ/mol Mg</td>
<td>_____</td>
<td>_____</td>
</tr>
</tbody>
</table>

Mean value of \( \Delta H_1 \) ____________

Show one complete calculation for \( \Delta H_1 \) above.
### III. Determination of $\Delta H_2$

<table>
<thead>
<tr>
<th>Trial</th>
<th>Weight of MgO + vial</th>
<th>Weight of vial + residue</th>
<th>Mass of MgO used</th>
<th>Mass of HCl solution</th>
<th>$T_i$ (initial T of HCl)</th>
<th>$T_f$ (final T of HCl)</th>
<th>$\Delta T_{HCl} = T_f - T_i$</th>
<th>$q_2$ (heat released by rxn)</th>
<th>Moles of MgO used</th>
<th>$\Delta H_2$, kJ/mol MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial 1</td>
<td>________</td>
<td>________</td>
<td>________</td>
<td>________</td>
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<td>________</td>
</tr>
<tr>
<td>Trial 2</td>
<td>________</td>
<td>________</td>
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<td>________</td>
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</tr>
</tbody>
</table>

**Calculation of $\Delta H_2$**

Mean value of $\Delta H_2$

Show one complete calculation for $\Delta H_2$ above.

### IV. Determination of $\Delta H_f$ for MgO

Show your calculation below, including the deviation from the mean.

$$\Delta H_f$$ for MgO, ± deviation = ________________

**Calculation:**
1. When pure sulfuric acid dissolves in water, a great deal of heat is liberated. To determine the enthalpy of solution, 175 g of water was placed in an open calorimeter and cooled to 20.0°C. Then 5.00 g of pure, concentrated sulfuric acid, H\textsubscript{2}SO\textsubscript{4}(l), also at 20.0°C, was added and mixed in. The temperature rose rapidly to 25.4°C. Assume that the specific heat of the solution is 4.184 J \cdot g^{-1} \cdot \degree C^{-1}. C_{\text{cal}} = 19 J/\degree C. Calculate $q$. Then, calculate the $\Delta H$ of solution for one mole of H\textsubscript{2}SO\textsubscript{4}.

2. Suppose that during the determination of $\Delta H$ all the MgO did not dissolve in the HCl solution before the final temperature reading was obtained. What effect would this have on your calculated $\Delta H_f$ value?

3. The standard enthalpy of formation for MgO(s) is -601.7 kJ/mol. Calculate the % error for your experimental value.