The standard enthalpy of formation of a compound, ΔH_f^o , 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 ΔH_f^o value of zero. The overall heat change is:

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

The ΔH_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 ΔH_f^o of MgO is the heat produced when one mole of Mg combines with one-half mole of O₂ at standard conditions:

Overall Equation
$$Mg(s) + \frac{1}{2}O_2(g) ----> MgO(s)$$

When it is impossible or inconvenient to perform a single-step synthesis of one mole of a compound, chemists can still calculate the ΔH° 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 ΔH_f for MgO.

Equation 1	$Mg(s) + 2 H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_{2}(g)$	ΔH_1
Equation 2	$Mg^{2+}(aq) + H_2O(l) \rightarrow MgO(s) + 2 H^+(aq)$	ΔH_2
Equation 3	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(1)$	ΔH_3
Overall Equation	$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$	$\Delta H_f = \Delta H_1 {+} \Delta H_2 {+} \Delta H_3$

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 ΔH but opposite sign.

Also, we will not be working at standard conditions, so we cannot find ΔH° . 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.

<u>Step 1</u> 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 $0.1^{\circ}C$.

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:

$$q = c m \Delta T$$

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

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):

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

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

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 ΔT for the cold water and the calorimeter are equal since they were originally in contact.

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 ΔH_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 $4.184 \text{ J} \cdot \text{g}^{-1} \cdot {}^{\circ}\text{C}^{-1}$.

We will first calculate the heat, q_1 , in kJ for the amount of Mg used in the experiment. Then we calculate ΔH_1 for one mole of Mg. Note that q and ΔH_1 will be negative since the reaction is exothermic.

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

Then,

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

Step 3 Determination of ΔH_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 ΔH₂

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 ΔH_2 by calculating the amount of heat for one mole of MgO, using a calculation similar to step 2.

Calculation of ΔH_f for magnesium oxide

For your calculated values of ΔH_1 and ΔH_2 , find the mean value and range for each. Use the experimental values for ΔH_1 and ΔH_2 and the given value for ΔH_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.

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 ΔH° for the reaction: GeO(s) + ½ O₂(g) \rightarrow GeO₂(s) by combining the enthalpies of these two known equations, using Hess'ss Law.

$$Ge(s) + \frac{1}{2}O_2(g) \rightarrow GeO(s)$$
 $\Delta H^{\circ} = -255 \text{ kJ}$
 $GeO_2(s) \rightarrow Ge(s) + O_2(g)$ $\Delta H^{\circ} = +535 \text{ kJ}$

3. In determining ΔH_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?

Section	on Name			
	R	Report Sheet		
I. Determination of the Ca	lorimeter Co Trial 1	nstant Trial 2	Calorimeter # Trial 3 <u>Calculation of C_{cal}</u>	
T _c (cold water)			<u>Calculation of C_{cal}</u>	
T _h (hot water)				
T _{hc} (mixture)				
$\Delta T_c = \Delta T_{cal}$				
ΔT_h				
C_{cal}				
Mean value for calorimeter of	constant	(sho	ow units)	
Show one complete sample c	calculation of	C _{cal} above.		
II. Determination of ΔH_1	Trial 1	Trial 2		
Weight of Mg + vial			Calculation of ΔH_1	
Weight of vial				
Weight of Mg				
Mass of HCl solution				
T _i (initial T of HCl)				
T _f (final T of HCl)				
$\Delta T_{HCl} = T_f - T_i$				
q ₁ (heat released by rxn)				
Moles of Mg used				
ΔH_1 , kJ/mol Mg				
Mean value of ΔH_1				
Show one complete calculati	on for ΔH_1 ab	ove.		

Report (continued)

III. Determination of ΔH_2	Trial 1	Trial 2	
Weight of MgO + vial			Calculation of ΔH_2
Weight of vial + residue			
Mass of MgO used			
Mass of HCl solution			
T _i (initial T of HCl)			
T _f (final T of HCl)			
$\Delta T_{HCl} = T_f - T_i \label{eq:deltaTHCl}$			
q2 (heat released by rxn)			
Moles of MgO used			
ΔH_2 , kJ/mol MgO (remember the sign change!)			
Mean value of ΔH_2			
Show one complete calculation	on for ΔH_2 abo	ove.	
IV. Determination of ΔH_f for	or MgO		
Show your calculation below.	, including the	e deviation from the me	ean.
ΔH_f for MgO,	± deviation =		
Calculation:			

Name
Post Laboratory Questions
ssolves in water, a great deal of heat is liberated. To determine the water was placed in an open calorimeter and cooled to 20.0°C. ated sulfuric acid, H ₂ SO ₄ (l), also at 20.0°C, was added and mixed lly to 25.4°C. Assume that the specific heat of the solution is °C. Calculate q. Then, calculate the ΔH of solution for one mole
ermination of ΔH_2 all the MgO did not dissolve in the HCl erature reading was obtained. What effect would this have on your
ormation for MgO(s) is -601.7 kJ/mol. Calculate the % error for
te