

## Experiment 12 – Determination of an Enthalpy of Reaction, Using Hess's Law

### Object:

To measure the standard heat of formation,  $\Delta H_f^0$ , of  $\text{MgO (s)}$ , and to become familiar with calorimetry as a tool for measuring heats of reaction.

### Theory:

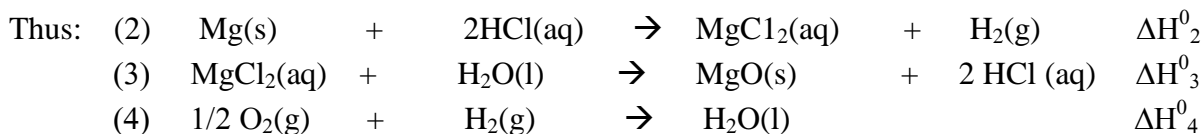
The standard heat of formation,  $\Delta H_f^0$ , of a compound is defined to be the heat evolved or absorbed when one mole of the compound in its standard state is formed from the elements in their standard states. The standard state of a compound or element is taken to be the most stable form of the substance at one atmosphere pressure and  $25^\circ\text{C}$ . Naturally, the heat of formation of an element in its most stable form is defined to be zero, since there is no change in enthalpy in forming an element from itself.

The heat of formation,  $\Delta H_f^0$ , which we will determine today is simply the change in enthalpy for the reaction (1) below:



Note that the reaction is written for formation of one mole of  $\text{MgO(s)}$ , which requires the use of a fractional coefficient for  $\text{O}_2$ , and that all physical states must be specified, since enthalpy depends on the physical state of the substance.

Experimentally it would be very difficult to measure the heat of formation of this compound directly, especially in a Styrofoam calorimeter. Fortunately, we can employ a law formulated by Hess to evaluate this  $\Delta H$  indirectly by finding a series of reactions which are easier to measure, or for which the values of  $\Delta H$  are available in standard tables. As you may recall, Hess's law simply states that if a series of reactions can be added together to get a certain reaction, their  $\Delta H$ 's can be added together in the same manner to get the  $\Delta H$  for the reaction of interest.



Since these reactions add up to give the formation reaction for  $\text{MgO(s)}$ , reaction (1) above, their  $\Delta H^0$ 's can be summed to get  $\Delta H_f^0$  for magnesium oxide, i.e.

$$\Delta H_f^0(1) = \Delta H_2^0 + \Delta H_3^0 + \Delta H_4^0 \quad (\text{Eq.1})$$

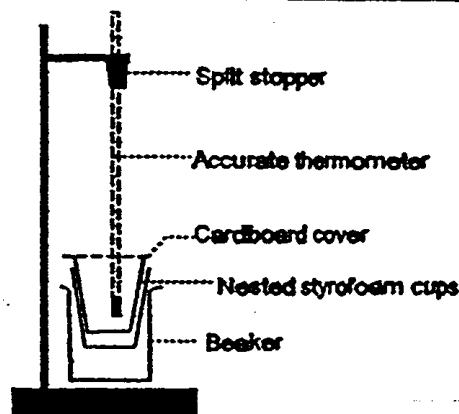
If  $\text{Mg(s)}$  is dissolved in  $\text{HCl(aq)}$ ,  $\Delta H^0_2$  can be obtained. If  $\text{MgO(s)}$  is dissolved in  $\text{HCl(aq)}$ ,  $\text{MgCl}_2\text{(aq)}$  will be formed, which is the reverse of reaction (3), thus its  $\Delta H$  will be the negative  $\Delta H^0_3$ . The fourth reaction is simply the formation reaction of liquid water which has a value of  $-285.85 \text{ kJ/mol}$ . If the value for reaction (4), the value for  $\Delta H^0_f$  for  $\text{MgO(s)}$  can be calculated.

### **Experimental Procedure and Calculations:**

**Precautions:** Hot water is a serious cause of burns. Handle with care.  $\text{HCl}$  is an acid; contact with skin, clothing, and especially eyes is to be avoided.  $\text{MgO}$  can form a caustic solution with water, and its dust can be extremely irritating. Avoid breathing the dust as well as contact of dust or solutions with skin, clothing or eyes. Wash hands with water immediately if skin contact is suspected.  $\text{H}_2$  gas produced in reaction (2) is explosive when mixed with air. Avoid ignition sources. As always, wear safety goggles in the lab. Dispose of chemicals as directed. Clean up any spills as directed by your instructor.

#### **1. Determination of the Calorimeter Constant (or Heat Capacity)**

Check out a calorimeter as directed by the instructor and assemble as shown. The thermometer is very expensive as shown. The thermometer is very expensive and must be handled with extreme care. The beaker is to provide support to the tippy styrofoam cups, and the split stopper is to support the thermometer. A small iron ring may be substituted for the stopper and clamp, and provides less opportunity for breakage.



The number of joules (or kilojoules) required to raise the temperature of the calorimeter one degree Celsius is called the calorimeter constant ( $C$ ), and may be determined as follows:

Weigh the dry, empty calorimeter and cover. Add to the calorimeter 70.0 mLs of cold water and reweigh the calorimeter and water as before. Measure about 30.0 mLs of water into a suitable beaker and heat it with a burner and ringstand to boiling, and then remove the heat. Immediately measure the temperature of the cold water in the calorimeter ( $T_c$ ) as precisely as possible, estimating one place beyond calibrations on the thermometer. Then measure the temperature of the hot water ( $T_h$ ), quickly add the hot water sample to the cold water in the calorimeter, cover the calorimeter to promote mixing, and then measure the maximum temperature ( $T_f$ ) of the hot and cold water mixture after about one minute. Finally measure the total mass of the calorimeter as before to determine the mass of hot water added, since we don't know how much evaporation occurred during the heating process. Since the calorimeter is assumed to be perfect insulator (a fairly good approximation), there must be no heat ( $q$ ) lost from the calorimeter system. Therefore all the heats of the system must add to zero, i.e.:

$$\sum q = 0 = q_{\text{HOT}} + q_{\text{COLD}} + q_{\text{CAL}} \quad (\text{Eq.2})$$

or:  $q_{\text{CAL}} = -\{ q_{\text{HOT}} + q_{\text{COLD}} \}$

$$\text{and in more detail: } C\Delta T_{\text{CAL}} = -m_{\text{COLD}} c_{\text{sp}} \Delta T_{\text{COLD}} - m_{\text{HOT}} c_{\text{sp}} \Delta T_{\text{HOT}} \quad (\text{Eq.3})$$

where  $m$  is mass,  $c_{\text{sp}}$  is the specific heat of water ( $4.184 \text{ J/g}^\circ\text{C}$ ), and  $\Delta T$  is the change in temperature,  $(T_{\text{F}} - T_{\text{I}})$ . Note that  $T_{\text{F}}$  is the same for all terms, but that  $T_{\text{I}}$  is different for the hot water.

Since the values of all variables in Eq. 3 are known except  $C$ , it can be calculated. Repeat this measurement 1 or 2 more times as time allows, using 25 and 35 mLs of hot  $\text{H}_2\text{O}$  respectively and drying the calorimeter between trials. You may assume the dry weight of the calorimeter to be constant for each trial, but you must determine the weight of the cold water sample in the calorimeter and the final weight of both hot and cold water, after you've determined  $T_{\text{F}}$ , determine a mean value for  $C$  from your trials.

## 2. Determination of $\Delta H^\circ_2$

Dry your calorimeter, measure into the calorimeter approximately 60.0 mLs of 1 M HCl Solution, and determine the weight of calorimeter and HCl solution. Let the calorimeter stand while you weigh the Mg metal.

Weigh a plastic weigh boat on the analytical balance. Place approximately 0.55-0.60 g Mg turnings in the boat and determine the total weight. ***Be sure to record all these values in your lab book in your lab book in ink.*** Carefully record the temperature of the HCl solution in the calorimeter, then transfer the Mg metal from the paper into the HCl. Immediately cover the opening with the thermometer and cover. **CAUTION:** hydrogen gas is being generated; avoid flames.

After one minute, gently swirl the liquid in the calorimeter, taking care not to spill any. Record the maximum temperature attained by the solution. Inspect the interior of the calorimeter for any Mg metal stuck to the sides above the solution. If any is found, return it to the liquid with the tip of the thermometer, reclose the calorimeter and see if there is any further increase in temperature. If time allows, carry out a second trial.

Calculate  $\Delta H^\circ_2$  as follows:

$$\begin{aligned} \text{As reasoned above:} \quad q_{\text{RXN}} &= -q_{\text{CAL}} - q_{\text{SOLUTION}} \\ \text{and in more detail:} \quad q_{\text{RXN}} &= -C\Delta T - m_{\text{SOLN}} c_{\text{sp}} \Delta T \end{aligned} \quad (\text{Eq.4})$$

The mass of solution,  $m_{\text{SOLN}}$ , may be calculated by adding the mass of Mg to the mass of HCl.

The specific heat of the solution is approximately that of water, and will be assumed to be the same.

The value of  $\Delta H^0_2$  in kJ/mol is determined by converting  $q_{\text{RXN}}$  to kJ and then dividing by the moles of Mg used in the experiment: 
$$\Delta H^0_2 = \frac{q_{\text{RXN}}(\text{kJ})}{\text{Moles Mg}} \quad (\text{Eq.5})$$

### 3. Determination of $\Delta H^0_3$

Again measure 60 mLs of 1 M HCl into the dried calorimeter, and weigh the calorimeter and HCl. Accurately weigh out 0.90-1.00 g MgO onto a previously weighed weigh boat. Record the temperature of the HCl in the calorimeter. All at once, transfer the weighed MgO into the calorimeter, taking care to get it all into the HCl solution, rather than hung up on the sides of the cup. Immediately replace the cover and thermometer on the calorimeter, *mix the solution well* and record the maximum temperature reached in the calorimeter. It may take a while to dissolve, so track the temperature until it stops rising. If time allows, carry out a second trial.

Calculate  $q_{\text{RXN}}$ , and  $\Delta H^0_3$  in the same manner as  $\Delta H^0_2$  was calculated above. Assume specific heat of the solution to be the same as water, and add the mass of MgO to that of the HCl solution to get the mass of solution. Be careful to carry the correct number of significant figures through the calculation. Use 40.31 as the formula weight of MgO. Note, however, that the value of  $\Delta H^0_3$  to be used in the Hess's Law calculation is the *negative* of  $\Delta H_{\text{RXN}}$  because we ran the *reverse* of reaction (3). It should end up positive (endothermic)!

# REPORT SHEET

## 1. Determination of the Calorimeter Constant:

	Trial 1	Trial 2	Trial 3
Mass of cal. And cold H <sub>2</sub> O			
Mass of empty cal.			
Mass of cold H <sub>2</sub> O			
Mass of cal. And total H <sub>2</sub> O			
Mass of hot H <sub>2</sub> O			
T <sub>C</sub> (T <sub>I</sub> cold H <sub>2</sub> O, cal)			
T <sub>H</sub> (T <sub>I</sub> hot H <sub>2</sub> O)			
T <sub>F</sub> (mixture)			
ΔT <sub>HOT</sub> (T <sub>F</sub> - T <sub>H</sub> )			
ΔT <sub>COLD</sub> (T <sub>F</sub> - T <sub>C</sub> )			
ΔT <sub>CAL</sub> (T <sub>F</sub> - T <sub>C</sub> )			
C (Cal constant)			

Mean Value of C (with units) \_\_\_\_\_

Show calculation of C (1<sup>st</sup> trial only):

$$C = \frac{-(m_{\text{HOT}} C_{\text{sp}} \Delta T_{\text{HOT}}) - (m_{\text{COLD}} C_{\text{sp}} \Delta T_{\text{COLD}})}{\Delta T_{\text{CAL}}}$$

Chemistry 1AL  
Hess's Law

Name \_\_\_\_\_

2. Determination of  $\Delta H^0_2$

	Trial 1	Trial 2
Mass of cal. and HCl sol'n		
Mass of empty calorimeter **		
Mass of HCl solution		
Mass of Mg and weigh boat		
Mass of weigh boat		
Mass of Mg		
Total mass of solution		
T <sub>I</sub> of HCl solution		
T <sub>F</sub> HCl + Mg		
$\Delta T$ (T <sub>F</sub> - T <sub>I</sub> )		
*q <sub>RXN</sub> (J)		
Moles Mg		
* $\Delta H^0_2$ (kJ/mole)		

\* Show set-ups for indicated calculations for trial 1

\*\* Assume unchanged

**Chemistry 1AL**  
**Hess's Law**

Name \_\_\_\_\_

**3. Determination of  $\Delta H^0_3$**

	Trial 1	Trial 2
Mass of cal. and HCl sol'n		
Mass of empty calorimeter**		
Mass of HCl solution		
Mass of MgO and weigh boat		
Mass of weigh boat		
Mass of MgO		
Total mass of solution		
$T_i$ of HCl solution		
$T_f$ of HCl + MgO		
$\Delta T$ ( $T_f - T_i$ )		
* $q_{RXN}$ (J)		
* Moles MgO		
* $\Delta H_{RXN}$ (kJ/mol MgO)		
* $\Delta H^0_3$ ( $-\Delta H_{RXN}$ )		

\* Show set-ups for indicated calculations for trial 1

\*\* Assume constant

Chemistry 1AL  
Hess's Law

Name \_\_\_\_\_

**Calculation of  $\Delta H_f^0$  for MgO:**

$$\Delta H_f^0 (1) \text{ MgO(s)} = \Delta H_2^0 + \Delta H_3^0 + \Delta H_4^0$$

(1) Based on Trial 1 values.

(2) Based on Trial 2 values.

**Summary of Results:**

	Trial 1	Trial 2	Trial 3
$\Delta H_2^0$			
$\Delta H_3^0$			
$\Delta H_4^0$	-285.85 kJ/mol	-285.85 kJ/mol	
$\Delta H_f^0$			

**Post-Lab Assignment – Experiment 12**

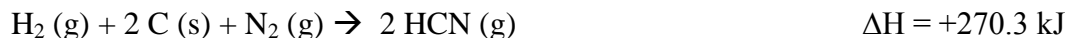
Name\_\_\_\_\_

**(Show calculations clearly on an attached separate sheet of paper)**

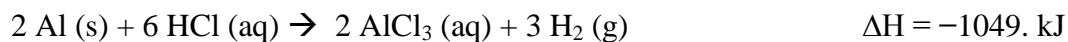
1. Athletes use cold packs containing an ammonium nitrate solution to ice their injuries.

1.25 grams of ammonium nitrate is dissolved in enough water to form 25.0mL of a solution in a calorimeter. The temperature of the solution falls from 25.8°C to 21.9°C. **What is the enthalpy of the reaction in kJ/mole?** Assume the density of the solution to be 1.0g/mL and its specific heat capacity to be 4.18 J/g°C. (assume the calorimeter heat capacity to be negligible)

2. Calculate  $\Delta H$  for the reaction  $\text{CH}_4 (\text{g}) + \text{NH}_3 (\text{g}) \rightarrow \text{HCN} (\text{g}) + 3 \text{H}_2 (\text{g})$ , given:



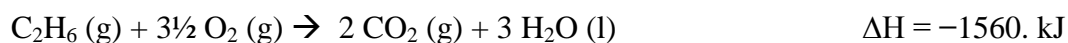
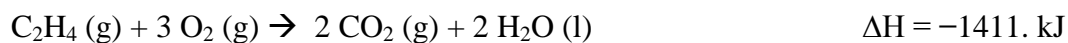
3. Calculate  $\Delta H$  for the reaction  $2 \text{Al} (\text{s}) + 3 \text{Cl}_2 (\text{g}) \rightarrow 2 \text{AlCl}_3 (\text{s})$ , given:



**Pre-Lab Assignment – Experiment 12**

Name \_\_\_\_\_

1. State Hess's Law:

2. Calculate  $\Delta H$  for the reaction:  $\text{C}_2\text{H}_4 (\text{g}) + \text{H}_2 (\text{g}) \rightarrow \text{C}_2\text{H}_6 (\text{g})$ , from the following data.3. Calculate  $\Delta H$  for the reaction  $4 \text{NH}_3 (\text{g}) + 5 \text{O}_2 (\text{g}) \rightarrow 4 \text{NO} (\text{g}) + 6 \text{H}_2\text{O} (\text{g})$ , given: