CALORIMETRY AND HESS'S LAW:
FINDING ΔH° FOR THE COMBUSTION OF MAGNESIUM

MATERIALS: Styrofoam coffee cup and lid, thermometer, magnetic stirrer, magnetic stir bar, 50-mL and 100-mL graduated cylinders, 150 mL beaker, aluminum slug, magnesium ribbon, magnesium oxide, 1.00 M HCl, 1.00 M NaOH, copper wire.

PURPOSE: The purpose of this experiment is to determine the ΔH° for the combustion of magnesium by determining the ΔH°'s for reactions which can be combined together according to Hess's Law, yielding the ΔH° for the desired reaction.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Construct and use a calorimeter.
2. Use a calorimeter to examine heat transfer.
3. Determine a set of reactions which, after applying Hess's Law, yield the ΔH° for the desired reaction.
4. Use a spreadsheet program for data manipulation, graphing, and regression analysis.

DISCUSSION: The First Law of Thermodynamics is the Law of Conservation of Energy, which states that energy can neither be created nor destroyed – the total energy of the universe is a constant. A fire or a chemical explosion is just the result of converting the chemical energy of the fuel or explosive into thermal and mechanical energy of the products and the surrounding air. Objects near a fire increase in temperature because energy is transferred in a process called heating; the energy exchanged is the amount of heat ($\mathbf{q}$). Objects near an explosion are moved because energy is transferred in a process called doing work; the energy exchanged is the amount of work done ($\mathbf{w}$). Our primary interest here is with heat transfers (the "thermo" in thermodynamics). These heat transfers can take place between two objects at different temperatures, and they also can accompany physical or chemical changes (i.e., reactions). **Calorimetry** is a technique for measuring heat transfers; it makes use of an insulated container called a calorimeter.

Qualitatively, the process of heat transfer that occurs in a calorimeter is very familiar to us. We all recognize that a cup of hot coffee left in a cool room will get colder, and eventually will become the same temperature as the room. Of course, the thermal energy of the coffee cannot be lost; it is simply moved into the rest of the room. The coffee gets measurably colder, while the room gets warmer, albeit imperceptibly. The air (and the walls, furniture, etc.) of the room serves as a "thermal bath" to absorb the heat released by the coffee. The same thing happens in a calorimeter. If a hot object, like an aluminum slug, is dropped into a cold sample of water, the water acts the thermal bath and absorbs the heat; the process stops when both water and slug are at the same temperature, a situation called "thermal equilibrium". If the whole process is conducted in an insulated container, like a Styrofoam cup, then no heat is lost to the room. In a thermodynamic sense, the hot Al slug is the "system", and the water the "surroundings". Energy "lost" by the system is "gained" by the surroundings. The insulated cup acts as the whole experimental universe, and the total energy within the cup must remain constant, as dictated by the First Law.

As long as there is no phase change, a transfer of energy into or out of a sample of matter will result in a temperature change. The magnitude of the temperature change will depend on the kind of material, its amount (i.e., the mass $\mathbf{m}$ or number of moles $\mathbf{n}$), and how much energy is transferred. The relation between the amount of energy transferred in the form of heat, $\mathbf{q}$, and the temperature change of the object, $\mathbf{\Delta T}$, can be written as:

$$\mathbf{q = m\,c_s\,\Delta T} \qquad \text{or} \qquad \mathbf{q = n\,c_p\,\Delta T} \qquad \text{or} \qquad \mathbf{q = C_p\,\Delta T} \tag{1}$$

$\mathbf{\Delta T}$ represents a difference between the final and initial values: $\mathbf{\Delta T = T_{final} - T_{initial}}$. The "$\mathbf{c}$" values in the equations above are different versions of the "heat capacity" of the object. These values are specific to the substance being studied. In the first equation, the constant $\mathbf{c_s}$ is the **specific heat capacity** (commonly called just "specific heat"). Typical units for the specific heat are Joules per gram per degree Celsius, or J g^{-1} °C^{-1}. This tells us how many Joules of heat we have

to add or remove to change the temperature of one gram of the material by one °C. The constant c_p in the second equation is the **molar heat capacity**; it relates similar information, except it pertains to warming or cooling of one mole of material, rather than one gram. Which equation (and constant) we use depends only on our choice of using mass or moles to describe the quantity, but we must be consistent. The third equation, which gives heat transfer q in terms of a total heat capacity C_p, is used when heat is absorbed or released by a calorimeter assembly (described below); in this case, the value of C_p represents the amount of heat transfer required to change the temperature of the whole assembly by one °C.

In this experiment, the calorimeter assembly will consist of a Styrofoam cup and plastic lid, together with the dilute acid solution, magnetic stir bar and thermometer within it. We will carry out an exothermic reaction by adding a known amount of either Mg(s) or MgO(s) to the acid solution, and the heat released by the reaction will be absorbed by the calorimeter. We will measure the temperature increase of the calorimeter assembly. For simplicity we will assume that no heat is lost from the calorimeter during the reaction; while this is not strictly true, the error introduced by this assumption is relatively small.

The heat transfer associated with the reaction will be designated as q_{rxn}; that associated with the calorimeter is q_{cal}. Assuming that no heat is lost, the heat released by the reaction (q_{rxn}) must be equal to the heat gained by the calorimeter (q_{cal}). The total energy of the universe is constant, so:

$$q_{rxn} + q_{cal} = 0 \qquad \text{or} \qquad q_{rxn} = -q_{cal} \tag{2}$$

Because the calorimeter described above is an assembly of several different materials, its heat equation q_{cal} is written in terms of the total heat capacity (C_p), and

$$q_{rxn} = -q_{cal} \qquad \text{becomes} \qquad q_{rxn} = -C_p \Delta T_{cal} \tag{3}$$

Again, the negative sign is required because of the direction of the heat change, and reflects the fact that an exothermic reaction (negative q) results in a positive ΔT (temperature increase) in the calorimeter. In a calorimetry experiment, a reaction is performed inside a calorimeter and the resulting temperature change of the calorimeter is measured. The chemical reaction comprises the **system**; the calorimeter and thermometer are part of the **surroundings**. If we know the total heat capacity (C_p) of the calorimeter and its contents, and can measure the temperature change when the reaction occurs, then we can determine the amount of heat liberated by the reaction. Alternately, if we know the amount of heat transferred, we can determine the heat capacity of the calorimeter by using the equation in reverse. As a final theoretical detail, if the heat of reaction is measured in a constant-pressure calorimeter (e.g., a coffee-cup calorimeter), then

$$q_{rxn} = n \, \Delta H \tag{4}$$

For the exothermic reactions being studied here, the **enthalpy of reaction**, ΔH, is a negative quantity representing the amount of heat released per mole of reactant (Mg or MgO) that is consumed. Every reaction has an associated ΔH value.

Note that in this experiment, we will determine the *maximum* temperature reached during reaction and use this as the "final" temperature (T_{final}) value when calculating ΔT for each run. Because the reactions studied here are heterogeneous (with both solid and solution reactants), the reactions require several minutes to complete, and some heat is certainly lost from the system during this period. Now, if the calorimeter were perfectly insulated and this small amount of heat was not lost, the final temperature would be a few tenths of a degree higher, and thus the corresponding DT values would be a little larger. While it is important to recognize this source of systematic error, in practice it is not large enough to impact the usefulness of the procedure as a means of demonstrating the principles of calorimetry and the application of Hess's Law.

PROCEDURE:

Part A: How to determine ΔH° for the combustion of one mole of magnesium

1.   Observe the combustion reaction of magnesium metal, as demonstrated by your instructor. The objective of this experiment is to determine the ΔH° for this reaction. (The superscript "o" indicates that all of the reactants and products are in their standard states.) Make any notes needed for later use.

✎ **Answer in-lab questions #1 and #2 on page E12K-8.**

2.   Direct measurement of ΔH° for the combustion of magnesium is difficult. However, because ΔH° is a *state function* (independent of path), we can determine the value of ΔH° for this reaction indirectly (via an alternate path) using an alternate set of reactions that add together to yield the desired reaction. If the ΔH° values for these alternate reactions can be measured, then by applying Hess's Law, we can calculate ΔH° for the desired reaction. While there are many sets of reactions that could accomplish this objective, here we will focus on a particular set of three reactions. One of these will **not** be experimentally determined during this lab; instead, the required ΔH° value is provided below:

$$H_2(g) + \tfrac{1}{2}\ O_2(g) \rightarrow H_2O(l) \qquad \Delta H° = -285.83\ kJ$$

The other two reactions to be studied here involve magnesium and magnesium oxide as reactants.   Many metals and metal oxides react with strong acids. In this experiment, we will react Mg and MgO separately with hydrochloric acid (HCl) but need to write out the reactions in advance to ensure our experimental plan is valid.

✎ **Answer in-lab questions #3, #4, and #5 on page E12K-8.**

Part B: Measuring ΔH° for the reaction of Mg or MgO with HCl - Record data on pages E12K-5 and E12K-6.

In this experiment, students will determine the ΔH° values for the two reactions involving magnesium metal or magnesium oxide with hydrochloric acid.   **Work in pairs**. Following the direction of your instructor, **each pair will be assigned *one* of the two reactions** to study by carrying out the appropriate procedures described below. **Each pair will also be assigned a specific mass of reactant** to use for their first trial, and will also carry out a second trial using a different mass of their choice. Class data will then be combined for later analysis and final determination of the ΔH°'s for the two reactions.

→ *For Magnesium Metal (Mg) and Hydrochloric Acid (HCl) reaction:*

1.   Each pair of students will be assigned a "target" mass of **0.1, 0.2, 0.3, 0.4 or 0.5 g of Mg** to be used to carry out the following procedures:

2.   Trim a piece of Mg strip using scissors to approximately the correct assigned mass (pre-weigh on toploading balance), then measure the mass using the **analytical balance.** Record this mass (±0.0001 g) on the data sheet. Make a loose ball of the Mg and wrap it in a long piece of copper wire to secure it, leaving a tail of copper wire long enough to suspend the Mg ball in the HCl solution in the Styrofoam cup. The copper will not react in the solution; its purpose is to prevent the magnesium from floating to the surface during the reaction. Do not wrap the magnesium too tightly or it will not react quickly enough with the HCl solution. Do not wrap the magnesium too loosely since it may escape the copper "cage" and float.

3.   Measure 100 mL of 1.0 M HCl solution in a graduated cylinder. Place a magnetic stir bar in a dry Styrofoam cup and place the cup on the magnetic stir plate. Transfer the acid to the Styrofoam cup. Add a plastic lid to the cup and insert the digital thermometer through the hole in the lid until it is in the solution. **Do NOT poke a hole in the Styrofoam cup!** Turn the stir plate on the *lowest* setting that allows rotation of the stir bar. Measure the temperature of the acid and record the value (°C). This is the **initial temperature** ($T_{initial}$).

4.   When you are ready to carry out the experiment, lift the lid and suspend the copper wire containing the Mg ball in the Styrofoam cup so that the Mg ball is submerged fully in the acid. Replace the lid with the thermometer

and continue stirring to mix. Working quickly, record the **time <u>and</u> temperature of the solution every 30 seconds for 5 minutes.** Note that the temperature will rise quickly, reach a plateau, and then decrease slowly after that. The **maximum temperature** reached is the one we will use as T_{max}.

5. Repeat steps 1-5 for Trial 2 using a ***different mass*** of Mg (your choice, must not exceed 1.0 g).

6. Report your mass of **Mg**, $T_{initial}$, and T_{max} values to your instructor for each run (a shared Google sheet may be provided for this purpose).

7. When data collection is completed, rinse the calorimeter and thermometer with distilled water and dry as completely as possible. Place the piece of copper in the container labeled "copper waste."

→ *For Magnesium Oxide (MgO) and Hydrochloric Acid (HCl) reaction:*

1. Each pair of students will be assigned a "target" mass of **0.3, 0.6, 0.9, 1.2 or 1.5 g of MgO** to be used to carry out the following procedures:

2. On a **<u>top-loading balance,</u>** transfer approximately the correct mass of MgO to a clean weighing boat (no need to record this mass).

3. Next, determine the mass of the MgO and the weighing boat on the **<u>analytical balance</u>** and record this mass (±0.0001 g) on the data sheet.

4. Measure 100 mL of 1.0 M HCl solution in a graduated cylinder. Place a magnetic stir bar in a dry Styrofoam cup and place the cup on the magnetic stir plate. *Carefully* transfer the acid to the Styrofoam cup. Replace the plastic lid on the cup and insert the digital thermometer through the hole in the lid until it is in the solution. **Do NOT poke a hole in the Styrofoam cup!** Turn the stir plate on the lowest setting that allows rotation of the stir bar. Measure the temperature of the acid and record the value (°C). This is the **initial temperature** ($T_{initial}$).

5. When you are ready to carry out the experiment, transfer the MgO from the weigh boat into the acid. Replace the lid with the thermometer and begin stirring to mix. Working quickly, record the **time <u>and</u> temperature of the solution every 30 seconds for 5 minutes.** Note that the temperature will rise quickly, reach a plateau and then drop slowly after that. The **maximum temperature** reached is the one we will use as T_{max}.

   <u>NOTE</u>: In this reaction all the MgO should react since HCl is used in excess. *However, if the solid MgO is allowed to sit on the bottom or sticks to the sides of the cup it will not dissolve and hence it will not react. **Make sure the solution is mixed constantly but gently***. Before discarding this solution, check to see that all of the MgO has reacted. If solid MgO remains, the results from the trial are not accurate and the experiment must be repeated.

6. Using the same **<u>analytical balance,</u>** record the mass (±0.0001 g) of the "empty" weighing boat after the transfer and calculate the mass of MgO actually transferred to the calorimeter.

7. Repeat steps 1-5 for Trial 2 using a ***different mass*** of MgO (your choice, must not exceed 1.8 g).

8. Report your mass **MgO**, $T_{initial}$, and T_{max} values to your instructor for each run (a shared Google sheet may be provided for this purpose).

9. When data collection is completed, rinse the calorimeter and thermometer with distilled water and dry as completely as possible.

Cleanup:
1. All solutions are dilute aqueous solutions and can be disposed down the sink with plenty of water.
2. Rinse your calorimeter and lid, and leave it to dry for the next lab section.
3. Return all equipment to their original locations.
4. Clean up your work area.

Name: _____   **Section:** _____

Partner: _____   **Date:** _____

DATA AND ANALYSIS SECTION
Experiment 12K

Part B: Measuring ΔHº for the reaction of Mg with HCl

Heat capacity of the calorimeter: _____ **(your instructor will provide this value)**

Assigned "target" mass of Mg metal for Trial 1: _____

	Trial 1		Trial 2	
Mass of Mg metal used (g)				
Volume of 1.00 M HCl (mL)				
Initial Temperature, $T_{initial}$ (°C)				
	Time (sec)	**Temperature (°C)**	**Time (sec)**	**Temperature (°C)**
Maximum Temperature, T_{max} (°C)				
ΔT ($T_{max} - T_{initial}$) (°C)				

Part B: Measuring ΔH° for the reaction of MgO with HCl

Heat capacity of the calorimeter: _____ **(your instructor will provide this value)**

Assigned "target" mass of MgO for Trial 1: _____

	Trial 1		Trial 2	
Mass of MgO sample and weighing boat (g)				
Mass of weight boat AFTER transfer (g)				
Mass of MgO used (g)				
Volume of 1.00 M HCl (mL)				
Initial Temperature, T$_{initial}$ (°C)				
	Time (sec)	**Temperature (°C)**	**Time (sec)**	**Temperature (°C)**
Maximum Temperature, T$_{max}$ (°C)				
ΔT (T$_{max}$ – T$_{initial}$) (°C)				

CLASS DATA

Mg Reaction with HCl

Midshipman	Mass of Mg (g)	Initial Temperature, $T_{initial}$ (°C)	Maximum Temperature, T_{max} (°C)	ΔT (°C)

MgO Reaction with HCl

| Midshipman	Mass of MgO (g)	Initial Temperature, $T_{initial}$ (°C)	Maximum Temperature, T_{max} (°C)	ΔT (°C)

IN-LAB QUESTIONS

Part A: How to determine ΔH^o for the combustion of one mole of magnesium

1. Write the balanced chemical equation for combustion of **one mole** of magnesium metal in oxygen, O_2. (The coefficient in front of Mg must be 1, but other coefficients may be fractional coefficients. Fractions are allowed here because we want to find ΔH^o for the combustion of 1 mole of Mg.

    _____ Mg (s) + _____ O_2 (g) → _____ _____ (s)
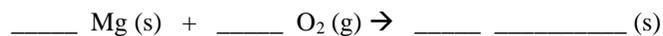
2. Write your observations of the Mg combustion demo. Why would it be difficult to study the combustion of magnesium directly using a simple water-filled calorimeter?

3. Write the balanced molecular, complete ionic, and net ionic equations for the reaction of magnesium metal with hydrochloric acid. One product is provided. You must figure out the other product (hint: BUBBLES form!)

    Molecular: _____ Mg (s) + _____ HCl (aq) → _____ $MgCl_2$ (aq) + _____ _____ (g)
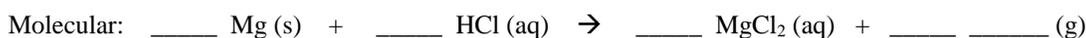
    Complete ionic:

    Net ionic:

4. Write the balanced molecular, complete ionic, and net ionic equations for the reaction of solid magnesium oxide with hydrochloric acid. Note that water is formed in this reaction (alas, no gas bubbles! The magnesium is already in the Mg^{2+} state in MgO, unlike Mg in the previous reaction.)

    Molecular: _____ MgO (s) + _____ HCl (aq) → _____ $MgCl_2$ (aq) + _____ H_2O (ℓ)

    Complete ionic:

    Net ionic:

5. Combine the deduced reactions (as net ionic equations) from #3 and #4 and the given reaction below so that the 3 reactions add to give the goal reaction from #1 (combustion of one mole of magnesium). You will need to rearrange some of the reactions, but not the goal reaction! Show how some reactants and products cancel out to yield the goal reaction. We will combine these reactions with ΔH values derived from our data later.

    Reminder: the given reaction is: H_2 (g) + ½ O_2 (g) → H_2O (l)
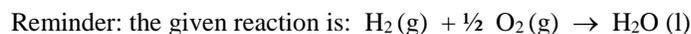
    Mg reaction (from #3; rearrange if needed):

    MgO reaction (from #4; rearrange if needed):

    Given reaction (rearrange if needed):

    _____

    Goal reaction (from #1; use **as is**):

DATA ANALYSIS
Experiment 12K

Part B: Measuring ΔH^o for the reaction of Mg or MgO with HCl

1. Calculate the number of moles of Mg and MgO used for **trial one** for each reactant. You will need to find the relevant molar masses. **Show your work in the space provided below.**

    a. For _____ g Mg, calculate moles Mg. For Mg, molar mass = _____ g/mol.

    b. For _____ g MgO, calculate moles MgO. For MgO, molar mass = _____ g/mol.

2. Using the heat capacity for the calorimeter provided (C_p = _____ **J/°C**) and the ΔT for **trial one** for each reactant, calculate q_{cal} (in kJ) and q_{rxn} (in kJ) for each run using the equations:

    $$q_{cal} = C_p, \Delta T \quad \text{and} \quad q_{rxn} = - q_{cal}$$

    Show your work in the space provided below.

    a. For _____ g Mg and ΔT = _____ °C.

        i.   Calculate q_{cal} (in kJ)

        ii.   Calculate q_{rxn} (in kJ)

    b. For _____ g MgO and ΔT = _____ °C.

        i.   Calculate q_{cal} (in kJ)

        ii.   Calculate q_{rxn} (in kJ)

3. Create an Excel spreadsheet that lists the results from the entire class (including moles of reactant and ΔH^o for **each** of the two reactions studied) using the template shown below for each reactant.

Data for reaction of Mg with HCl

MIDN	Mass Mg (g)	Moles Mg (g)	$T_{initial}$ (°C)	T_{max} (°C)	ΔT (°C)	q_{cal} (kJ)	q_{rxn} (kJ)

Data for reaction of MgO with HCl

MIDN	Mass MgO (g)	Moles MgO (g)	$T_{initial}$ (°C)	T_{max} (°C)	ΔT (°C)	q_{cal} (kJ)	q_{rxn} (kJ)

4. Use Excel to make plots of **q_{rxn} vs. moles of reactant** using the collected class data for both reactions (two graphs). Calculate the linear trendline and display both the equation and the R^2 value on each graph.

5. From the trendline equations, determine the average value for **ΔH^o per mole of magnesium**, and the average value for **ΔH^o per mole of magnesium oxide**. Recall: **ΔH^o = q_{rxn} / mole reactant.**
   (Hint: Look at the axis units!)

   a. For the Mg reaction with HCl, **ΔH^o** = _____ (include units)

   b. For the MgO reaction with HCl, **ΔH^o** = _____ (include units)

6. Rewrite your answers from In-lab question 5 on page E12K-8 in the spaces below and **add your ΔH^o results** from Data Analysis #5 (from above). Remember to modify a ΔH^o value as needed if you reverse a reaction or multiply it by some factor. Your goal reaction should consume **1 mole** of Mg.

   The ΔH^o value for the given reaction is: $H_2(g)$ + ½ $O_2(g)$ → $H_2O(\ell)$ ΔH^o = -285.83 kJ/mol

   WRITE REACTIONS   **INCLUDE VALUES & UNITS**
   ↓   ↓

   Mg reaction: ΔH^o = _____

   MgO reaction: ΔH^o = _____

   Given reaction: ΔH^o = _____

   _____

   Goal reaction for Mg combustion: ΔH^o = _____

6.(cont). Show your calculation for ΔH° of the goal reaction:

Determine the % error for your calculated value of ΔH° of combustion of Mg.
The accepted value for ΔH° is -601.24 kJ/mol.

POST-LAB QUESTIONS
Experiment 12K

1. Using the ΔH°_f (standard enthalpy of formation) values for reactants and products listed below, calculate ΔH° values for the magnesium/HCl and magnesium oxide/HCl molecular reactions and calculate a percent error (% error) of the experimentally determined values relative to the calculated values. **Show your work.**

Substance	ΔH°_f (kJ/mol)
Mg (s)	0
MgO (s)	-601.0
H_2O (ℓ)	-285.8
O_2 (g)	0
H_2 (g)	0
HCl(aq)	-167.0
$MgCl_2$(aq)	-800.1

a. For the Mg and HCl reaction:

ΔH° (experimental) = _____ (from page E12K-10, #4a)

ΔH° (calculated using ΔH°_f values) =

% error =

b. For the MgO and HCl reaction:

ΔH° (experimental) = _____ (from page E12K-10, #4b)

ΔH° (calculated using ΔH°_f values) =

% error =

2. Determine ΔH° for $2\ Al\ (s)\ +\ 3/2\ O_2\ (g)\ \rightarrow\ Al_2O_3\ (s)$

given: $H_2\ (g)\ +\ \frac{1}{2}\ O_2\ (g)\ \rightarrow\ H_2O\ (l)$ $\Delta H^{\circ} = -286$ kJ/mol

$2\ Al\ (s)\ +\ 6\ H^+\ (aq)\ \rightarrow\ 2\ Al^{3+}\ (aq)\ +\ 3\ H_2\ (g)$ $\Delta H^{\circ} = -1050$ kJ/mol
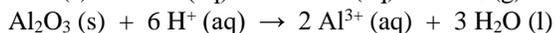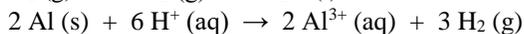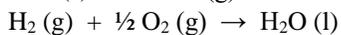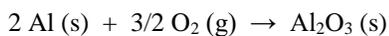
$Al_2O_3\ (s)\ +\ 6\ H^+\ (aq)\ \rightarrow\ 2\ Al^{3+}\ (aq)\ +\ 3\ H_2O\ (l)$ $\Delta H^{\circ} = -238$ kJ/mol

Name: _____   **Section:** _____

Date: _____

PRE-LAB QUESTIONS
Experiment 12K

1. Review the following websites:

    https://www.military.com/video/forces/air-force-training/c-17-formation-deploys-countermeasure-flares/3909670130001

    https://www.youtube.com/watch?v=gAhsvOP5yaM

    http://science.howstuffworks.com/mre.htm

a. List 2 military applications for the reaction studied in this experiment. $Mg\ (s) + ½\ O_2\ (g) \rightarrow MgO\ (s)$
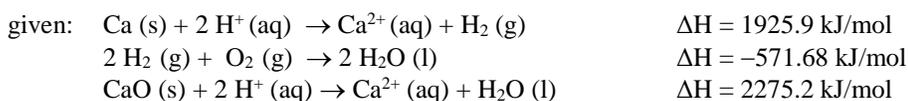
    i.

    ii.

b. TRUE or FALSE: Use water to put out a Magnesium fire (Hint: watch the youtube video at the link above)

c. In our experiment, why can't we determine ΔH for $Mg\ (s) + ½\ O_2\ (g) \rightarrow MgO\ (s)$ by <u>direct</u> measurement? Explain.

2. Use Hess's Law to determine the ΔH_{rxn} for the reaction: $Ca(s)\ +\ ½\ O_2(g)\ \rightarrow\ CaO(s)$

    given: $Ca\ (s) + 2\ H^+\ (aq)\ \rightarrow Ca^{2+}\ (aq) + H_2\ (g)$ $\Delta H = 1925.9$ kJ/mol

              $2\ H_2\ (g) +\ O_2\ (g)\ \rightarrow 2\ H_2O\ (l)$ $\Delta H = -571.68$ kJ/mol

              $CaO\ (s) + 2\ H^+\ (aq) \rightarrow Ca^{2+}\ (aq) + H_2O\ (l)$ $\Delta H = 2275.2$ kJ/mol

    $\Delta H_{rxn} =$ _____