# Chemistry 120 Laboratory
Solution Calorimetry: A Hess' Law Investigation

Objectives:
- To measure the heat capacity of a calorimeter
- To measure the heat of reaction for two chemical reactions
- To use Hess' Law, in conjunction with the above measurements, to calculate the heat of reaction for the combustion of magnesium metal
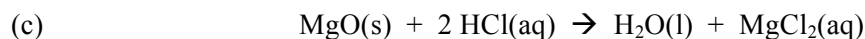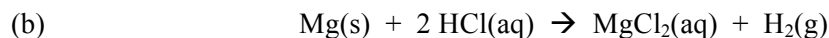
Background:

The heat of reaction is defined as the heat gained or lost by a chemical system as a reaction proceeds from reactants to products. It is often given as part of a thermochemical equation, such as that shown for the combustion of hydrogen gas:

(a) $\qquad\qquad\qquad$ $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286$ kJ
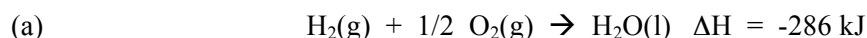
The negative sign indicates that the chemicals lose thermal energy to the surroundings in the reaction. Thus when one mole of hydrogen combines with one-half mole of oxygen to make one mole of water, 286 kilojoules of energy are released to the surroundings. This is an example of an ***exothermic*** reaction. The symbol "H" stands for the ***enthalpy***, the thermal energy at constant applied pressure. The symbol "Δ" refers to change. So "ΔH" refers to the enthalpy change for the combustion of two moles of hydrogen gas. Conditions of constant pressure are achieved by carrying out the reaction in a calorimeter that is open to the constant applied pressure of the atmosphere. The heats of reaction are reported for 25°C, although they vary only minimally with temperature.

In this experiment you will measure the ΔH values for the following reactions:

(b) $\qquad\qquad\qquad$ $Mg(s) + 2\ HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

(c) $\qquad\qquad\qquad$ $MgO(s) + 2\ HCl(aq) \rightarrow H_2O(l) + MgCl_2(aq)$

Using the thermochemical equations for these two reactions along with that previously given for the hydrogen/oxygen reaction, you will then calculate ΔH for the formation of magnesium oxide (which is the same as the heat of combustion of magnesium)

$$Mg(s) + 1/2\ O_2(g) \rightarrow MgO(s) \qquad \Delta H_f$$
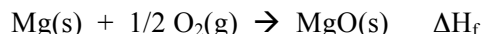
by applying Hess' Law as described below and in your textbook.

A ***solution calorimeter*** is a device for measuring heats of reactions that occur in solution. For aqueous solutions, a Styrofoam coffee cup works well. One carries out the reaction in the cup and measures the temperature change (Δt) over the course of the reaction. Assuming ***adiabatic*** conditions – that is, all of the heat of reaction is confined to the insulated cup and its contents with no heat leak to the outside of the cup – one can calculate the heat of reaction in the calorimeter as follows:

1. Total heat from the reaction is equal to the product of the heat capacity of the calorimeter and the temperature change of the calorimeter and its contents:

$$Q = C_{calorimeter} \times \Delta t$$

2. The heat capacity of the calorimeter is obtained from the heat capacity of the {cup, lid, thermistor, and magnet} assembly plus the heat capacity of the solution. The approximate heat capacity of the cup assembly can be estimated to be about 30 joules/°C; and that of the 100 mL of HCl and Mg to be
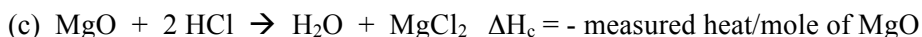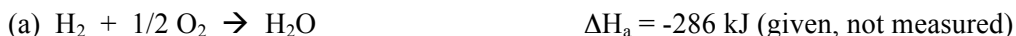
$$C_{contents} \approx 3.86 J/g/°C \times 100 mL \times 1.00 g/mL = 386 J/°C$$

Thus the total heat capacity of the system is about

$$C_{calorimeter} \approx 386 J/°C + 30 J/°C = 420 J/°C$$

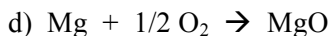See the next page for a method by which you will determine the actual heat capacity.

3. The temperature change is obtained by determining the difference between the extrapolated pre-addition and post addition baselines at the point where a vertical line connecting them passes through the midpoint of the temperature rise.

4. The balanced equations are used to confirm that the limiting reagents for each reaction are, respectively, Mg and MgO. From the actual moles of limiting reagent and the actual number of joules of energy released, you can determine the heat evolved per mole of limiting reagent.

5. The chemical equations are as follows:

   (a) $H_2 + 1/2 O_2 \rightarrow H_2O$ $\qquad\qquad$ ΔH_a = -286 kJ (given, not measured)

   (b) $Mg + 2 HCl \rightarrow MgCl_2 \quad + H_2$ $\qquad$ ΔH_b = - measured heat/mole of Mg

   (c) $MgO + 2 HCl \rightarrow H_2O + MgCl_2$ $\quad$ ΔH_c = - measured heat/mole of MgO

Note the (-) sign indicates an exothermic process. Heats need to be converted from Joules to kiloJoules. Adding the chemical equations (a) + (b) – (c) gives:

$Mg + 2 HCl + H_2 + 1/2 O_2 + H_2O + MgCl_2 \rightarrow MgCl_2 + H_2 + H_2O + MgO + 2 HCl$

which simplifies to:

   d) $Mg + 1/2 O_2 \rightarrow MgO$

This is the reaction for the formation of one mole of MgO. To get the heat of reaction for this process, we add the heats of reaction for the equations in the same sense that we added the equations:
$$\Delta H_d = \Delta H_a + \Delta H_b - \Delta H_c$$
ΔH_d is the molar heat of formation of MgO. Thus $\Delta H_{f MgO}$ (kJ/mole MgO) $\equiv \Delta H_d$.

To determine the heat capacity of the calorimeter assembly, one can add a metal of known heat capacity at the temperature of boiling water (t_{hot}) to the calorimeter cup containing 100 mL of HCl at room temperature (t_{cold}). The whole system comes to some final temperature in between the two temperatures, t_{final}.

The assumption is that **all of the heat is transferred from the hot metal ingot to the calorimeter**, and all is contained within the cup, so **none escapes to the surroundings**:

$$Q_{metal} + Q_{calorimeter} = 0 \qquad\qquad (eq. 1)$$
$$c_{metal} \times mass_{metal} \times (t_{final} - t_{hot}) + C_{calorimeter} \times (t_{final} - t_{cold}) = 0$$
$$C_{calorimeter} = -c_{metal} \times mass_{metal} \times (t_{final} - t_{hot})/(t_{final} - t_{cold}) \qquad (eq. 2)$$

To get a reasonable temperature change, you would need at least 30 grams of metal. You need a metal that will not react with the HCl. Copper is a good choice, since it is inert to action by acids. Its specific heat capacity $c_{Cu} = 0.3851$ joules/°C/gram.

Pre-Laboratory Assignment:
Answer the following questions, showing all steps in the solutions. The correct answers are given for each.

Q. 1 Suppose 30.0 grams of copper at 99.0°C are added to a calorimeter containing 100 mL of 1.00M HCl at 23.5°C and the temperature rises to a final value of 25.2°C. What is the heat capacity of the calorimeter in Joules/°C? (Answer 500 J/°C)

Q. 2 What is the experimentally measured heat of reaction between Mg and HCl per mole if 0.25 grams of magnesium added to 100 mL of 1M HCl in the calorimeter from Q 1 causes a temperature rise of 12.3°C? (Answer -600 kJ/mole Mg)

Q. 3 To how many significant figures should the heat capacity of the calorimeter and the heat of reaction of Mg with HCl each be reported? Explain.

Procedure:

All solutions can be discarded in the drains. Solids should be discarded into the trash receptacles. Copper should be returned to the location from which it was taken. Proper safety precautions should be taken and goggles should be worn throughout the lab period.

1. Thermistor Calibration
[Note 1] This process is the same that you used the first week of lab. Turn on the MicroLAB unit, then the PC. Plug the thermistor temperature sensor into the jack. Open the MicroLAB program and design a program that measures time and temperature every half second. When you add the temperature sensor, you will be given the option to read from a calibration file or do a new calibration of the thermistor temperature probe. You may wish to use your earlier calibration file, but only if you are using the same PC and thermistor probe. If you choose to recalibrate, use at least three points spanning the range of the experiment, roughly 0 to 40°C. Be sure to add a line fit and save the calibration to a file with a name that makes sense.

Add the time to column A and to the x-axis; add the temperature to column B and the y-axis. It might be a good idea to add the temperature to the Digital Display window as well.
Run the program once to make sure all is well, moving the thermistor from ice to warm water.

2. Heat Capacity of the Calorimeter:
Bring 100 mL of DI water to a boil in a 250 mL beaker. Weigh about 30 grams of Cu to the nearest mg; alternatively, just weigh one or two copper cylinders to get about 30 grams. (If the copper is tarnished, *first* clean the tarnish off with some dilute HCl, followed by a rinse with DI water, and a thorough drying.) Add the weighed Cu metal to a 150 mm test tube and place the test tube in the boiling water bath for at least 10 minutes. The Cu should then be at the temperature of the boiling DI water. You can measure that temperature or look it up if you know the atmospheric pressure.

Set up the calorimeter: place nestled Styrofoam cups into a supporting beaker. Add magnetic stir bar. Measure 100 mL of 1.00M HCl in a graduated cylinder. Pour the HCl into the calorimeter cup. Position the assembly over the magnetic stirrer securely. Adjust the stirring to a moderately brisk speed – fast enough but no sloshing or tornados inside the cup. Insert the thermistor into the lid, using a rubber band looped about the probe to adjust its height. Put the lid on the cup and allow a minute or so to let everything thermally equilibrate.

START the program. Collect readings for at least 2 minutes to establish a baseline on the temperature/time plot. [See NOTE 2 at end of handout.]

Now work quickly but carefully: remove the lid from the calorimeter and the hot test tube from the water bath. Add the copper to the HCl and replace the lid assembly.

You should see the temperature begin to climb and then level off to a constant temperature plateau. Collect data for at least 5 minutes and then STOP the experiment. Turn off the stirrer. **Save your data** to the hard drive and to your flash drive. EXPORT your data as well.

Determine the initial and final temperatures of the calorimeter and contents. A really good way to do this is to get best linear fit equations for the baseline and for the final temperature line. Compute the two values for temperature (y) at that common time (x) that represents about the midpoint of the temperature change region of the plot. The difference between these two temperature values is the best-fit temperature change, Δt, for the calorimeter in that run.

Place this Δt into equation 2 to determine the heat capacity of the calorimeter. It would be reasonable to assume that your heat capacity would be about 400 to 600 joules/°C. ***Repeat at least once and determine the average heat capacity of the calorimeter.***

3. The Mg/HCl Reaction:
It is important to maintain the experimental conditions of this part of the experiment as close as you can to those used in getting the heat capacity of the calorimeter. Clean and dry the calorimeter cup, stir bar, thermistor probe, and lid. Add the stir bar to the cup. Measure 100 mL of 1.00M HCl and add it to the cup as before. Insert the thermistor into the lid and place the lid on the Styrofoam cup assembly and begin stirring. Allow the system to equilibrate thermally for several minutes. Meanwhile, weigh to the **nearest 0.001 gram about 0.25 grams of Mg** turnings.

Begin data logging and collect data for at least two minutes to establish an initial baseline. Remove the lid and quickly add all of the Mg to the calorimeter. As the reaction occurs, the temperature should increase, since the reaction is exothermic. Continue taking data until a final constant temperature plateau is reached and maintained for at least three minutes. Stop the experiment and turn off the stirrer. **Save and Export your data** to the hard drive and a flash drive. Rinse the calorimeter and all contents with DI water and dry everything. ***Repeat the calorimetry run at least once.*** The Δt can be determined in the same way as in Part 2.

4. The MgO /HCl Reaction
This experiment is carried out the same as Part 3 above except that **1 gram** of magnesium oxide, MgO, weighed to the nearest 0.001 gram, is used in place of Mg. MgO is a fine powder. Take care that the powder is transferred as completely as possible to the HCl solution, leaving as little as possible in the weighing tray or on the sides of the Styrofoam cup. It should be completely reacted and dissolved at the end of the run. Do at least two runs. The Δt can be determined in the same way as in Part 2.

Data analysis:
Obtain printouts of one thermogram of each type.
Calculate the heat capacity of the calorimeter in Joules/^{o}C.
Use the heat capacity and measured temperature changes from parts 3 and 4 to determine the number of joules of energy released in each run.
Convert the amount of Mg and MgO into moles of each in each run.
Calculate the heats of reaction per one mole of Mg and per one mole of MgO.
Use Hess' Law to calculate the heat of formation of MgO as shown on page 2 of this handout.

Report:
Your report should include the page that follows as a cover sheet as well as the following:
- sample thermogram from each section of the experiment
- sample calculations from good runs of Δt, calorimeter heat capacity, heats of reaction, and heat of formation of MgO
- tables of raw data (mass, temperature changes) used in calculations
- table of results for heat capacity, heat of reaction between Mg and HCl and between MgO and HCl
- average heat of formation of MgO and a comparison with the accepted value

Hess's Law Grading Sheet   Name:_____

Attach this as the cover sheet to your lab report

<div align="center">

Points Possible Points Earned

</div>

Objective: 1   _____

Data:

     Thermograms   3   _____

     Table of Raw Data   2   _____

     Masses   2   _____

     Temperatures   1   _____

Sample Calculations:

     Δt 1   _____

     C_{cal} 2   _____

     q_{Mg} 2   _____

     $\Delta H_{Mg\ rxn}$ 1   _____

     q_{MgO} 2   _____

     $\Delta H_{MgO\ rxn}$ 1   _____

     ΔH_f 2   _____

     % Error   3   _____

Results:

     Table of Results with ave. ΔH_{fMgO} 2   _____

     Ave. C_{cal} 1   _____

     Ave. ΔH_{Mg} 1   _____

     Ave. ΔH_{MgO} 1   _____

Summary Discussion of Results: 1   _____

Reference to Source of Accepted Value: 1   _____

Total Points   30   _____