CHM201 General Chemistry and Laboratory I
Laboratory 8 – Thermochemistry and Hess's Law
Spring 2021

Purpose:

In this laboratory, you will measure heat changes arising from chemical reactions. You will use Hess's Law to calculate enthalpies of reaction from the heat of formation data. Since the heat of formation for magnesium oxide, MgO, is difficult to measure without using a bomb calorimeter, you must use a series of reactions to compute the result.

Introduction:

Nearly all chemical reactions generate or consume heat while forming products. We depend on the heat liberated in the combustion of fossil fuels to sustain a technological society. We observe applications of thermochemistry every day, and these applications are not limited to heat generating (exothermic) reactions. Cold-packs drain heat from the surrounding in a heat consuming (endothermic) reaction, using heat from the environment.

To determine an enthalpy change in the laboratory, you must be very careful to define "the system" and "the surroundings" precisely. The system is that part of the universe or the lab that you are going to measure while the surroundings is everything else (in the universe!). There is a boundary between the system and the surroundings, and you will only measure ***what exists in the system***. You need not account for what happens to the surroundings. As a result, you must understand what the system is and where the boundary between the system and the surroundings exists.

In our case this distinction is clear, since you will be using nested coffee cups as a constant-pressure calorimeter. The system is the calorimeter and everything inside the calorimeter, and the surroundings is everything outside the calorimeter. You will use a pair of Styrofoam coffee cups (a good heat insulator) nested inside one another, a coffee cup top and a thermocouple for measuring temperature. The thermocouple is connected to a data collection device, which is, in turn set up to communicate with a computer running a graphing and analysis program. To calculate your results correctly you will need to account for all heat changes within the system. You may make the following simplifying assumptions:

1. The room temperature does not change greatly during the experiment.
2. The only source of heat generated is from the chemical reaction being studied.
3. The heat generated by the chemical reaction is absorbed by the other components of the system which we can assume to be the mass of water present and the calorimeter (styrofoam cups). We make the further assumption that even though in this case the cup contains hydrochloric acid, we will assume that this solution, which is mostly water, will have the same heat properties as pure water, which is well documented.

Using the symbols q (heat) and H (enthalpy),

$$q_{total} = 0 = q_{rxn} + q_{water} + q_{calorimeter} \qquad \textbf{\textit{or}}$$

$$q_{rxn} = -q_{water} + -\ q_{calorimeter}; \qquad \Delta H = q_{rxn}/\text{moles of limiting reagent}$$

So what are these heats? What units do they have? You may not know the q_{rxn} (that's what you must calculate), but you can use the equation below for a heat change by measuring the change in temperature. The heat that causes temperature change is equal to the quantity of material times the change in temperature times its specific heat (s). Thus, for the heat terms given above we can rewrite the water and calorimeter terms as follows:

$$q_{water} = ms\Delta T \textit{ and } q_{calorimeter} = C\Delta T$$

where m is mass, s is the specific heat of the material (water), C is the heat capacity of the calorimeter and ΔT is the temperature change in degrees Celsius. For these calculations, you may assume that the heat liberated by the reaction is equal to the heat gained by the mass of water (HCl solution) in the calorimeter + the heat gained by the calorimeter. The specific heat of water is well known (4.184 J/g-ºC); you may assume the heat capacity for the calorimeter is 10.0 J/ºC. After determining the temperature change (ΔT), you can calculate the heat change of the water and calorimeter and the heat liberated by the reaction. Remember that the heat generated in a reaction and the enthalpy of that reaction are not the same. To determine enthalpy, you must take into account the number of moles of the limiting reagent.

To complete the calculations outlined above, you must measure the mass of the reagents, and temperature change for each of the constituent reactions. You should need no help with the first, but temperature change is a little more complex.

You will produce graphs of the temperature changes over time, and from these graphs (and some simple linear algebra) you can determine the initial and final temperatures. The initial temperature is easy to read from the graph, by finding the point when the temperature begins its rise. The final temperature is not directly measurable, since the system will start losing heat to the environment when the reaction begins. The problem is determining when the reaction was complete and what the temperature was at that time. To understand the method, the following theoretical discussion may help.

The figures below represent typical exothermic reactions and their heat profiles. In Figure 1, the reaction started and completed at the same time (instantaneous), and the heat never escapes from the isolated system. In that case, you simply need to measure the lowest and highest temperatures. Unfortunately, we live in the real world and reactions do not complete instantaneously and heat eventually escapes even the best insulated container, as in Figures 2 and 3. Notice that a fast reaction, approximates the theoretical better than the slow reaction, but the following assumptions may be used in either case.

Figure 1.
Instantaneous reaction and liberation of heat (theoretical)

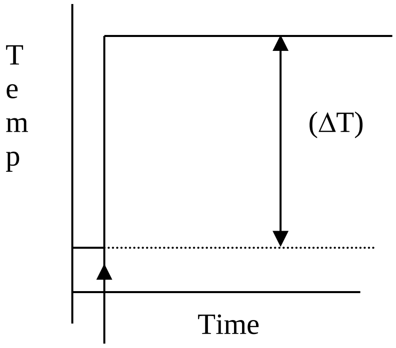


Figure 2.
Fast reaction

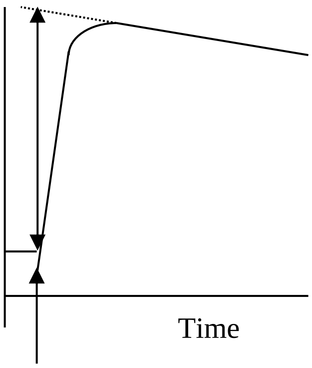
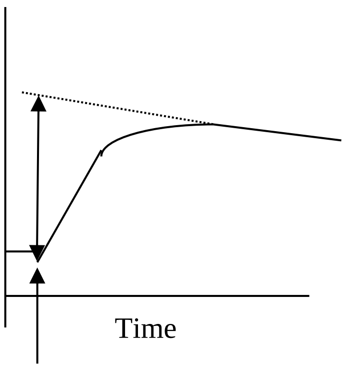


Figure 3.
Slow reaction



It would be convenient if you could simply subtract the lowest temperature from the highest to arrive at ΔT, but, as you can see from the diagrams, the real systems have already "leaked" heat to the surroundings by the time the maximum temperature was recorded. The question you must ask is, "At what temperature would the system be if the reaction happened instantaneously and no heat leaked?" To do this, you must look backward in time! That is, by looking at the changes in the system over time, you should be able to make a very good estimate of what happened previously, even though you were unable to record the actual data. The mathematical method is called extrapolation, and you should be familiar with it.

When you examine the graph produced by your experiment, you should observe that the temperature change after the reaction is complete (this is called the decay curve) looks very nearly linear over the first several minutes. By assuming it is linear, you can extend the line back in time to determine the temperature at the time the reaction began, which is the same time as it started if the reaction happened instantaneously (by definition). Now you have both the initial and final temperatures. It is tempting to try to determine the value graphically, but that method is error prone, and must be avoided.

Your data for the reactions of Mg and MgO with HCl will resemble Figures 2 and 3, respectively. You must complete the *mathematical* extrapolations to determine the initial and final temperatures.

Procedure:

1. General setup, use of the Macintosh computer/LabQuest system and reaction of Mg with HCl.

1.1 Set up the calorimeter apparatus as shown at the instructor's desk. You will need two styrofoam coffee cups nested inside one another, a ring stand and support ring to keep the cups upright, a 100mL graduated cylinder and the computer/LabQuest system including a temperature probe and USB cable. Set up the LabQuest as far from the coffee cups as possible to avoid damage.

1.2 Transfer 100.0 mL of 3.0 M HCl to each of two Styrofoam cups and label the cups #1 and #2. Create your calorimeter by placing cup #1 inside an empty cup mounted on the ringstand. Insert the temperature probe through the lid of the calorimeter. Do not remove the waxy coating on the temperature probe. This covering is to protect the probe from the HCl solution. Set aside the second cup of HCl for use on the second trial.

1.3 Turn on the computer. Connect the power supply to the LabQuest, connect the temperature probe in Channel 1 of the LabQuest and connect the USB cable to both the LabQuest and the computer.

1.4 On the computer, look to the bottom of the screen and move the cursor onto the caliper and graph icon. Double click on this icon to open the LoggerPro application on the computer. You should see the LoggerPro screen, a data table on the left and an empty graph window on the right. On the line that says LoggerPro is a series of pull down menus (File, Edit, Experiment, etc.).

1.5 You will now run a short temperature vs. time acquisition using the LabQuest system to determine the room temperature and to test the connections of the computer/LabQuest system. Move the cursor to the Experiment pull down menu and select Data Collection. Make the Length of the trial 960 seconds and set the sampling speed to 2 samples per second. Select Done from the bottom of the window.

1.6 Go back to the Experiment pull down menu and select Start Collection. The data table should fill with data and the graph should show a relatively straight horizontal line across the window. The temperature should be shown actively above the data table. Record this temperature in the data table as Room Temperature. After you have collected about a minute's worth of data, you may stop the collection.

1.7 Using weighing paper determine the mass on the ***analytical balance*** to within 0.1 mg (0.0001g) of approximately 0.25 g of magnesium ribbon that has been cut into ~1 cm pieces. ***Determine the mass on the analytical balance to four decimal places. Data from the top loading balance will result in large point deductions for the entire group.***

1.8 Select Experiment from the pull-down menu and from that menu select Data Collection. Confirm that the data collection parameters are the same as before (960 sec @ 2 samples per sec).

1.9 Start the data collection and **let it run for about 30 seconds**.

1.10 You may now quickly add all the magnesium to the calorimeter, cover it and stir the contents continually until the temperature has reached a peak and is beginning to decrease steadily. Do not stir too vigorously.

1.11 Allow the data collection to continue for the entire 16 minutes unless you are instructed to stop.

1.12 Once the data have been collected for the ***first*** trial, notify the instructor to show you the method for analyzing the data. For all subsequent trials, you may proceed on your own, but I will be available to help or to confirm your analysis.

1.12.1 Select the Analyze pull down menu and select Examine from this menu.

1.12.2 Move the cursor to the highest point on the graph (highest temperature) and drag the cursor to form a darker blue window that starts at the highest point on the graph and ends with a point collected several minutes into the decay curve.

1.12.3 Perform a Linear Fit on the selected data. If the linear correlation is very close to unity you have captured a nearly linear portion of the curve.

1.12.4 Record the slope and intercept of this line and move the box that displays these values to a portion of the graph that does not contain data.

1.12.5 Select the File pull down menu and the Print Graph option. The number of copies should equal the number of members in your group plus one for the group data to be turned in. Print the graph and get the hard copies from the printer in the lab.

1.13 Before moving on to the next trial, record the starting time and temperature of the reaction. You can get this by positioning the cursor at the point where the temperature starts to rise rapidly. You will use the time value of this point to solve the linear regression equation for the final temperature.

1.14 Remove cup #1 and set it aside to cool. ***Do not discard,*** you will be using it again! Repeat 1.7 – 1.13 for a second trial using a second sample of magnesium and cup #2 of HCl.

2. Reaction of Magnesium Oxide with HCl.

Repeat 1.7-1.14 substituting approximately 0.5 grams of MgO for the magnesium metal. Remember to record the mass of MgO on the analytical balance to within 0.1 mg! Perform two determinations (using cup #1 and then cup #2) for the reaction of MgO with HCl. In these reactions you may find that there is no significant temperature decrease. You should still determine the linear fit line (linear least squares fit or linear regression line) using the maximum temperature and the time points after the maximum. In these trials (Trial 3 and 4) the slope will probably be close to zero.

3. Calculation of the Heat of Reaction

3.1 Convert the number of grams of magnesium and magnesium oxide used in this experiment to moles and enter these values into the table provided.

3.2 From each graph, determine the final temperature by solving the linear fit equation for temperature at the time the reaction was started.

3.3 You should now have the following data for each reaction:

T_0, T_f, mass of Mg or MgO and the moles of Mg or MgO. ***We will assume that the heat properties and density of the HCl solution in the calorimeter are the same as pure water. Thus for calculation purposes 100.0 mL of HCl = 100.0 mL of pure water***.

3.4 Calculate the heat given off by the reaction using the s of water to be 4.184 J/g-ºC, the density of water as 1.00 g/mL, and the heat capacity of the calorimeter as 10.0 J/ºC.

$$q_{water} = ms\Delta T = \text{(mass of water used)} \times 4.184\ \text{J/g-°C} \times (T_f - T_0)$$

$$q_{calorimeter} = ms\Delta T = 10.0\ \text{J/°C} \times (T_f - T_0).$$

Determine these values and enter them into the table provided.

$$q_{total} = 0 = q_{rxn} + q_{water} + q_{calorimeter}$$

$$q_{rxn} = -q_{water} + -q_{calorimeter}$$

3.5 Calculate the value for q_{rxn} and enter it into the table provided. The enthalpy change for the reaction is the heat given off divided by the number of moles of limiting reagent. Divide the qrxn by the moles of material used and enter this value as the ΔH_{rxn} in the table.

3.6 You should have two values for the enthalpy of reaction as described in Trial 1 (manual graph and from the linear curve fit). Determine the percent error between each of these Trial 1 values and your Trial 2 value.

$$\%error = \frac{Trial\ 1\ value - Trial\ 2\ value}{Trial\ 2\ value} \times 100\%$$

3.7 Using the average calculated values for the enthalpy of reaction for each of the reactions (use the value for Trial 1 with the smaller % error as described in 3.6) studied and the accepted value for the reaction between H_2 and O_2 to form water given below, determine the enthalpy of reaction for the formation of ***one mole*** of MgO from Mg and oxygen (Hess's Law). Determine this same value from heat of formation data and record this value as the theoretical value. Calculate the %error between your experimental value and the theoretical value from the equation below. Be sure to use units for all your calculations!

$$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O; \qquad \Delta H = -286\ kJ$$

$$\%error = \frac{\Delta H_{theory} - \Delta H_{experimental}}{\Delta H_{experimental}} \times 100\%$$