## Experiment 9-Heats of Reactions

## Introduction

The most important applications of chemistry (from factories to your body) involve making chemicals that are useful, or burning chemicals for energy. To do either one efficiently, we have to understand energy changes associated with chemical reactions: how much energy it costs to make a compound, or how much energy we can gain from a reaction. This part of chemistry is called calorimetry, which means "heat measurement". The most important concept to remember is the Conservation of Energy, which means that energy is not created or destroyed, it just changes form and moves between substances. For example, when gasoline is burned in a car engine, it gets hot because energy is released by the combustion reaction. The reactants had more internal energy than the products, and the energy released by the reaction heats up the products, and their surroundings, and is used to drive the car. (Don't get confused: the engine gets hot because of energy released by the fuel, not because energy is entering from the surroundings. In fact, heat leaves the engine and warms the surroundings, because the engine is hotter.)

If we want to know how much heat (and thus how much energy to do work, like driving the car) we can get from burning a gallon of gasoline, we have to collect the energy released by the reaction in some measurable way. Usually this is done using a calorimeter. The calorimeter is an insulated container in which we run the reaction. The calorimeter, or the material inside it, has a known heat capacity. Heat capacity (unit $\mathrm{J} /{ }^{\circ} \mathrm{C}$ ) is the amount of energy required to raise the temperature of the material by $1^{\circ} \mathrm{C}$. Since the container is insulated, we assume that the energy absorbed or released by the reaction is all used to change the temperature of the calorimeter and the material inside it. If we measure the temperature change, and know the heat capacity, then we can calculate the energy absorbed or released by the reaction.

In this experiment, we will measure heats of reaction using styrofoam cups as calorimeters. Our reactions will run in aqueous solution. Because water has a high heat capacity, we can assume that the heat capacity of the whole system (cups, products and water) is equal to the heat capacity of the (mostly water) solution. The heat capacity of the solution is just the specific heat " $C s$ " of the solution (or heat capacity/gram which has units of $\mathrm{J} / \mathrm{g} \cdot{ }^{\circ} \mathrm{C}$ ) times the mass of the solution. Then

$$
\begin{equation*}
q_{\text {surr }}=q_{\text {soln }}=m_{\text {soln }} \cdot C_{s} \Delta T \tag{Eq 1}
\end{equation*}
$$

where $q_{\text {soln }}$ is the heat required to cause temperature change $\Delta T$ (where $\Delta T=T_{\text {final }}-T_{\text {initial }}$ ) in the $m$ grams of a solution with specific heat denoted " $C s$ ".

From the $1^{\text {st }}$ Law

$$
\begin{equation*}
q_{s y s}+q_{\text {surr }}=0 \quad \text { or } \quad q_{\text {sys }}=-q_{\text {surr }}=-q_{\text {soln }} \tag{Eq 2}
\end{equation*}
$$

where $q_{s y s}$ is the enthalpy change of the particular amount of reaction in a student's experiment and $q_{\text {soln }}$ is the heat required for the observed temperature change of the solution. If $q_{\text {soln }}$ is positive (temperature increase for the surroundings) then $q_{s y s}$ must be negative (i.e. an exothermic state change). Likewise, if $q_{\text {soln }}$ is negative (temperature decrease for the surroundings) then $q_{\text {sys }}$ must be positive (endothermic state change). The enthalpy of reaction is just $q_{s y s}$ divided (or normalized) by moles of reaction (which in your case will be either moles of limiting Mg or moles of limiting MgO used in your particular experiment):

$$
\begin{equation*}
\Delta H_{r x n}=\mathrm{q}_{\mathrm{rxn}} / \mathrm{n}_{\mathrm{rxn}} \quad \text { hence units of } \mathrm{kJ} / \mathrm{mol} \tag{Eq 3}
\end{equation*}
$$

The reactions studied here are:

$$
\begin{array}{ll}
\mathrm{Mg}(s)+2 \mathrm{HCl}(a q) \rightarrow \mathrm{MgCl}_{2}(a q)+\mathrm{H}_{2}(g) & \text { Rxn 1 } \\
\mathrm{MgO}(s)+2 \mathrm{HCl}(a q) \rightarrow \mathrm{MgCl}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) & \operatorname{Rxn} 2
\end{array}
$$

In each case, the solid reactant $(\mathrm{Mg}$ or MgO$)$ will be the limiting reactant. Since both have a coefficient of 1 in the equation, moles of Mg or MgO is equal to moles of reaction.

Finally, once we have measured the $\Delta H_{r x n}$ for Rxn 1 and Rxn 2, we can use the fact that enthalpy is a state function, hence the path independence of $\Delta H$ in the form of Hess' Law, to find the $\Delta H_{r x n}$ for Rxn 3:

$$
\operatorname{Mg}(s)+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{MgO}(s)+\mathrm{H}_{2}(g) \quad \operatorname{Rxn} 3
$$

Hess' Law says that if you add 2 reactions together, the total enthalpy of reaction will be the sum of the individual $\Delta H_{r x n}$ values. Remember that if you reverse the direction of a reaction (swap the reactants and products) the sign of $\Delta H_{r x n}$ will change (multiply by -1 ).

| $\mathrm{Mg}(s)+2 \mathrm{HCl}(a q) \rightarrow \mathrm{MgCl}_{2}(a q)+\mathrm{H}_{2}(g)$ | $\Delta H_{l}$ |
| :---: | :---: |
| $\mathrm{MgCl}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{MgO}^{2}(s)+2 \mathrm{HCl}(a q)$ | $-\Delta H_{2}$ |
| $\mathrm{Mg}(\mathrm{s})+2 \mathrm{HCl}(a q)+\mathrm{MgCl}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{MgCl}_{2}(a q)+\mathrm{H}_{2}(g)+\mathrm{MgO}(s)+2 \mathrm{HCl}(a q)$ |  |

Add up the reactions, then cancel "spectators" to get reaction 3:

$$
\mathrm{Mg}(s)+\mathrm{H}_{2} \mathrm{O}(l) \rightarrow \mathrm{MgO}(s)+\mathrm{H}_{2}(g) \quad \Delta H_{3}=\Delta H_{l}-\Delta H_{2}
$$

## Safety Precautions:

- Wear your safety goggles.
- Solutions of hydrochloric acid $(\mathrm{HCl})$ are corrosive. If HCl splashes on you, rinse it off immediately with plenty of running water.


## Waste Disposal:

- Neutralize your liquid waste with sodium bicarbonate in a large beaker, then pour it down the sink with plenty of running water.
- Please be careful when weighing the MgO . If you spill any, clean it up!
- Rinse and save the styrofoam cups unless they are broken.


## Part 1

First, we will measure the enthalpy of Rxn 1. A measured amount of hydrochloric acid solution will be placed in a calorimeter. Magnesium ribbon will be added, and the heat produced by the reaction will be measured by observing the temperature change $(\Delta \mathrm{T})$ of the HCl solution. Record all your raw data (masses and temperatures) directly into a table in your notebook.

## Procedure - Part 1

1. Weigh a dry, empty calorimeter (two Styrofoam cups in a stack).
2. Measure out about 100 mL of 1 M HCl in a graduated cylinder.
3. Add the 1 M HCl solution to the calorimeter and weigh it again. Subtraction gives the mass of the HCl solution. The specific heat of 1 M HCl solution is $4.04 \mathrm{~J} / \mathrm{g} \cdot{ }^{\circ} \mathrm{C}$.
4. Allow the temperature of the acid and the calorimeter to equilibrate for a few minutes. While you are waiting, proceed with step 5.
5. Obtain a strip a magnesium ribbon that weighs between 0.2 and 0.3 grams. If the magnesium doesn't look shiny, clean it with steel wool before weighing. Weigh the magnesium strip to the nearest $\pm 0.001$ or $\pm 0.0001$ grams on a digital balance and record the mass.
6. Wind the magnesium ribbon around a pencil to give it a compact, spiral shape.
7. Set up a ring stand with an iron ring, and set the calorimeter under the ring. (This ring will be used to help support the thermometer.) Read and record the temperature of the HCl in the calorimeter. The temperature should be read to the nearest $\pm 0.1^{\circ} \mathrm{C}$. Leave the thermometer in the calorimeter for the rest of the experiment, supported inside the ring on the ring stand so that it doesn't fall over and break.
8. Drop the magnesium into the acid solution in the calorimeter. If necessary, use the thermometer to hold the ribbon under the surface of the acid.
9. Stir or swirl the calorimeter frequently. As the magnesium reacts, observe the temperature. Record the maximum temperature attained (again, to the nearest $0.1^{\circ} \mathrm{C}$ ). This should be reached as the reaction is ending. Wait for a while after the magnesium has completely reacted to be sure you have observed the maximum temperature.
10. Pour the contents of the calorimeter into a large beaker. Neutralize the solution with sodium bicarbonate, if available, and discard the solution in the sink.
11. Repeat the entire procedure to collect a second data set.

## Calculations - Part 1

1. Use your experimental data to calculate the energy absorbed by the solution, using Eqn. 1. Assume the specific heat of the solution is $4.04 \mathrm{~J} / \mathrm{g} \cdot{ }^{\circ} \mathrm{C}$.
2. Calculate the number of moles of reaction that occurred (using the moles of the limiting reactant).
3. Find $\Delta H_{r x n}$ using Eqn 3 , in units of $\mathrm{kJ} / \mathrm{mol}$.
4. Repeat calculations 1-3 for your second trial.
5. Calculate the average value of $\Delta H_{r x n}$ and the percent difference between the two values.
6. Write your name and results on the board.

## Part 2

Second, we will measure the enthalpy of reaction for Rxn 2 . The procedure for studying this reaction is essentially the same as that used in Part 1 . Magnesium oxide $(\mathrm{MgO})$ is a white powder. The MgO will be poured into an excess of HCl in a calorimeter and the temperature change will be measured. In this part of the experiment, 2 M HCl (specific heat $=3.89 \mathrm{~J} / \mathrm{g} \cdot{ }^{\circ} \mathrm{C}$ ) will be used instead of 1 M HCl . In this part, you will calculate how much of the reactants to use using an approximate value for the enthalpy of reaction, then find the experimental enthalpy of reaction using your actual data.

## Pre-Calculations - Part 2

Assuming that you use about 100 mL of solution, and the enthalpy of reaction for Rxn 2 is approximately $-130 \mathrm{~kJ} / \mathrm{mol}$, follow these steps to calculate the mass of MgO that would cause the solution to increase in temperature by $25^{\circ} \mathrm{C}$.

1. How many kJ are needed to heat the 100 mL of solution by $25^{\circ} \mathrm{C}$ ? Assume the solution has a density of about $1 \mathrm{~g} / \mathrm{mL}$.
2. How many moles of the reaction-and, by extension, moles of MgO - are needed to produce this much heat?
3. How many grams of MgO does this correspond to?
4. Check that MgO is the limiting reactant under these conditions (there should be plenty of excess HCl ).
5. Check your calculations with the instructor before proceeding.

## Procedure - Part 2

1. Before you start, you have to do the pre-calculations! See above. You will use approximately the same amount of MgO you calculated. It doesn't need to be exactly the same amount.
2. Repeat the same procedure you used in Part 1, but use 2 M HCl and the mass of MgO that you calculated (to within 0.05 g ). Weigh the MgO on a weigh boat and slowly pour it directly from the paper to the calorimeter, then stir vigorously. Record the masses and temperatures in a table in your notebook, as you did in Part 1. Again, be sure to observe the maximum temperature reached by the system $\left( \pm 0.1^{\circ} \mathrm{C}\right)$. Record the mass after the reaction is complete, and find the amount of MgO you used by subtraction. This way you don't have to worry if some sticks to the weigh boat.
3. When the reaction is complete, check to see that a clear solution remains in the calorimeter. If the solution isn't clear, then some unreacted MgO remained, and you will have to repeat the experiment with less MgO so that it is the limiting reactant.
4. Repeat the procedure, as before. The amount of MgO can be changed, if desired, for the second run, but make sure it is still the limiting reactant.

## Calculations - Part 2

Calculate $\Delta H_{r x n}$ for Part 2 as you did in Part 1. Again, calculate $\Delta H_{r x n}$ separately for each trial, and report the average and the percent difference of the two trials. Although you've been told that it is close to $-130 \mathrm{~kJ} / \mathrm{mol}$, you can't assume this value in your calculations: the purpose of the experiment is to measure this value!

## Part 3

If you want to know $\Delta H_{r x n}$ for Rxn 3, what do you do?

1. Try putting a small scrap ( 1 cm or less) of Mg ribbon in plain water. Does anything happen? Could you measure a heat change for this reaction as you did in Part 1 and Part 2? Why or why not? If you could, would the heat you measured correspond exactly to Rxn 3 as written?
2. Predict whether Rxn 3 is endothermic or exothermic. Explain (you can use your observations, general knowledge, etc).
3. Use Hess's Law to find $\Delta H_{r x n}$ for Rxn 3 using your average $\Delta H_{r x n}$ values for Rxn 1 and Rxn 2. (Figure out how to add Rxn 1 and Rxn 2 to give you Rxn 3. You can cancel formulas that appear on both sides of the reaction; they are "spectator substances" just like when you write net ionic equations.)
4. Your instructor may require you to calculate the percent error for your three $\Delta H_{r x n}$ values, in which case you will need to use standard enthalpies of formation to find the true values.

## Experiment 9 Pre-Lab Sheet

1. (2 pts) Write the reactions whose $\Delta H_{r x n}$ will be determined directly in this experiment.
2. ( 5 pts ) Determine all the raw data you will need to collect for each trial. Draw a sample data table, with appropriately labeled rows and columns, that organizes your raw data sensibly. You should use this table to collect the data directly into your notebook!
3. ( 3 pts ) Sample calculation. You add 0.782 g of Na metal to 100.00 g of $\mathrm{H}_{2} \mathrm{O}$ (specific heat $4.18 \mathrm{~J} / \mathrm{g}^{\circ} \mathrm{C}$ ), and the solution temperature increases from $23^{\circ} \mathrm{C}$ to $36^{\circ} \mathrm{C}$. Find $\Delta H_{r x n}$ for the reaction

$$
2 \mathrm{Na}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow 2 \mathrm{NaOH}(\mathrm{aq})+\mathrm{H}_{2}(\mathrm{~g})
$$

