Name:____

Chemistry 117 Laboratory
University of Massachusetts Boston

HEATS OF REACTION

LEARNING GOALS

1. Become familiar the technique of calorimetry to measure heats of reaction
2. Become familiar with the concept of heat transfer between the reaction occurring in solution and the solvent
3. Become familiar with using the heat capacity of water to estimate the heat absorbed or released during a reaction in solution.
4. Learn to use standard heats of formation to calculate standard heats of reaction

INTRODUCTION

Chemical and physical changes usually involve the absorption or liberation of heat, given the symbol q. When heat is absorbed, the change is said to be *endothermic*, and the numerical value of the heat is given a positive sign ($q > 0$). When heat is liberated, the change is said to be *exothermic*, and the numerical value of the heat is given a negative sign ($q < 0$). Under standard conditions of temperature and constant pressure (exactly 25 ^{o}C and 1 atmosphere) with all reactants in their usual physical states, the measured heat of a reaction is called the *standard enthalpy*, given the symbol ΔH^{o}.

Whether under standard conditions or not, the heats of reactions can often be measured using an apparatus called a *calorimeter*. One of the most useful kinds of heats of reaction to measure and tabulate is the *standard enthalpy of formation* of a substance, ΔH^{o}_{f}, the enthalpy involved in the formation of one mole of a substance from its elements under standard conditions. For example, ΔH^{o}_{f} for $H_2O(l)$ is defined by the following thermochemical reaction:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^{o}_{f} = -285.83 \text{ kJ/mol}$$

This indicates that under standard conditions the formation of one mole of liquid water from its elements liberates 285.83 kJ in an exothermic reaction. By definition, the standard enthalpies of formation of all elements in their standard states are taken to be zero. Therefore, $\Delta H^{o}_{f} = 0$ for both $H_2(g)$ and $O_2(g)$. The reason for tabulating standard enthalpies of formation is that the data can be used to calculate the enthalpy of any reaction under standard conditions, if we know the ΔH^{o}_{f} values for all the reactants and products. For any reaction under standard conditions, the enthalpy of the reaction, $\Delta H^{o}_{\text{rxn}}$, is the sum of the standard enthalpies of formation of the products, multiplied by their stoichiometric coefficients in the reaction equation, minus the sum of the standard enthalpies of formation of the reactants, multiplied by their stoichiometric coefficients in the reaction equation. Mathematically, this can be stated as

$$\Delta H^{\circ}_{\mathrm{rxn}} = \Sigma n_p \Delta H^{\circ}_p - \Sigma n_r \Delta H^{\circ}_r$$

where n_p and n_r are the stoichiometric coefficients of each of the products and each of the reactants, respectively. For example, for a reaction $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$, we would have

$$\Delta H^{\circ}_{\mathrm{rxn}} = [c\Delta H^{\circ}_f(\mathrm{C}) + d\Delta H^{\circ}_f(\mathrm{D})] - [a\Delta H^{\circ}_f(\mathrm{A}) + b\Delta H^{\circ}_f(\mathrm{B})]$$

One of the heat changes we will measure in this experiment results from the reaction of metallic magnesium metal with dilute hydrochloric acid to form hydrogen gas and a solution of magnesium chloride:

$$\mathrm{Mg}_{(s)} + 2\mathrm{HCl}_{(aq)} \rightarrow \mathrm{H}_{2(g)} + \mathrm{MgCl}_{2(aq)}$$

The appropriate data from the short table of standard enthalpies of formation shown below can be used to calculate the value of $\Delta H^{\circ}_{\mathrm{rxn}}$ for this reaction.

Species	ΔH°_f, kJ/mol
$\mathrm{HCl}(g)$	–92.30
$\mathrm{HCl}(aq)$	–167.2
$\mathrm{MgCl_2}(s)$	–641.6
$\mathrm{MgCl_2}(aq)$	–796.9
$\mathrm{H_2O}(l)$	–285.83

$$\begin{aligned}\Delta H^{\circ}_{\mathrm{rxn}} &= [\Delta H^{\circ}_f(\mathrm{MgCl}_{2(aq)}) + \Delta H^{\circ}_f(\mathrm{H}_{2(g)})] - [\Delta H^{\circ}_f(\mathrm{Mg}_{(s)}) + 2\Delta H^{\circ}_f(\mathrm{HCl}_{(aq)})] \\ &= [-796.9 + 0] - [0 + 2(-167.2)] = -462.5 \text{ kJ/mol}\end{aligned}$$

Your calculated value of $\Delta H^{\circ}_{\mathrm{rxn}}$ for this reaction is -462.5 kJ per mole of Mg(s) reacted. This reaction is quite exothermic.

PROCEDURE

Principles of Calorimeter Measurements

Precision calorimeters are very expensive and extremely tedious to use. Therefore, in this experiment we will use a simple "coffee-cup calorimeter." The coffee-cup calorimeter, as shown in Fig. 1 below, consists of two expanded polystyrene (Styrofoam$^{\mathrm{TM}}$) cups, nested together (one inside the other). The cups are stabilized with a ring on a ring stand and are covered with a 10-cm square piece of fiber board with a small hole in it, through which the probe of a digital thermometer is inserted. A Teflon$^{\mathrm{TM}}$-coated magnetic stir bar inside the inner cup allows continuous stirring of any solution, using the spinning magnet inside the motorized stirrer underneath the cups. The thermometer probe should fit snugly in the hole in the cover, and its tip should be just high enough above the bottom of the cup to avoid being hit by the spinning stir bar.

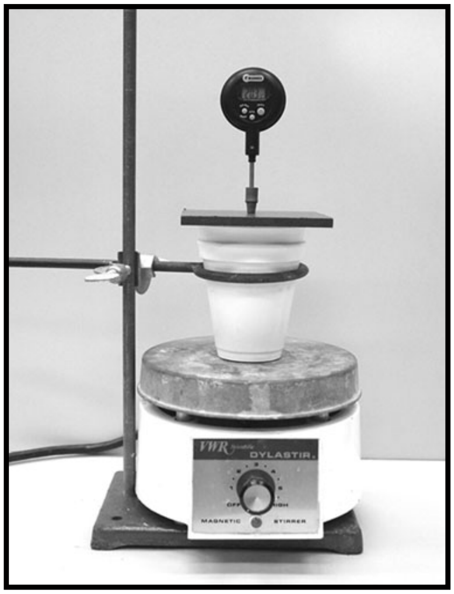

Fig. 1. Experimental set-up of a "coffee-cup calorimeter"

Regardless of design, a calorimeter is used to determine heats of reaction by calculating the heat change experienced *by the calorimeter* (not the reaction itself), using the equation

$$q_{\mathrm{cal}} = C_{\mathrm{cal}}\Delta T$$

where q_{cal} is the heat change for the calorimeter, C_{cal} is the heat capacity of the calorimeter (the apparatus and its contents), and ΔT is the temperature change of the calorimeter, defined as the final temperature (T_{f}, after the heat change) minus the initial temperature (T_{i}, before the heat change); i.e.,

$$\Delta T = T_{\mathrm{f}} - T_{\mathrm{i}}$$

In precise calorimeter studies the heat capacity of the apparatus is carefully obtained as an instrument constant. To arrive at a working value of the heat capacity of our coffee-cup calorimeter, we will need to make some simplifying assumptions. Expanded polystyrene is a good insulator, which is why it keeps hot or cold liquids from changing temperature rapidly. However, polystyrene itself has a relatively low heat capacity, so very little heat is needed to change the temperature of the inside of the cup to that of the liquid it contains. Therefore, we will assume that the heat capacity of the apparatus is essentially that of the liquid in it.

Moreover, in this experiment we will be creating dilute solutions, whose heat capacities are not significantly different from pure water, which has a specific heat of 4.184 J/$^{\circ}$C·g. In each case, then, we will obtain the heat capacity of the calorimeter as the product of the mass of the solution in the cup times the specific heat of water:

$$C_{\text{cal}} \;.\; (\text{grams of solution}) \times 4.184\ \text{J/}^{\circ}\text{C}\cong\text{g}$$

In a precision laboratory calorimeter, the temperature change, ΔT, is measured as the change for the water used to surround the reaction chamber and fill the apparatus. In our experiments, we can obtain the ΔT value by measuring the temperatures of the liquid in the cup before and after the chemical reaction or physical process we are studying, using the digital thermometer. If the temperature of the liquid in our coffee-cup calorimeter rises as a result of a chemical reaction or physical change, the calorimeter itself has absorbed heat, an endothermic heat change. By the First Law of Thermodynamics, heat is not lost, but rather is transferred from one body to another. This means that the endothermic heat change of the calorimeter is the result of an exothermic reaction or process, which gives off the same amount of heat as the calorimeter takes in. In the same manner, if the temperature of the calorimeter falls as a result of some chemical reaction or physical process, the calorimeter has experienced an exothermic change in which it has given an equal amount of heat to the reaction or process. In this case, the chemical reaction or physical process is endothermic. In general, then, the heat change for the calorimeter is equal but opposite in sign to the heat change for the chemical reaction or physical process taking place in it; i.e.,

$$q_{\text{cal}} = -q_{\text{rxn}}.$$

Part A: Heat of Solution

When an ionic compound is dissolved in water, the resulting solution may be warmer or cooler than the initial temperature of the pure water, depending on the particular ionic compound dissolved. The *heat of solution* of a substance is defined as the heat absorbed or liberated when one mole of solute is dissolved in an infinite amount of water. The phrase “infinite amount of water” simply means an amount of solvent so large that further addition of solvent causes no measurable change in the observed heat of dissolving the solute. The conditions in the following procedure only approximate infinite dilution. As a result, the measured heat of solution will be slightly lower than the actual value at infinite dilution.

1. On a triple-beam balance, determine the mass of one polystyrene cup with the stir bar placed inside it. Record this mass to ±0.01 g on the data sheet.

2. With a graduated cylinder, measure 100 mL of deionized water, and transfer it to the previously weighed polystyrene cup. On the same triple-beam balance used in step 1, determine the mass of the cup, stir bar, and water. Record this mass to ±0.01 g on the data sheet. Determine the mass of water by subtraction.

3. On a triple-beam balance, determine the mass of an aluminum weighing dish. Add to the weighing dish a sample of potassium nitrate whose mass is in the range of 2.0 to 2.5 g. Record the mass of the weighing dish and sample to ±0.01 gram on the data sheet. Determine the mass of the sample by subtraction.

4. Assemble the coffee-cup calorimeter as shown in Fig. 1, being careful not to spill any of the previously weighed water. Start the stirrer motor, and adjust the speed to obtain vigorous stirring without splashing. Record the temperature of the water in the polystyrene cup just prior to adding the sample of potassium nitrate (next step). This is the initial temperature, T_i.

5. Quickly add *all* of the potassium nitrate sample to the water (tap the bottom of the weighing dish, if necessary), and immediately cover the cup with the lid. Continuously stir the mixture for about one minute until the temperature remains constant for 15 seconds. Record this as the final temperature, T_f, on the data sheet.

6. Check to be sure that all the solid potassium nitrate dissolved. If it did, carry out the remaining calculations on the data sheet. If it did not, repeat the experiment.

Heats of Reaction

Name____ Lab Section____________________

Partner(s)_______________________________________

DATA SHEET

Part A: Heat of Solution

a. Mass of empty cup with stir bar _________________ g

b. Mass of cup, stir bar, and 100 mL water _________________ g

c. Mass of water _________________ g

d. Mass of weighing dish _________________ g

e. Mass of weighing dish plus $KNO_3(s)$ _________________ g

f. Mass of $KNO_3(s)$ _________________ g

g. Mass of solution _________________ g

h. Heat capacity of calorimeter _______________ J/^{o}C

i. Initial temperature, T_i ________________ ^{o}C

j. Final temperature, T_f ________________ ^{o}C

k. Temperature change, ΔT ________________ ^{o}C

l. Calorimeter's heat change, q_{cal} _________________ J

m. Solution heat change, $q_{soln} = - q_{cal}$ _________________ J

n. Moles of $KNO_3(s)$ dissolved (f.w. KNO_3 = 101.11 u) _______________ mol

o. Heat of solution per mole of $KNO_3(s)$ dissolved ____________ kJ/mol

p. Is dissolving of KNO_3 in water exothermic or endothermic? __________________

q. Assuming the correct heat of solution is +34.89 kJ/mol, calculate
the percent error in your result. ____________% error

B. Heat of Neutralization

Whenever a strong acid and strong base are mixed, a neutralization reaction occurs in which hydronium ion, H_3O^+, from the acid reacts with hydroxide ion, OH^-, from the base to form water:

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2H_2O_{(l)}$$

The *heat of neutralization* for this reaction is a measure of the heat change when one mole of hydronium ion reacts with one mole of hydroxide ion.

1. Empty your calorimeter, and rinse the inner polystyrene cup, stir bar, and thermometer probe with deionized water. Allow the excess water to drain from the cup, then dry the cup, stir bar, and thermometer probe with a paper towel.

2. Assemble the coffee-cup calorimeter as shown in Fig. 1, and place the stir bar in the inner cup.

3. With a graduated cylinder, measure approximately 50 mL of 1.00 M hydrochloric acid solution, and record the exact volume to 0.1 mL on the data sheet. Transfer this to the inner polystyrene cup of the calorimeter.

4. With another graduated cylinder (not previously used for hydrochloric acid solution), measure between 30 and 40 mL of 1.00 M sodium hydroxide solution, and record the exact volume to 0.1 mL on the data sheet.

5. Start the stirrer motor, and adjust speed to obtain vigorous stirring without splashing. Measure and record the temperature of the hydrochloric acid solution in the cup just prior to adding the sodium hydroxide solution (next step). This is the initial temperature, T_i. (The temperature of the sodium hydroxide solution can be assumed to be the same, because both solutions have been standing in the laboratory for the same amount of time.)

6. Add all of the sodium hydroxide solution to the cup containing the hydrochloric acid solution, and place the lid over the cup. Continue stirring until the temperature becomes constant. Record this as the final temperature, T_f, on the data sheet.

7. Carry out the calculations indicated on the data sheet.

Heats of Reaction

Name____ Lab Section____________________

Partner(s)_______________________________________

DATA SHEET

B. Heat of Neutralization

a. Exact volume of 1.00 M HCl(*aq*) (~50 mL) _______________ mL

b. Exact volume of 1.00 M NaOH(*aq*) to be added (30 - 40 mL) _______________ mL

c. Moles of NaOH ______________ mol

d. Assuming 1.00 mL = 1.00 g, mass of solution produced on mixing ________________ g

e. Heat capacity of calorimeter, C_{cal} ______________ J/°C

f. Initial temperature, T_{i} _______________ °C

g. Final temperature, T_{f} _______________ °C

h. Temperature change, ΔT _______________ °C

i. Calorimeter's heat change, q_{cal} ________________ J

j. Neutralization heat change, $q_{\text{rxn}} = -\, q_{\text{cal}}$ ________________ J

k. Moles of H_3O^+ neutralized with OH^- ______________ mol

l. Heat of neutralization per mole of H_3O^+ neutralized ____________ kJ/mol

m. Is the heat of neutralization exothermic or endothermic? __________________

n. Assuming the correct value of the heat of neutralization is
–57.36 kJ/mol, calculate the percent error in your result. ____________% error

C. Heat of Reaction of Magnesium and Hydrochloric Acid

In this experiment you will measure the heat of the reaction of metallic magnesium metal with 1.00 M hydrochloric acid solution to form hydrogen gas and a solution of magnesium chloride:

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + MgCl_{2(aq)}$$

1. Empty the previous solution in your calorimeter into the appropriate chemical waste container. Rinse the inner polystyrene cup, stir bar, and thermometer probe with deionized water. Allow the excess water to drain from the cup, then dry the cup, stir bar, and thermometer probe with a paper towel.

2. On a triple-beam balance, determine the mass of the inner polystyrene cup with the stir bar placed inside it. Record this mass to ±0.01 g on the data sheet.

3. With a graduated cylinder, measure 75 mL of 1.00 M hydrochloric acid solution, and transfer it to the previously weighed polystyrene cup. On the same triple-beam balance used in step 2, determine the mass of the cup, stir bar, and hydrochloric acid solution. Record this mass to ±0.01 g on the data sheet. Determine the mass of the hydrochloric acid solution by subtraction.

4. With sandpaper, clean a 15-cm strip of magnesium ribbon weighing about 0.1 g until it is shiny. Shape the strip into a zig-zag pattern, so that it will fit the bottom of the cup when you eventually add it to the hydrochloric acid solution (step 6, below). Then determine the mass of the strip on an analytical balance to ±0.0001 g. Record this mass on the data sheet.

5. Assemble the coffee-cup calorimeter as shown in Fig. 1, being careful not to spill any of the previously weighed hydrochloric acid solution. Start the stirrer motor, and adjust the speed to obtain vigorous stirring without splashing. Record the temperature of the hydrochloric acid solution in the polystyrene cup just prior to adding the sample of magnesium (step 6, below). This is the initial temperature, T_i.

6. Add the previously weighed magnesium strip to the cup containing the hydrochloric acid solution, and place the lid over the cup. Continue stirring until the temperature becomes constant. Record this as the final temperature, T_f, on the data sheet.

7. Carry out the calculations indicated on the data sheet.

8. Clean up by emptying the contents of your calorimeter into the appropriate chemical waste container. Rinse the cup, stir bar, and thermometer probe with deionized water. Allow the excess water to drain from the cup, then dry the cup, stir bar, and thermometer probe with a paper towel. Reassemble the apparatus so it is ready for the next laboratory section.

Heats of Reaction

Name____ Lab Section___________________

Partner(s)_____________________________________

DATA SHEET

C. Heat of Reaction of Magnesium and Hydrochloric Acid

a. Mass of empty cup with stir bar ________________ g

b. Mass of cup, stir bar, and 75 mL of 1.00 M $HCl(aq)$ ________________ g

c. Mass of $HCl(aq)$ solution ________________ g

d. Mass of $Mg(s)$ ________________ g

e. Mass of solution ________________ g

f. Heat capacity of calorimeter, C_{cal} ______________ J/°C

g. Initial temperature, T_{i} _______________ °C

h. Final temperature, T_{f} _______________ °C

i. Temperature change, ΔT _______________ °C

j. Calorimeter's heat change, q_{cal} ________________ J

k. Reaction heat change, $q_{\text{rxn}} = - q_{\text{cal}}$ ________________ J

l. Moles of $Mg(s)$ reacted ______________ mol

m. Heat of reaction per mole of $Mg(s)$ reacted ____________kJ/mol

n. The heat of reaction of this reaction was calculated in the introduction. Using this as the theoretical value, calculate the percent error in your experimental result. ___________% error

Lab Report:

Your lab report will consist of your data sheets (pgs 6, 8 and 10) and a discussion of your results in paragraph form. Points to be addressed in your discussion.

- Provide a summary of your results (10 pts)
- Discuss any experimental difficulties you encountered. (5 pts)
- How large was your experimental errors for the three different reactions (5 pts)
- For each trial determine what temperature change would have resulted in the theoretical value for the heat of reaction. (5 pts) Based on this calculation, postulate a likely source of error based on “expected” temperature change? (5 pts)