Experiment 6: CALORIMETRY AND THE ENTHALPY OF REACTION

PRELIMINARY READING: Chang, section 6.5

INTRODUCTION

Heat, symbolized $q$, is a form of energy transfer occurring between two objects that are initially at different temperatures. Many chemical reactions are accompanied by either the absorption or release of heat. Reactions in which heat is absorbed are described as endothermic ($q$ is positive), while those in which heat is released are termed exothermic ($q$ is negative). The process by which heat transfer is measured is known as calorimetry.

When pressure is held constant (e.g., in an open container), the measured quantity of heat $q$ transferred is equal to the change in enthalpy, $\Delta H$.

$$q_p = \Delta H$$

(1)

Enthalpy change is a measure of the relative stability of reactants versus products. For exothermic reactions, the products are more stable than the reactants; for endothermic reactions, the reactants are more stable than the products. In this experiment the enthalpy change of an acid-base neutralization reaction will be measured in a calorimeter.

$$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{NaCl(aq)}$$

(2)

The enthalpy change $\Delta H$ of the reaction will be equal to the amount of heat lost by the reactants. This heat is transferred to the products of the reaction. However, while the calorimeter is well-insulated from the surroundings, the interior of the calorimeter (including the temperature probe and stirrer) also absorbs some heat. Thus, the heat-balance expression for this experiment is as follows:

$$\Delta H = q_{\text{reactants}} = -(q_{\text{products}} + q_{\text{calorimeter}})$$

(3)

We will be measuring the heat gained by the products and by the calorimeter.

Now, how is $q$ actually measured? For this purpose we make use of a quantity called the specific heat capacity, or just specific heat for short. This quantity is symbolized $s$ in your course textbook (advanced texts more commonly use the symbol $C_p$). The specific heat is defined to be the amount of heat necessary to raise the temperature of 1 gram of a given substance by 1 °C. In symbolic terms, this definition appears as:

$$s = \frac{q}{m \cdot \Delta T}$$

(4)

Note that $\Delta T$ is defined as $T_{\text{final}} - T_{\text{initial}}$. If this equation is solved for $q$, the method for measuring heat becomes apparent:

$$q = m \cdot s \cdot \Delta T$$

(5)

The mass of the products and the temperature change may be determined experimentally. The specific heat of the products will be given. The heat gained by the calorimeter is a bit more problematic. A specific heat for any given calorimeter must be determined experimentally. Since the mass of the calorimeter itself does not change, the product of the mass and the specific heat is designated as a property of the calorimeter called the calorimeter constant, $C_{cal}$, which has units of J / °C. The heat balance expression now looks as follows:

$$q_{\text{reaction}} = \Delta H = -[(m_{\text{products}} \cdot s \cdot \Delta T) + (C_{cal} \cdot \Delta T)]$$

(6)

The calorimeter constant may be measured by carrying out a reaction of known enthalpy change in the calorimeter and noting the difference between the experimental and theoretical enthalpy changes. In this case, measured
samples of hot water and cold water will be mixed in the calorimeter and come to temperature equilibrium. The total heat loss by the hot water equals the total heat gain by the cold water and the calorimeter. In symbolic terms

\[-q_{\text{hot water}} = q_{\text{cold water}} + q_{\text{calorimeter}}\]  \hspace{1cm} (7)

Expanding each term according to the information above yields

\[-(m_{\text{hot}} \cdot s(H_2O) \cdot \Delta T_{\text{hot}}) = (m_{\text{cold}} \cdot s(H_2O) \cdot \Delta T_{\text{cold}}) + (C_{\text{cal}} \cdot \Delta T_{\text{cal}})\]  \hspace{1cm} (8)

The masses of the two water samples and the temperature changes are measured experimentally, and the specific heat of water is a known value.

We will measure the calorimeter constant in part A and the enthalpy of neutralization of the acid-base reaction in part B.

PRELAB QUESTIONS:

1. Consider the following thermochemical equation:

\[A + B \rightarrow C \hspace{1cm} \Delta H = +21 \text{ kJ/mol}\]

If solutions of A and B initially at 25°C are combined in a beaker, will the beaker get hotter or colder? Is this reaction endothermic or exothermic?

2. If 4250 joules of heat is added to 65.0 g of water initially at 25.0°C, what is the final temperature of the water? The specific heat of water is 4.184 J/g °C.

3. A calorimeter contains 95.0 g of water initially at 24.7°C. To this is added 40.0 g of water at 65.3°C. The final temperature of the mixture is 36.4°C. The specific heat of water is 4.184 J/g °C. Determine the calorimeter constant of this calorimeter. Note that the cold water and calorimeter undergo exactly the same temperature change. Note: read the calculations section below.

EQUIPMENT AND MATERIALS: two styrofoam coffee cups, 4” x 4” x 3/8” piece of corrugated cardboard or foam board with small hole in center, two 100- or 150mL beakers, two 50- or 100-mL graduated cylinders, thermometer, ring stand, iron ring, wire gauze, burner, lighter, computer with Logger Pro interface and two temperature probes, 100 mL each of 1.00 M HCl and 1.00 M NaOH.

PROCEDURE

A. Determination of Calorimeter Constant

The calorimeter will be a doubled styrofoam coffee cup. A 4” x 4” x 3/8” piece of cardboard with a hole for the temperature probe will be used as a cover.

1. Plug the temperature probes into port 1 and port 2 of the Vernier interface. Start the Logger Pro program; a window will open that has time on the x-axis and temperature (channels 1 and 2) on the y-axis. On the Experiment menu, choose Data Collection. On the Collection tab, set the length to 300 seconds. On the Data menu choose Column Options, then Temperature. Under the Options tab, set the displayed precision as 2 decimal places.

2. Use a graduated cylinder to accurately measure 50.0 mL of deionized water into a dry 100-mL beaker and measure another 50.0 mL of deionized water into the clean, dry calorimeter. Cover the calorimeter and insert
the channel 1 temperature probe through the hole in the cover. Place the beaker on a wire gauze on a ring stand with the channel 2 temperature probe in the water, and heat the water to about 60 °C. Turn off the burner when the temperature is slightly below your target value, as the temperature will continue to rise for a short time.

3. When the temperature of the hot water begins to fall you may begin data collection by clicking on the **Collect** button on the computer screen. Collect temperature data on the two channels for about 60 seconds, then proceed to step 4 without stopping the data collection.

4. Quickly and carefully pour the hot water into the calorimeter and quickly replace the cover and temperature probe. (Cooperation by the two partners will help here.) If you allow too much heat to be lost to the atmosphere from the hot water you will get poor results. Swirl the calorimeter and contents gently to mix and allow the computer to record the temperature of the mixture for the remainder of the 300 seconds.

5. To analyze and print your data;

   a) Rescale the graph in order to have data fill the page by clicking on the **Autoscale** button.

   b) Click the **Statistics** button. In the box that appears on the graph, several statistical values are displayed for Temp 1, including the minimum and maximum. Record these values in your lab notebook. The minimum should represent the initial temperature of the cold water (the flat portion of the Temp 1 trace) and calorimeter, and the maximum represents the final temperature for the entire system. Click and drag the box until it is in a convenient position that does not obscure the temperature curves.

   c) Use the **Examine** feature to move the cursor to the point on the Temperature 2 plot just at the point of mixing; this is the point just before the Temp 1 trace begins to rise. Record this temperature as the initial temperature of the hot water.

   d) Print a copy of the Graph window. In order to have the data from the Examine box printed, you can not use the mouse for the print command. Instead, type **Alt+F** to access the file menu. Scroll down using the arrow keys to the command “Print Graph.” Enter your name(s) and the number of copies. You may wish to add additional title information, such as “Part A, Trial 1.”

   e) When you collect a new set of data, the original set will be lost if it is not saved or stored. You may do this by choosing Store Latest Run from the Data menu, and the data will be stored as Run 1. Subsequent trials will be plotted on the same graph. In order to hide the earlier runs, click on the Temperature axis label and uncheck Run 1, then click OK.

6. Dry the calorimeter, temperature probe, and beaker, and repeat steps 1-5 in order to obtain two values of \( C_{cal} \), which will be averaged.

Part B: Enthalpy of Neutralization

1. Dry the calorimeter, probe, and beaker again. Carefully measure 50.0 mL of 1.00 M NaOH solution into the calorimeter. Add the cover and channel 1 probe and prepare the computer to record the temperature of this solution.

2. Pipet 50.0 mL of 1.00 M HCl solution into a clean, dry 100-mL beaker. Place the channel 2 probe in this solution.

3. Begin data collection as before and record the temperatures in the calorimeter for 30 seconds, then, without halting data collection, quickly and carefully pour the acid solution into the calorimeter and replace the cover with temperature probe on the calorimeter. Swirl the mixture gently and continue to record the temperature for
the remainder of the 300 seconds.

4. Autoscale the graph, then analyze and print out your data as described in part A.

5. Clean and dry the equipment and carry out a repeat determination.

CALCULATIONS

Part A:

Do a complete set of calculations for each trial (don’t average the temperatures from the two trials). Rearrange equation (8) to solve for the calorimeter constant. Recall that the temperature changes are all defined to be final value minus initial value. Again, note that the cold water and calorimeter undergo exactly the same temperature change. The specific heat of liquid water is 4.184 J/g °C. Look up the density of water at 25°C (reference your source) and use this value to calculate the masses of the water samples. Solve for C_{cal} in each trial, then average your two values for C_{cal} and use this average value in part B. Be sure to use significant figures properly.

Part B:

1. Use equation (6) to determine q for the neutralization reaction. Be careful about the signs of quantities. The product solution is a 0.500 M solution of NaCl. We may assume that the specific heat of this dilute NaCl solution is equal to that of pure water. However, note that the mass of products should be 100.9 g, since an additional 0.901 g of water was formed in the reaction.

2. Since enthalpy changes are normally reported on a per mole basis, we will do the same. Determine the number of moles of water formed in the reaction (see step 1 above). Divide the total q for the reaction that was calculated in step 1 by the number of moles of water formed to yield the molar enthalpy change ΔH. Report the results of the two trials, plus the average value.

3. Write the net ionic equation for the neutralization reaction (recall that HCl and NaOH are both strong electrolytes). Look up the appropriate standard enthalpies of formation and calculate ΔH° for this reaction.

Compare your results for the ΔH of neutralization with the theoretical value that you calculated in number 3 and calculate the percent error. Is the neutralization endothermic or exothermic? What is the significance of this result? Discuss possible sources of systematic error. Be sure to label all of your graphs clearly and include them with your report.

REPORT

Fill in the attached data sheet and attach your calculations, graphs, and discussion of results.

(Revised 5/07)
# CHE 131L: Calorimetry

Name______________________________

## Data and Results:

### A. Calorimeter Constant

<table>
<thead>
<tr>
<th></th>
<th>Trial 1</th>
<th>Trial 2</th>
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<tbody>
<tr>
<td>Initial temp of cold water &amp; calorimeter, °C</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>Initial temp of hot water, °C</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>Final temp of mixture, °C</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>ΔT of cold water &amp; calorimeter, °C</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>ΔT of hot water, °C</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>$q_{\text{cold}}$, J (heat gained by cold water)</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>$q_{\text{hot}}$, J (heat lost by hot water)</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>$q_{\text{calorimeter}}$, J (heat gained by calorimeter)</td>
<td>_______</td>
<td>_______</td>
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<tr>
<td>$C_{\text{cal}}$, J/°C</td>
<td>_______</td>
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<tr>
<td>Average $C_{\text{cal}}$, J/°C</td>
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<td></td>
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</tbody>
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### B. Enthalpy of Neutralization

<table>
<thead>
<tr>
<th></th>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_i$ of HCl, °C</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>$T_i$ of NaOH, °C</td>
<td>_______</td>
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<tr>
<td>Average $T_i$, °C</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>$T_f$ of NaCl solution, °C</td>
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<td>_______</td>
</tr>
<tr>
<td>ΔT, °C</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>q of NaCl solution, J</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>q of calorimeter, J</td>
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<td>_______</td>
</tr>
<tr>
<td>total q of reaction, J (note sign)</td>
<td>_______</td>
<td>_______</td>
</tr>
<tr>
<td>ΔH of reaction, kJ/mol</td>
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<td>_______</td>
</tr>
<tr>
<td>Average ΔH, kJ/mol</td>
<td>_______</td>
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<tr>
<td>% Error in ΔH</td>
<td>_______</td>
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