Calorimetry

Objectives:

After completing this lab, you should be able to:
- Assemble items of common laboratory equipment and collect experimental data
- Perform calculations involving thermodynamic functions and variables
- Begin to develop an appreciation for the fact that almost all chemical reactions are accompanied by a change in energy
- Write the Experimental section of a formal laboratory report

Resources:

Lab Text – Chapter IV and Appendix A
Lecture Text – Chapter 6
Constant Pressure Calorimetry Video
Purdue University Chemistry Lab Resources

Safety:

Eye protection must be worn at all times in the lab. Hydrochloric acid and sodium hydroxide are extremely corrosive in case of skin or eye contact and toxic when ingested. Concentrated hydrochloric acid should be opened and dispensed only in the fume hood. MSDS sheets for all of the compounds used in this experiment are available in the lab.

Introduction:

With very few exceptions, all chemical and physical changes that matter undergoes are accompanied by a change in energy. The branch of science that was developed during the 18th and 19th centuries to study that change in energy is thermodynamics. Fortunately, thermodynamics deals with macroscopic variables like temperature, volume and pressure that are relatively easy to measure in the lab. It assumes no knowledge of the nature of matter at the atomic or molecular level.

As the name suggests, thermodynamics often involves changes in energy in the form of heat. We can define heat as the “flow of internal energy from one object to another due to a difference in temperature”, as illustrated in the diagram shown below.
In a calorimeter experiment, we are usually measuring the heat produced by a chemical or physical change indirectly; that is we are keeping track of the changes taking place in the surroundings, not in the system. The law of conservation of energy tells us that all of the heat released by the system must be gained by the surroundings. If we can monitor the temperature change of the surroundings and keep track of everywhere the heat goes after being released by a chemical reaction (the system), we can determine how much heat was released. Keep in mind that some chemical and physical processes are endothermic; that is heat is absorbed rather than being released.

\[
\text{Endothermic} \\
\Delta H > 0
\]

\[
\text{Exothermic} \\
\Delta H < 0
\]

The master equation for calorimetry calculations is given below:

\[ q = m \ C \ \Delta T \]

Where

\[ q \] is the heat released or absorbed. Because heat is a form of energy, the SI unit of heat is the joule (J).

\[ m \] is the mass of the substance undergoing a change in temperature as a result of releasing or absorbing heat. Common units are grams (g).

\[ C \] is the specific heat (capacity) of the substance undergoing a change in temperature. Common units are joules per gram degree celsius (J/g °C) or joules per gram kelvin (J/g K). Specific heat is a characteristic intensive physical property of a substance. The specific heat of water is 4.184 J/g °C.

\[ \Delta T \] represents the change in temperature (always \( T_{\text{final}} - T_{\text{initial}} \)). Units can be either °C or K.

You should convince yourself that the units of these terms are consistent with the equation given above.
We will be using a simple coffee cup calorimeter for determining the heat of neutralization for an acid-base reaction and heat of solution for a soluble salt. Because the cups are not tightly sealed, we are working under conditions of constant pressure.

The thermodynamic function which represents the heat of a reaction under conditions of constant pressure is enthalpy (H). For our neutralization reaction therefore, we can write

\[ q_{\text{rxn}} = \Delta H_{\text{rxn}} \]

Procedure:

Part I: Preparation of Solutions

Prepare 250 mL of a 1.00 M solution of hydrochloric starting with the concentrated reagent (12.1 M). **Caution: concentrated hydrochloric acid should be opened and dispensed only in the fume hood.**

Prepare 250 mL of a 1.00 M solution of sodium hydroxide starting with the solid reagent. Keep in mind that the heat of solution of sodium hydroxide is exothermic. This solution should be transferred to an appropriate plastic bottle for storage.

Part II: Construction of Calorimeter

Gather all of the components for constructing a constant pressure coffee cup calorimeter. You will need to fashion your own stirring device from a piece of solid glass rod. Placing the coffee cups inside a beaker of appropriate size will help to stabilize the setup. Think about the details of your calorimeter in terms of what you are trying to accomplish.

Part III: Calibration of the Calorimeter

In order to account for all of the heat produced by a reaction in the calorimeter, it is important to determine how much heat the calorimeter itself absorbs. This can be accomplished by combining two masses of water, one “hot” and one “cold”. If the coffee cups were perfect insulators, the final temperature of the combined mass of water would be midway between the hot and cold temperatures, assuming equal masses were used. Because the cups are not perfect insulators, the hot water will lose slightly more heat than the cold water gains. The difference represents the heat capacity of the calorimeter, often referred to as the “calorimeter constant”.

Give it Some Thought:
What is the source of the "constant pressure" referred to above?
Determine the calorimeter constant by using the master equation for calculating the amount of heat lost by the hot water and the amount of heat gained by the cold water.

**Give it Some Thought:**
What are the units of the calorimeter constant?

**Part IV: Measuring Enthalpy of Neutralization**

Measure the enthalpy of neutralization for the reaction of HCl and NaOH and express it on a kJ per mole of HCl basis. Repeat the measurement for a total of three trials. Calculate the average enthalpy of neutralization and the standard deviation. Be sure to include the calorimeter constant in your calculations.

**Give it Some Thought:**
How have you chosen to define the system and the surroundings in your calorimeter setup?

**Part IV: Measuring Enthalpy of Solution**

The solution of a soluble salt such as sodium chloride involves a physical change rather than a chemical change. We can conveniently represent the solution process by the following, in which water is shown as the solvent and not explicitly as a reactant.

\[
\text{NaCl} \quad \overset{\text{H}_2\text{O}}{\longrightarrow} \quad \text{Na}^{+} \quad \text{Cl}^{-}
\]

Choose one of the soluble salts provided in the laboratory. Using about 100 g of water and about 10 g of the soluble salt, set up a calorimeter experiment to measure the enthalpy of solution for the salt. Perform three replicate trials and express your results on a kJ per mole of salt (kJ/mol) basis. Calculate the average and standard deviation.

**Give it Some Thought:**
Although you are asked to use "about" 100 g of water and "about" 10 g of salt, does it matter how accurately you weigh each of these substances? You have encountered this situation before!
Clean Up:

Soluble salts and neutralized solutions of acids and bases may be flushed down the drain with plenty of water.

Pre-Lab Preparation:

1) Write the molecular equation, complete ionic equation and net ionic equation for the reaction of hydrochloric acid and sodium hydroxide

2) Show the calculation for preparing 250 mL of a 1.00 M solution of hydrochloric starting with the concentrated reagent (12.1 M).

3) Show the calculation for preparing 250 mL of a 1.00 M solution of sodium hydroxide starting with the solid reagent.

4) The master equation for calculating enthalpies of reaction in a calorimeter experiment is $q = m C \Delta T$. What are the units for each of these terms?

5) What is the numerical value for the specific heat of water in units of calories? In units of joules?

Assessment:

Pre-Lab Preparation responses – 20 pts. (Due at the beginning of the lab period)
Successful completion of procedure – 40 pts.
Final Lab notes – 40 pts. (Due at the end of the lab period)