Constant Pressure Calorimetry

Purpose

To use changes in temperature to determine 1) the enthalpy of a neutralization reaction, 2) the enthalpy associated with dissolving a compound and 3) the specific heat capacity of a metal.

Learning Objectives

Use a coffee-cup calorimeter to monitor temperature changes during various chemical and physical processes.

Calculate the change in enthalpy for a neutralization reaction by determining the change in temperature.

Calculate the change in enthalpy for the dissolution of an ionic compound by determining the change in temperature.

Calculate the specific heat capacity of a metal by determining the change in temperature.

Laboratory Skills

Set up a constant pressure calorimeter.

Monitor and record data at specific times while carrying out steps in a procedure.

Equipment

- Coffee cup calorimeter
- 1 cardboard lid
- Thermometer
- 50.0 mL graduate cylinder
- 150.0 mL beaker

Chemicals

- Metal pieces: Zinc, Aluminum, steel
- 1.00 M HCl solution
- NH_4NO_3
- 1.00 M NaOH solution
- $MgSO_4$
- DI Water

Introduction

Chemical reactions are often accompanied by changes in heat energy. When heat is released, the reaction is called **exothermic**. When heat is absorbed, the reaction is called **endothermic**. If substances mixed in a flask undergo an exothermic reaction, the contents of the flask become warmer. If the substances undergo an endothermic reaction, the flask contents become colder. The heat energy change of a reaction is generally called the heat of reaction. For a reaction performed at constant pressure, the heat of reaction is equal to the enthalpy change, ΔH, for the reaction.

Every substance has an enthalpy, H. Generally, the sum of the enthalpies of the products differs from the sum of the enthalpies of the reactants. The enthalpy change, ΔH, is equal to the sum of the enthalpies of the products minus the sum of the enthalpies of the reactants. When ΔH is negative, heat is released by the reaction and thus, the reaction is exothermic.

Heat is commonly measured in units of calories or joules. One calorie (cal) is the amount of heat needed to raise the temperature of one gram of water one degree Celsius. One kilocalorie (kcal) equals 1000 calories. The SI unit of heat is the joule; one calorie is equal to 4.184 joules.

Calorimetry is the study of heat transferred in a chemical reaction, and a *calorimeter* is the tool used to measure this heat. Thus, calorimetry can be used to measure heats of reaction. In a calorimeter, a chemical reaction is generally performed in a water bath. The heat of reaction will change the temperature of the calorimeter, increasing the temperature for an exothermic reaction and decreasing it for an endothermic reaction. The heat change associated with the temperature change of the calorimeter is equal to the **heat capacity** of the calorimeter ($C_{\text{calorimeter}}$) times the temperature change ($\Delta T = T_{\text{final}} - T_{\text{initial}}$) as seen in Equation 2.1:

$$q_{\text{calorimeter}} = C_{\text{calorimeter}} \times \Delta T \qquad \text{(Equation 2.1)}$$

In this experiment, students will determine a heat of reaction in a coffee cup calorimeter. A coffee cup calorimeter consists of two Styrofoam cups, a lid, and a thermometer. Two solutions are mixed in the calorimeter and the temperature change of the mixed solution is measured. Since styrofoam cups act as excellent insulators, it is reasonable to assume that all the heat transferred or generated inside the calorimeter remains inside the calorimeter without the calorimeter itself absorbing any of the heat. Thus, $q_{\text{calorimeter}}$ can be neglected. The heat capacity of the solution can be assumed to be equal to the heat capacity of water as its density is quite close to that of water. Thus, the heat of reaction can be calculated by Equation 2.2, the heat equation for water.

$$q = m_{\text{sol}} \times c_{\text{sol}} \times \Delta T \qquad \text{(Equation 2.2)}$$

In this equation, m_{sol} is mass in grams, g, of the solution and c_{sol} is the specific heat capacity of the solution, which due to the dilute nature of the solution, can be approximated by the specific heat capacity of water, $4.184 \frac{\text{J}}{\text{g}\cdot{}^{\circ}\text{C}}$. For this experiment, it is also reasonable to assume that the density of the solution is approximately equal to the density of water, about $1.00 \frac{\text{g}}{\text{mL}}$. For example:

$$50.0 \text{ mL } H_2O \times \frac{1.00 \text{ g}}{\text{mL}} = 50.0 \text{ g } H_2O$$

Thus, the volume of the solution in mL is equal to the mass of the solution in grams, m_{sol}. Putting the equations together, the heat of the reaction is calculated by Equation 2.3:

$$q_{\text{rxn}} = -(m_{\text{sol}}) \times (c_{\text{sol}}) \times \Delta T \qquad \text{(Equation 2.3)}$$

Calorimetry can measure the heat changes associated with many types of reactions. In this experiment, three processes involving heat transfer can be studied: **Heat of Neutralization, Enthalpy of Solution of Salts, and Specific Heat Capacity of a Metal**. You will be performing all three procedures.

A. Heat of Neutralization

The transfer of heat that results from an acid/base neutralization reaction carried out at constant pressure is called the *enthalpy of neutralization*, $\Delta H_{\text{neutralization}}$, and is expressed in units of kcal/mol or kJ/mol. The reaction to be studied is shown in Reaction 2.1:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \text{(Reaction 2.1)}$$

Since HCl and NaOH are strong electrolytes, this net ionic equation associated with this molecular equation is given in Reaction 2.2:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \text{(Reaction 2.2)}$$

As with any chemical reaction, *the extent of the reaction is dependent on the amount of limiting reactant present.* Given the amount in moles of the limiting reactant undergoing reaction and the measured amount of heat generated during the reaction, $\Delta H_{\text{neutralization}}$can be determined as shown in Equation 2.4, keeping in mind that $q_{\text{rxn}} = -(m_{\text{sol}}) \times (c_{\text{sol}}) \times \Delta T$.

$$\Delta H_{\text{neutralization}} = \frac{q_{\text{rxn}}}{\textit{amount(mol) of limiting reagent}} \qquad \text{(Equation 2.4)}$$

B. Enthalpy of Solution of Salts

When a salt dissolves in water at constant pressure, there is a transfer of heat associated with the reaction called the enthalpy of solution, $\Delta H_{solution}$, as seen in Equation 2.5. It is expressed in units of kcal/mol or kJ/mol of salt.

$$\Delta H_{solution} = \frac{q_{rxn}}{moles_{salt}} \quad \text{(Equation 2.5)}$$

The solution process can be written as shown in Reaction 2.3:

$$NH_4NO_3(s) \longrightarrow NH_4{}^+(aq) + NO_3{}^-(aq) \quad \text{(Reaction 2.3)}$$

Heat may be given off or absorbed by the salt as it dissolves as ions in water.

In this experiment, students will measure the enthalpy of solution for two salts, ammonium nitrate (NH_4NO_3) and magnesium sulfate ($MgSO_4$). The equation for the solution process for ammonium nitrate was given in Reaction 2.3. The equation describing the solution process for magnesium sulfate is shown here in Reaction 2.4:

$$MgSO_4(s) \longrightarrow Mg^{2+}(aq) + SO_4{}^{2-}(aq) \quad \text{(Reaction 2.4)}$$

C. Specific Heat Capacity of a Metal

Students will find the specific heat capacity of a metal by equating the heat lost by the metal (at high temperature) to the heat gained by the water reservoir at a lower temperature when they are mixed in the calorimeter. The metal must first be heated, and its temperature measured, $T_{initial}$(metal). The temperature of the water reservoir is measured prior to, $T_{initial}$(water), and after, T_{final} (water), adding the solid to it. The heat transferred to the water is the opposite sign of the heat lost by the metal, as seen in Equation 2.6.

$$q_{metal} = -q_{water} \quad \text{(Equation 2.6)}$$

The formula for q given by Equation 2.6 can then be substituted on each side of the equation to give Equation 2.7

$$(c_{metal})\,(m_{metal}) \times \Delta T_{metal} = -\,(c_{water})\,(m_{water}) \times \Delta T_{water} \quad \text{(Equation 2.7)}$$

Rearranging this equation to solve for the specific heat capacity of the metal, results in an experimentally determined specific heat capacity of the metal that can be compared to the actual value of the specific heat capacity of the metal (Equation 2.8).

$$c_{\text{metal}} = \frac{-(c_{\text{water}})(m_{\text{water}}) \times \Delta T_{\text{water}}}{(m_{\text{metal}}) \times \Delta T_{\text{metal}}} \qquad \text{(Equation 2.8)}$$

Procedure

Safety Precautions

Safety goggles are required throughout the lab.

Avoid pouring any acid or base above eye-level, and be cautious as acids and bases can be hazardous.

Heat of Neutralization

1. Obtain 2 Styrofoam cups and a piece of cardboard from the supply table. Nest the cups and insert the thermometer through the small hole in the center of the cardboard.

2. Carefully measure, using a graduate cylinder, 50.0 mL of 1.00 M HCl solution and transfer it to the inner cup. Record the temperature of the HCl to the nearest 0.1°C.

3. Rinse the graduated cylinder with deionized (DI) water, then rinse it with small amount of NaOH solution, then carefully measure 50.0 mL of 1.00 M NaOH solution. Assume that the temperature of the NaOH is the same as that of the HCl solution.

4. Follow these steps to determine the heat of neutralization:
   - Add the 50.0 mL of the NaOH solution to the HCl in the cup and swirl gently while monitoring the temperature.
   - Record the temperature to the nearest 0.1°C, when the temperature reaches a maximum.
   - Assume that the liquid in the cup has the same density as water and determine the mass of the liquid in the calorimeter.
   - Use the mass and the heat capacity ($4.184 \frac{\text{J}}{\text{g}\cdot{}^{\circ}\text{C}}$) to calculate the heat in joules evolved by the reaction.

5. Calculate the amount in moles of H^+(aq) (or HCl(aq)) that was neutralized.

6. Calculate the enthalpy per mole of $H^+(aq)$ neutralized.

7. Repeat everything for a second trial. Record the average of the enthalpy per mole of $H^+(aq)$ neutralized on your report sheet, $\Delta H_{\text{neutralization}}$.

Enthalpy of Solution of Salts

1. Weigh out approximately 2.000 grams of NH_4NH_3 and record the exact amount to the nearest 0.001 g.

2. Measure 50.0 mL of DI water and place it in a clean calorimeter. Record the exact volume and measure the initial temperature of the DI water, recording this to the nearest 0.1°C.

3. Follow these steps to determine the enthalpy of solution of NH_4NH_3:
   - Remove the lid from the coffee cup calorimeter and quickly add the salt to the calorimeter and begin swirling while holding the thermometer about 3 cm from the bottom of the cup.
   - Continue to stir for at least 1 minute to ensure all the salt has dissolved and to avoid faulty temperature readings.
   - Monitor the temperature and record the values on your report sheet.
   - Note that in calculating the total mass of the solution needed for calculation of q_{res}, you must add the mass of the salt to the mass of water.
   - Recall that the density of water is 1.00 $\frac{\text{g}}{\text{mL}}$. Calculate the $\Delta H_{\text{solution}}$.

4. Dispose of the solution in the waste container down the sink and rinse the calorimeter with tap water and then DI water.

5. Clean the calorimeter and repeat this procedure with $MgSO_4$.

Specific Heat Capacity of a Metal.

1. Prepare a hot water bath by filling a 400 mL beaker with tap water, placing it on a hot plate, and bringing the water to a boil.

2. Measure about 20 grams of the metal assigned by your Instructor. Record the exact mass **and identity** of the metal used in your report sheet.

3. Measure 50.0 mL of DI water and place it in a clean calorimeter. Record the exact volume in your report sheet.

4. Transfer the metal to a large test tube and place it in the boiling water bath to raise the metal temperature to about that of the bath, which should take about fifteen minutes.
   - Measure and record the temperature of the metal by placing the thermometer probe into the test tube in contact with the metal and wait for the temperature reading to stabilize (less than 1°C change in two minutes).
   - This will serve as the ***initial temperature*** of the metal T_{initial} (metal).
   - Keep the metal in the test tube in the hot water bath until just before mixing (next step)

5. Cool the temperature probe to room temperature by placing it in a cold-water bath. Then measure and record the initial temperature of the water, T_{initial} (water), in the calorimeter. Ensure that the temperature has stabilized and record this value on your report sheet.

6. Measure the specific heat capacity of the metal as follows:
   - Using a test tube holder, carefully remove the hot test tube containing the metal from the bath.
   - Quickly dry the outside of the test tube. Then pour the metal out of the test tube into the calorimeter.
   - Immediately begin swirling the calorimeter contents, while monitoring the temperature. Record the values on your report sheet.
   - Recall that the density of water is 1.00 $\frac{\text{g}}{\text{mL}}$. Calculate the specific heat capacity of the metal c_{metal}.

A. Heat of Neutralization

Report Table 2.1: Heat of Neutralization

	Trial 1	Trial 2
Volume of HCl		
Temperature of HCl		
Volume of NaOH		
Temperature of mixture after reaction		

Show calculations for heat in joules evolved

Show calculations for amount in moles of H^+ neutralized

Show calculations for enthalpy per mol of H^+

B. Enthalpy of Solution of Salts

Show enthalpy of solution calculation starting with the data above for NH_4NO_3, showing the full calculation for the Enthalpy of solution (ΔH)

Report Table 2.2: Enthalpy of Solution of Salts

	NH_4NO_3	$MgSO_4$
Mass of salt	__________	__________
Volume of DI water	__________	__________
Temperature of DI water	__________	__________
Temperature of mixture after dissolution	__________	__________

C. Specific Heat Capacity of a Metal

Identity of metal __________

Mass of metal __________

Volume of DI water __________

$T_{initial}$ (metal) __________

$T_{initial}$ (water) __________

Temperature of mixture after addition of metal __________

Show calculations for specific heat capacity of the metal

Discussion

Your discussion should be at most 2 pages, double spaced, 10-12 point font (minimum is 1 paragraph). Your discussion should contain at least 3 paragraphs, one for each of the experimental parts. You may choose to have one additional paragraph which either explains what you will be writing, which summarizes what you wrote or which ties the 3 parts of the experiment together. Your discussion for each part of the experiment should focus on explaining your results, interpreting your results and discussing whether they are reasonable (remember to use context – for example, literature values for any results you have calculated). Observations should be used to interpret what is happening chemically. (For example, instead of stating, "The temperature in the calorimeter decreased" (an observation), it is better to explain by stating, "The solution absorbed energy during the dissolution as the temperature in the calorimeter decreased".)

When writing your discussion, you should consider the following questions and make sure that your answer is incorporated into your discussion seamlessly (in other words, please do not number your responses or put them in separate paragraphs).

1. What sort of value do you expect to obtain for the enthalpy of neutralization of a strong acid and a strong base? How can you tell if your value is reasonable? Would you expect to obtain the same value if a different strong acid or strong base was used in the reaction? Why? Can you find a literature value with which you can compare your experimental result? Do you expect the values for different trials for the same experiment to give you different values? What do your results show?
2. What sort of value do you expect to obtain for the enthalpy of dissolution of a salt? What factors might affect the value of the enthalpy of dissolution? Can you find a literature value with which you can compare your experimental result?
3. What sort of value do you expect to obtain for the specific heat capacity of your metal? Why? Is the value you obtained reasonable? Why? Can you find a literature value with which you can compare your experimental result? Do you expect the values for different trials for the same experiment to give you different values? What do your results show?
4. What do the 3 parts of this experiment have in common? What is the chemical concept that relates them? How does this technique work? Are the results obtained using this technique scientifically accurate/precise? How do you know?

Real-Life Connections

Using any chemical concept in this experiment, make a connection to: 1) an event in the news, 2) your career plans, 3) a hobby of yours, 4) another course you are taking, or 5) your personal life. You may write as little as a paragraph to as much as a page (double spaced, 10-12 point font). Your writing should find at least one way, if not more, in which the chemical concept you have chosen is demonstrated.