Constant Pressure Calorimetry

Objective

To become acquainted with the use of a coffee cup calorimeter and determine the heat of reaction of a neutralization reaction, the enthalpy of solution of salts and the specific heat of a metal.

Equipment

- Coffee cup calorimeter
- 50.0-mL graduate cylinder
- 1 cardboard lid
- 400-mL beaker
- Vernier LabQuest2 w/ Thermometer probe
- Hotplate

Chemicals

- 1.00 *M* NaOH solution
- $MgSO_4$
- 1.00 *M* HCl
- DI Water

Introduction

Chemical reactions are accompanied by heat change. When heat is released, the reaction is called **exothermic** (exo-out, thermic-heat). When heat is absorbed, the reaction is called **endothermic** (endo-in, thermic-heat). 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 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. The Δ symbol means "change in".

Every substance has an enthalpy, H. Enthalpy is a thermodynamic quantity equivalent to the total heat content in the system and is equal to the internal energy plus the product of the pressure and volume (eq. 7.1).

$$H = E + \mathrm{PV} \qquad \mathbf{(7.x)}$$

Since we will be conducting this experiment at a constant pressure and volume for our purposes $H = E$. Be careful about confusing heat (H) with temperature (T). The temperature of a match flame and a bonfire flame may be equal however the heat within the match is vastly different from the heat found in the bonfire.

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.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \qquad (7.1)$$

When ΔH is negative, heat is released by the reaction and thus, the reaction is exothermic. This is key to understanding why the heat of reaction is equal to the negative of the heat change in the calorimeter (eq 7.3).

The SI unit of heat is the joule (J). It takes 4.184 joules to raise the temperature of one gram of water one degree Celsius, also known as the specific heat of water (C_s). Heat is also commonly measured in units of calories. One calorie (cal) is the amount of heat needed to raise the temperature of one gram of water one degree Celsius. One calorie is equal to 4.184 joules. One kilocalorie (kcal) equals 1000 calories.

You will be using the terms ***specific heat*** (C_s) and ***heat capacity*** (C). Specific heat has units of $J \cdot g^{-1}\ {}^{\circ}C^{-1}$ whereas heat capacity has units of $J \cdot {}^{\circ}C^{-1}$.

Calorimetry is the study of heat transferred in a chemical reaction, and a *calorimeter* is the tool used to measure this heat. Calorimetry can be used to find heats of reaction. In a calorimeter, a chemical reaction is generally performed in a water bath. The heat of reaction will change the temperature inside the calorimeter. For an exothermic reaction, the temperature inside the calorimeter will increase. For an endothermic reaction, the temperature inside the calorimeter will decrease. The heat change associated with the temperature change inside the calorimeter is equal to the heat capacity of the calorimeter contents ($C_{\text{contents.}}$) times the temperature change ($\Delta T = T_{\text{final}} - T_{\text{initial}}$):

$$q_{\text{contents}} = C_{\text{contents}} \times \Delta T \qquad (7.2)$$

Now what is this "q"? It is a term to describe the **change** in heat, i.e. $q = \Delta H$, in a system at constant pressure. To understand this more fully refer to *Enthalpy* in your textbook.

The heat of reaction is equal to the negative of the heat change of the calorimeter because heat flows out of the reaction into the calorimeter (notice the change of direction):

$$q_{\text{rxn}} = -q_{\text{contents}} \qquad (7.3)$$

In today's experiment, you will determine a heat of reaction in a coffee cup calorimeter. A coffee cup calorimeter is surprisingly efficient and consists of **two Styrofoam cups, a cardboard lid, and a thermometer**. Two solutions are mixed in the calorimeter and the temperature change of the mixed solution is measured. We will assume that the heat capacity of the solution is equal to the heat capacity of water. The heat capacity of water is equal to:

$$C_{\text{water}} = m_{\text{water}} \times C_{\text{s,water}} \qquad (7.4)$$

Where m is mass in grams, g, and $C_{\text{s,water}}$ is the specific heat of water 4.184 $\frac{\text{J}}{\text{g} \cdot {}^{\circ}\text{C}}$ We will also assume that the density of the solution is about 1.00 $\frac{\text{g}}{\text{mL}}$. For example:

$$50.0\ \text{mL H}_2\text{O} \times \frac{1.00\ \text{g}}{\text{mL}} = 50.0\ \text{g H}_2\text{O}$$

Therefore, the volume of the solution in mL is equal to the mass of the solution in grams, m_{sol}. Putting all the equations together, the heat of the reaction is equal to:

$$q_{\text{rxn}} = -q_{\text{contents}} = -(m_{\text{contents}}) \times (C_{\text{s,water}}) \times \Delta T \qquad (7.5)$$

Today you will investigate two processes involving heat transfer: **Heat of Neutralization** and **Enthalpy of Solution of Salts**.

A. Heat Capacity of the Calorimeter

Since our calorimeter isn't perfect, some the heat of reaction will be taken up (or given off) by the calorimeter. Because of this you must know the amount of heat absorbed by the calorimeter. To know this, you must first determine the heat capacity ($C_{calor.}$) of the calorimeter, meaning the amount of heat required to raise its temperature 1 ˚C.

In this experiment the temperature of the calorimeter and its contents is measured before and after the reaction. The total change in the enthalpy (Δ *H*) is equal to the negative product of the temperature change (Δ *T*) times the heat capacity of the calorimeter **and** its contents.

$$\Delta H = -\Delta T \times (C_{calor.} + C_{contents}) \qquad (7.6)$$

The heat capacity of the calorimeter can be determined by measuring the temperature change that occurs when mixing a known amount of hot water with a known amount of cold water in the calorimeter. The heat capacity of the calorimeter is the difference between the heat lost by the warm water and the heat gained by the cold water.

$$\Delta H_{warm\ water} - \Delta H_{cold\ water} = H\ gained\ by\ calorimeter \qquad (7.7)$$

If the warm water is added to the cold water already in the calorimeter, the change in temperature of the calorimeter would the difference between the cold water and the final temperature of the water. Putting this together we have:

$$H_{gained\ by\ calorimeter} = C_{calorimeter} \times \Delta T_{calorimeter} \qquad (7.8)$$

As an example:

Temperature of 50 mL warm water = 37.3 ˚C
Temperature of 50 mL cold water = 19.0 ˚C
Temperature of solution after mixing = 27.5 ˚C

Solution:

$\Delta T_{warm\ water} = 37.3\ ˚C - 27.5˚C = 9.8\ ˚C$
$\Delta T_{cold\ water} = 27.5\ ˚C - 19.0˚C = 8.5\ ˚C$

$$\Delta\, H_{warm\ water} = 4.184\ \frac{\mathrm{J}}{\mathrm{g \cdot {}^{\circ}C}} \bullet 50\ \mathrm{g} \bullet 9.8\ {}^{\circ}\mathrm{C} = 2.050 \times 10^{3}\ \mathrm{J}\ \textit{or}\ 2.050\ \mathrm{kJ}$$

$$\Delta\, H_{cold\ water} = 4.184\ \frac{\mathrm{J}}{\mathrm{g \cdot {}^{\circ}C}} \bullet 50\ \mathrm{g} \bullet 8.5\ {}^{\circ}\mathrm{C} = 1.778 \times 10^{3}\ \mathrm{J}\ \textit{or}\ 1.778\ \mathrm{kJ}$$

$$\mathrm{H}_{\text{gained by calorimeter}} = 2.050\ \mathrm{kJ} - 1.778\ \mathrm{kJ} = 0.2720\ \mathrm{kJ}\ \textit{or}\ \mathbf{272\ J}$$

This would be the amount of energy that is taken up by the calorimeter and is the amount of energy that needs to be added (exothermic reaction) or subtracted (endothermic reaction) to each reaction to give the total amount of energy released or absorbed by the system.

B. 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:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \qquad \mathbf{(7.9)}$$

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

$$\mathrm{H^{+}}(aq) + \mathrm{OH^{-}}(aq) \ \rightarrow\ \mathrm{H_2O}(l) \qquad \mathbf{(7.10)}$$

As with any chemical reaction, *the extent of the reaction is dependent on the amount of limiting reactant present.* Given the moles of limiting reactant undergoing reaction and the measured heat of the reaction, $\Delta H_{\text{neutralization}}$ can be determined as shown below, **keeping in mind that:** $\boldsymbol{q_{\mathrm{rxn}} = -\,q_{\mathrm{calorimeter}}}$.

$$\Delta H_{\text{neutralization}} = \frac{q_{\mathrm{rxn}}}{\text{moles reacted}} \qquad \mathbf{(7.11)}$$

C. 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, $\Delta H_{\text{solution.}}$ It is expressed in units of kcal/mol or kJ/mol of salt.

$$\boldsymbol{\Delta H_{solution} = \frac{q_{rxn}}{moles\ of\ salt}} \qquad \mathbf{(7.12)}$$

The solution process can be written as follows:

$$\mathrm{NH_4NO_3}(s) \rightarrow \mathrm{NH_4^{+}}(aq) + \mathrm{NO_3^{-}}(aq) \qquad \mathbf{(7.13)}$$

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

Procedure – Create data tables similar to the Report Sheet below in the *Data* section of your lab notebook.

A. Heat Capacity of a Calorimeter

1. Obtain 2 Styrofoam cups and a piece of cardboard from the supply table. Nest the cups and insert the LabQuest2 thermometer probe through the small hole in the center of the cardboard. Rest the entire apparatus in a 400 mL beaker for stability. On the LabQuest2 module select "Sensors" then "Data Collection". Interval should be set to 1 s/sample. Duration should be set to 180 s.
2. Using a graduated cylinder, place exactly 50.0 mL of distilled water in the inner cup of the calorimeter and replace the cardboard lid. Allow 5-10 minutes for the system to reach thermal equilibrium and record the temperature to the nearest 0.1 ˚C.
3. While waiting for the system to equilibrate, put exactly 50.0 mL of distilled water in a clean, dry 250 mL beaker. Heat the water on a hot plate until the temperature of the water is approximately 40 – 50 ˚C. Allow the water to stand for a minute or two on the bench and then record the temperature to the nearest 0.1 ˚C.
4. Once both water temperatures are recorded and immediately after recording the warm water temperature, quickly pour all of the warm water in the calorimeter, replace the lid with the temperature probe and start measuring the temperature by selecting the *start icon* on the LabQuest2. Observe the temperature curve until the temperature reaches a stable maximum, then stop.
5. Export your data to a USB stick.

Results section:

Create an Excel chart (graph) for inclusion with your results, plotting the temperature as a function of time. Determine ΔT from your plot and perform the calculations as described above to determine the heat capacity of your calorimeter. Use this value in the following experiments for determining the heat of reactions.

B. Heat of Neutralization

1. Using the calorimeter you prepared, carefully measure 50.0 mL of 1.00 *M* HCl solution with a graduate cylinder and transfer it to the inner cup. Put the probe into the HCl solution and use LabQuest2 to measure and record the temperature of the HCl to the nearest 0.1^{o}C.
2. Rinse the graduated cylinder with DI water, then rinse it with small amount of NaOH solution, then carefully measure 50.0 mL of 1.00 M NaOH solution. The temperature of the NaOH is assumed to be the same as the HCl solution.
3. On the LabQuest2 module select "Sensors" then "Data Collection". Interval should be set to 1 s/sample. Duration should be set to 180 s. Put the probe into the HCl solution. Start running and measuring the temperature by selecting the *start icon*. Observe the curve on LabQuest2. When you get 5 points (~5s) with the same temperature, add the 50.0 mL of the NaOH solution to the HCl in the cup, swirl gently, observe the temperature curve until the temperature reaches a maximum,

then stop. Assuming the liquid in the cup has the same density as water ($1.00\ \frac{g}{mL}$), find the mass of the sample containing both solutions. With this mass and the heat capacity of water ($4.184\ \frac{J}{g \cdot ℃}$) calculate the number of calories that were evolved by your reaction.

4. Export your data to a USB memory stick.
5. Repeat everything for a two more trials, <u>*or*</u> collect data from students you trust near you, as your TA directs.

Result section:

Create an Excel chart (graph) for inclusion with your results for each trial.

Calculate the number of moles of H^+(aq) (or HCl(aq)) that were neutralized for each trial.

Calculate the number of joules liberated per mole of H^+(aq) neutralized for each trial.

Record the average of the calories liberated per mole of H^+(aq) neutralized on your lab notebook, $\Delta H_{neutralization}$. Calculate and report the standard deviation and RSD.

C. Enthalpy of Solution of Salts

1. Weigh out ~ 2 grams of $MgSO_4$ and record the exact amount to the nearest 0.001 g. Consider which is the best balance to accomplish this with.
2. Measure 50 mL of DI water and place it in the clean calorimeter, after recording the exact volume. Measure the initial temperature of the DI water and record this to the nearest 0.1°C in your lab notebook.
3. As before, on the LabQuest2 module select “Sensors” then “Data Collection”. Interval should be set to 1 s/sample. Duration should be set to 180 s. Put the probe into DI water. Start running and measuring the temperature of DI water. After you get 5 points (~5s), quickly add the salt into the water. Continue to stir for at least 1 minute to ensure all the salt has dissolved and to avoid faulty temperature readings. Monitor the temperature curve until the temperature reaches a maximum, then stop and record the values on your lab notebook. Note that in calculating the mass of the reservoir needed for calculation of q_{res}, you must add the mass of the salt to the mass of water. Density of water ($1.00\ \frac{g}{mL}$). Calculate the $\Delta H_{solution}$.
4. Save your data on a USB memory stick for creating an Excel chart (graph) for inclusion with your results.

Result section:

Create an Excel chart (graph) for inclusion with your results for each trial.

Write a balanced chemical equation for the dissolution of your salt.

Calculate the number of moles of your salt that was dissolved.

Calculate the number of joules liberated per mole of salt dissolved.

Report Sheet EXP7: Constant Pressure Calorimeter

A. Heat Capacity of Calorimeter

Temperature of calorimeter and water before mixing. __________

Temperature of warm water. __________

Maximum temperature of mixture after reaction __________

Temperature difference __________

Heat gained by calorimeter (*J*) __________

B. Heat of Neutralization

	Trial 1	Trial 2	Trial 3
Volume of HCl	__________	__________	__________
Temperature of HCl	__________	__________	__________
Volume of NaOH	__________	__________	__________
Temperature of mixture after reaction	__________	__________	__________
Temperature difference	__________	__________	__________
Number of joules evolved	__________	__________	__________
Moles of H^+ that were neutralized	__________	__________	__________

Joules evolved per mole of H$^+$ __________ __________ __________

Average of the three trials of joules evolved per mole of H$^+$ __________

Standard Deviation and RSD __________ __________

C. Enthalpy of Solution of Salts

MgSO$_4$

Mass of salt __________

Volume of DI water __________

Mass of DI water __________

Temperature of DI water __________

Temperature of mixture after dissolution __________

Temperature difference __________

Total mass in reaction __________

Enthalpy of solution $\Delta H_{solution}$ __________