

## EXPERIMENT: CALORIMETRY AND HEAT OF NEUTRALIZATION

### INTRODUCTION

Heat is defined as the transfer of energy from or into a system because of a temperature difference between the system and its surroundings. Heat is often considered, inaccurately, as a form of energy existing as the result of the random motion of molecules.

Chemical reactions involving the transfer of heat are carried out in devices called calorimeters. Calorimeters are insulated to prevent loss or gain of heat between the calorimeter and its surroundings so that heat flow in the system can be measured.

The total amount of heat that is produced or absorbed by a chemical reaction, at constant pressure, is called the enthalpy of reaction ( $\Delta H$ ).

If the chemical reaction is exothermic, heat is released and the temperature of the system increases.

If the chemical reaction is endothermic, heat is absorbed and the temperature of the system decreases.

**Exothermic:** reactants  $\rightarrow$  products + heat  
( $\Delta H$  has a negative sign)

**Endothermic:** reactants + heat  $\rightarrow$  products  
( $\Delta H$  has a positive sign)

The quantity of heat is given the symbol  $q$ .

$$q = m \times \text{sp\_heat} \times \Delta t \quad \text{where:}$$

$q$  = amount of heat, measured in joules(J).

sp\_heat = the specific heat. The specific heat is the amount of heat required to raise the temperature of one gram of substance by one degree. The units of specific heat are

$$\text{J/g} \times ^\circ\text{C} \text{ or } \text{J/g} \times \text{K} \quad \text{since } 1^\circ\text{C} = 1 \text{ degree K.}$$

$m$  = mass, measured in grams

$\Delta t$  = temperature change,  $^\circ\text{C}$  or K.

**NOTE: All temperatures in this lab will be recorded in degrees Celcius,  $^\circ\text{C}$**

## Part I: Heat Capacity of the Calorimeter

The heat capacity,  $C$ , of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by 1 degree. The relationship between heat capacity and specific heat is  $C = m \times \text{sp\_heat}$ . Therefore,  $q = C \times \Delta t$  and  $C = q \div \Delta t$ .

In this experiment the calorimeter consists of the instrument and the 100.0 g of water contained within it. Ideally, the components of the calorimeter would absorb no heat, but the components of the calorimeters always absorb some energy from the system.

The heat capacity of the calorimeter is the quantity of heat absorbed by the calorimeter for each  $1^\circ\text{C}$  rise in temperature.

The heat capacity of the calorimeter must be determined experimentally. The easiest process is to study the mixing of warm and cold water.

Equal quantities of hot and cold water are mixed in the calorimeter and the final equilibrium temperature is measured. If the calorimeter absorbs no heat at all, the equilibrium temperature of the mixture is the average of the hot and cold temperatures. In reality, the hot water loses heat to both the cold water and the calorimeter. In other words, heat gained by the cold water should equal that lost by the hot water. Any difference is due to heat gained by the calorimeter. This assumes no heat is lost to the surroundings from the calorimeter.

**Heat lost by hot water = heat gained by cold water + heat gained by calorimeter.**

$$-q_{\text{hot}} = q_{\text{cold}} + q_{\text{cal}}$$

The minus sign indicates that the hot water is losing heat, whereas the cold water and the calorimeter are gaining heat.

From the amount of water in the calorimeter and the temperature change undergone by the water, the quantity of heat absorbed by the calorimeter,  $q_{\text{cal}}$ , can be determined.

The heat capacity of the calorimeter,  $C_{\text{cal}}$ , is determined by dividing  $q_{\text{cal}}$  by the temperature change.

For this experiment, the calorimeter used is a simple thermos jar and cover. The heat capacity of the calorimeter accounts for the heat absorbed by the thermometer as well as the heat absorbed by the actual calorimeter.

Since the density of water over the range of temperatures in this experiment is very close to  $1 \text{ g/mL}$ , the amount of water to be placed in the calorimeter can be more conveniently measured by volume with the assumption that the volume of water = mass of water.

### Sample Calculation: Heat Capacity of Calorimeter

50.0 mL of water at 40.5 °C is added to a calorimeter containing 50.0 mL of water at 17.4 °C. After waiting for the system to equilibrate, the final temperature reached is 28.3 °C. Calculate the heat capacity of the calorimeter. (sp\_heat of water = 4.184 J/g×°C)

$$\begin{aligned}\Delta t_{\text{hot}} &= 28.3\text{ }^{\circ}\text{C} - 40.5\text{ }^{\circ}\text{C} \\ &= -12.2\text{ }^{\circ}\text{C}\end{aligned}$$

$$\begin{aligned}\Delta t_{\text{cold}} &= 28.3\text{ }^{\circ}\text{C} - 17.4\text{ }^{\circ}\text{C} \\ &= 10.9\text{ }^{\circ}\text{C}\end{aligned}$$

$$\begin{aligned}q_{\text{hot}} &= m \times \text{sp\_heat} \times \Delta t \\ &= (50.0\text{ g}) \times (4.184\text{ J/g} \times ^{\circ}\text{C}) \times (-12.2\text{ }^{\circ}\text{C}) \\ &= -2550\text{ J}\end{aligned}$$

$$\begin{aligned}q_{\text{cold}} &= m \times \text{sp\_heat} \times \Delta t \\ &= (50.0\text{ g}) \times (4.184\text{ J/g} \times ^{\circ}\text{C}) \times (10.9\text{ }^{\circ}\text{C}) \\ &= 2280\text{ J}\end{aligned}$$

By rearranging the equation,  $q_{\text{hot}} = -(q_{\text{cold}} + q_{\text{cal}})$ , we can solve for  $q_{\text{cal}}$ :

$$\begin{aligned}q_{\text{cal}} &= -q_{\text{hot}} - q_{\text{cold}} \\ &= 2550\text{ J} - 2280\text{ J} \\ &= 270\text{ J}\end{aligned}$$

$$\text{Heat capacity of the calorimeter} \quad C_{\text{cal}} = \frac{270\text{ J}}{10.9\text{ }^{\circ}\text{C}} + 4.184\text{ J/g} \times ^{\circ}\text{C} \times 100.0\text{ g}$$

Remember the calorimeter includes the 100.0 g of water so we must include the heat capacity of this much water.

$$C_{\text{cal}} = 443\text{ J/}^{\circ}\text{C}$$

## Part II: Heat of Neutralization

In interactions between a system and its surroundings, the total energy remains constant:

$$q_{\text{system}} + q_{\text{surroundings}} = 0$$

Thus, heat **lost** by a system is **gained** by its surroundings, and vice versa.

$$q_{\text{system}} = -q_{\text{surroundings}}$$

In this part of the experiment, the reactions carried out are neutralization reactions between an acid and a base. The heat of reaction or neutralization,  $q_{\text{neut}}$ , is the negative of the heat gained by the calorimeter which includes the 100.0 g of water.

$$-q_{\text{neutralization}} = q_{\text{cal}}$$

The heat of neutralization is the heat evolved (released) when 1 mole of water is produced by the reaction of an acid and base.

The heat gained by the calorimeter,  $q_{\text{cal}}$ , is determined from the formula,  $q_{\text{cal}} = C_{\text{cal}} \times \Delta t$ , where  $\Delta t$  is the change in temperature undergone by the mixture. **NOTE:** To use the  $C_{\text{cal}}$  the exact same mass (100.0 g) must be used as in part I.

The heat capacity of the calorimeter,  $C_{\text{cal}}$ , is determined in Part I of the procedure.

Also, it is assumed that the specific heat capacity of the solution,  $sp\_heat$ , is approximately equal to that of water ( $sp\_heat_{\text{water}} = 4.184 \text{ J/g} \times ^\circ\text{C}$ ).

The moles of water produced in the neutralization are calculated using the volume and concentration (molarity) of the acid and base solutions.

Lastly, the enthalpy of neutralization per mole of water produced is calculated ( $\Delta H$  in kJ/mol).  $\Delta H$  is the enthalpy of reaction and it describes the amount of energy released or absorbed by a reaction under constant pressure conditions. Exothermic reactions, such as neutralization reactions, have a negative value of  $\Delta H$  and endothermic reactions have a positive value of  $\Delta H$ . The standard enthalpy change  $\Delta H^\circ$  is expressed in kJ/mol.

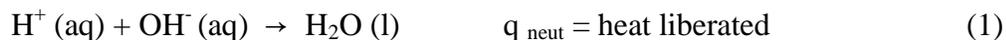
In the procedure, we mix solutions of:

- i) 2.0 M hydrochloric acid and 2.0 M sodium hydroxide, and
- ii) 2.0 M acetic acid and 2.0 M sodium hydroxide

The heat of neutralization for reactions i) and ii) is then determined.

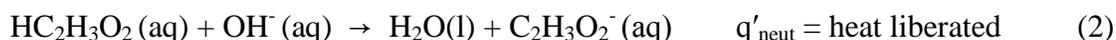
Reaction i) represents a neutralization reaction between a strong acid (HCl), and a strong base (NaOH). Strong acids and strong bases are completely dissociated in aqueous solution; hence

neutralization involves only the combination of  $H^+$  and  $OH^-$  ions:

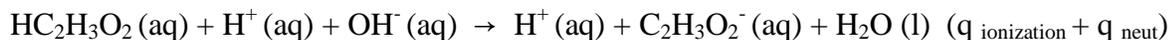
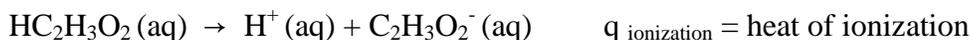


Because of this, the heat of neutralization is essentially constant and independent of the nature of the strong acid and strong base involved in the reaction. The above observation does not apply to the heat of neutralization involving a weak acid and/or a weak base. The heat of neutralization tends to be smaller because some energy must be expended to ionize the weak acid and/or the weak base.

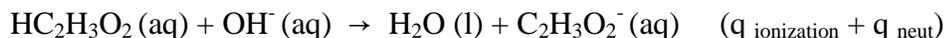
Reaction ii) represents a neutralization reaction between a weak acid, acetic acid, and a strong base, NaOH:



The above reaction is really the sum of the following reactions:



Since  $H^+$  appears on both sides of the equation, we may cancel it to get:



This equation is identical to Equation 2, therefore  $q'_{\text{neut}} = q_{\text{ionization}} + q_{\text{neut}}$ .

During the ionization of  $HC_2H_3O_2$ , some energy,  $q_{\text{ionization}}$ , must be consumed. It follows, therefore, that  $q'_{\text{neut}} < q_{\text{neut}}$ . because **some energy is used to ionize  $HC_2H_3O_2$** , the amount of heat released during the neutralization of  $HC_2H_3O_2$  is smaller than the amount of heat released during the neutralization of HCl.

The neutralization reaction is exothermic; the temperature of the solution in the calorimeter will increase as energy is transferred to it from the reactants. Heat is evolved and  $\Delta H$  has a negative sign.

### Sample Calculation: Heat of Neutralization

50.0 mL of 2.0 M HCl and 50.0 mL of 2.0 M NaOH both initially at 21.1 °C are added to a calorimeter and allowed to react. The temperature rises to 31.5 °C. The heat capacity of the calorimeter is 25 J/°C. Determine the enthalpy of reaction for the neutralization reaction, expressed in kJ per mol H<sub>2</sub>O formed.

Make two assumptions:

- 1) Assume the density of the resulting NaCl solution is 1 g/mL so that volume of solution = mass of solution.
- 2) Assume that the specific heat capacity of the solution is approximately equal to that of water ( $sp\_heat_{water} = 4.184 \text{ J/g}\times^{\circ}\text{C}$ ).

Change in temperature:

$$\Delta t = 31.5 \text{ }^{\circ}\text{C} - 21.1 \text{ }^{\circ}\text{C} = 10.4 \text{ }^{\circ}\text{C}$$

Heat gained by calorimeter during reaction:

$$\begin{aligned} q_{cal} &= C_{cal} \times \Delta t \\ &= 443 \text{ J/}^{\circ}\text{C} \times 10.4 \text{ }^{\circ}\text{C} \\ &= 4610 \text{ J} \end{aligned}$$

Heat of neutralization:

$$\begin{aligned} q_{\text{neutralization}} &= -q_{cal} \\ &= -4610 \text{ J} \end{aligned}$$

Moles of water produced in the reaction:

$$\text{moles H}^+ = 2.0 \text{ mol/L} \times 0.0500 \text{ L} = 0.10 \text{ mol}$$

$$\text{moles OH}^- = 2.0 \text{ mol/L} \times 0.0500 \text{ L} = 0.10 \text{ mol}$$

The H<sup>+</sup> and OH<sup>-</sup> combine to form 0.10 mol H<sub>2</sub>O. (The two are in stoichiometric proportions; neither is in excess.)

Enthalpy of neutralization per mole of water formed:

$$\begin{aligned} \Delta H &= \frac{-4610 \text{ J}}{0.10 \text{ mol}} \times \frac{\text{kJ}}{1000 \text{ J}} \\ &= -46 \text{ kJ/mol} = \text{Standard Enthalpy Change in kJ/mol} \end{aligned}$$

## Part I: Heat Capacity of the Calorimeter

### Procedure:

1. Using a graduated cylinder, measure 50.0 mL of distilled water. Pour the water into the calorimeter. Close the lid and install the thermometer. Use the thermometer to measure the temperature of the water in the calorimeter at 1-minute intervals for 3 minutes or until the temperature is steady. Measure the temperature to the nearest 0.1-degree and record this temperature as  $t_{\text{cold}}$ .
2. During the waiting period of step (1), measure 50.0 mL of distilled water using a graduated cylinder. Transfer the water to a beaker and heat on a hot plate. Heat the water to approximately 20°C above room temperature.
3. Remove the beaker of hot water from the hot plate and allow it to stand a minute or so. When the temperature of the hot water is approximately constant, measure to the nearest 0.1 degree and record this temperature as  $t_{\text{hot}}$ .
4. Pour the hot water quickly into the calorimeter and replace the lid. Insert the thermometer and stir gently by swirling the calorimeter. Observe the temperature rise and record the maximum temperature reached as  $t_{\text{final}}$ .
5. Empty the calorimeter, dry with paper towel, and proceed to Part II Procedure.

## Part II: Heat of Neutralization

### Procedure:

#### CAUTION:

Use caution in handling acids and bases. Dilute acids and bases will irritate or burn the skin. NaOH splashed in your eye can cause eye injury or blindness. Safety glasses required. Wash immediately if you spill these substances on your skin.

1. Using a graduated cylinder, measure 50.0 mL of 2.0 M HCl. Add the solution to the calorimeter and replace the lid. Record the temperature of the HCl solution as  $t_{\text{initial}}$ .
2. Measure 50.0 mL of 2.0 M NaOH into a graduated cylinder.
3. Pour the base quickly into the acid solution. Replace the lid, insert the thermometer, and stir gently by swirling.
4. Observe the temperature every 20 seconds or so until the temperature stabilizes. Record the maximum temperature reached by the mixture as  $t_{\text{final}}$ . (After the reaction is complete you will notice a slow cooling of the solution.)
6. Clean and dry the calorimeter and thermometer.
7. Repeat the Part II Procedure using acetic acid and sodium hydroxide.

**Quiz Hints:**

1. Define the terms: heat, enthalpy of reaction, heat capacity, specific heat.
2. Know the difference between an endothermic and exothermic reaction.
- 3.a) What is the heat of neutralization?  
b) How should the two heats of reaction for the neutralization of NaOH and the two acids compare? Why?
4. Know the experimental calculations.
5. The experimental procedure has you make several assumptions. List them and state how they could affect the calculated result.
6. Why must the exact same mass of solution(100.0 g) be used in the neutralization reactions?