Calorimetry

PURPOSE

To determine if a Styrofoam cup calorimeter provides adequate insulation for heat transfer measurements, to identify an unknown metal by means of its heat capacity and to determine a heat of neutralization and a heat of solution.

GOALS

1 To perform simple calorimetry experiments.

2 To use calorimetry results to calculate the specific heat of an unknown metal.

3 To determine heat of reaction (ΔH) from calorimetry measurements.

INTRODUCTION

Heat and work are the two most common ways for a system to exchange energy with its surroundings. The work term in reactions that do not involve gases is zero, so all of the energy change results in heat. The amount of heat that flows into or out of the surroundings is determined with a technique called calorimetry (heat measurement). A calorimeter is composed of an insulated container, a thermometer, a mass of water, and the system to be studied. The use of an insulated container (Styrofoam cup in this experiment) allows us to assume that there is no heat transferred through the calorimeter walls. In other words, we can assume that the thermodynamic universe is composed of the system and the surrounding water. In the experiment, we will test this assumption.

All of the heat absorbed or given off by a system (q_{sys}) is exchanged with its surroundings (q_{sur}), which is expressed mathematically in equation 1.

$$q_{sys} = -q_{sur} \tag{1}$$

Remember that q > 0 means that the heat flows into the system, while q < 0 means that heat flows out of the system. The minus sign in equation 1 simply implies that the heat flows in opposite directions relative to the system and its surroundings. That is, any heat that flows out of a reaction must flow into the surroundings, and vice versa.

In this experiment, water serves as the surroundings. We assume that no heat is exchanged through the walls of the insulated container, and we write the following:

$$q_{sur} = q_{water} \tag{2}$$

The heat that is exchanged with the water causes a temperature change of ΔT_{water} in the water as shown in equation 3.

$$q_{\text{water}} = C_{\text{water}} \cdot \Delta T_{\text{water}} \tag{3}$$

where C_{water} is the heat capacity of the water, the amount of heat needed to raise the temperature of the water by 1°C. The units of C are J/°C. ΔT is the temperature change, defined as $\Delta T = T_{final} - T_{initial}$. Heat capacities depend upon the mass of the sample, so the specific heat, the amount of heat needed to raise the temperature of one gram of a substance by 1°C, is often used instead. The symbol for specific heat is s. The specific heat of water is 4.18 J/g · °C. The heat capacity of the water equals the mass of water times the specific heat of water, i.e., $C_{water} = m_{water} \cdot s_{water}$. Substitution into equation 3 yields equation 4:

$$q_{\text{water}} = m_{\text{water}} \cdot s_{\text{water}} \cdot \Delta T_{\text{water}} \tag{4}$$

Finally, equations 1, 2 and 3 can be combined into the calorimetry equation:

$$q_{\text{sys}} = -q_{\text{water}} = -m_{\text{water}} \cdot s_{\text{water}} \cdot \Delta T_{\text{water}} = -m_{\text{water}} \cdot (4.18 \text{J/g} \cdot^{\circ} \text{C}) \cdot \Delta T_{\text{water}} \tag{5}$$

In the preceding discussion, we have assumed that all of the heat transfer involves the water in the calorimeter, and that the calorimeter apparatus (the Styrofoam cup, the air inside, the thermometer, etc.) is not involved in the heat transfer. We will test the validity of this assumption to convince ourselves that the data we get from subsequent calorimetry experiments is reliable.

This test will be conducted in Part A of this lab. Warm water will be added to cold water in the calorimeter. If we designate the warm water as the system, we can write:

$$m_{\text{warm water}} \cdot s_{\text{warm water}} \cdot \Delta > T_{\text{warm water}} = -m_{\text{cold water}} \cdot s_{\text{cold water}} \cdot \Delta T_{\text{cold water}} \tag{6}$$

The mass and temperature change of both the warm and cold water will be measured. If our assumption that the calorimeter apparatus is not involved in the heat transfer is correct, then the two sides of the equation should be equal. The extent to which they vary from equality will give an estimate of the validity of the assumption.

In Part B of this lab, the system is an unknown metal, and we can write:

$$m_{\text{metal}} \cdot s_{\text{metal}} \cdot \Delta T_{\text{metal}} = -m_{\text{water}} \cdot s_{\text{water}} \cdot \Delta T_{\text{water}} \tag{7}$$

The masses of water and metal, and the temperature changes they undergo, will be measured. With these values, the specific heat of the metal can be calculated. A table of specific heats of metals is included in this experiment to allow you to identify the metal.

In reactions carried out at constant pressure, the heat that is absorbed or given off is called the heat or enthalpy of reaction (ΔH). The enthalpy of reaction is the result of the difference in

potential energies of the reactants and the products. The sign of ΔH specifies the direction of heat flow. If ΔH < 0 (the potential energy of the reactants is greater than that of the products), heat is given off and the reaction is exothermic. If ΔH > 0 (the potential energy of the reactants is less than that of the products), heat is absorbed and the reaction is endothermic. In Part C of the lab, the system is an acid/base "neutralization" reaction.

$$NH_3(aq) + H_3PO_4(aq) \rightleftharpoons NH_4^+(aq) + H_2PO_4^-(aq) \tag{8}$$
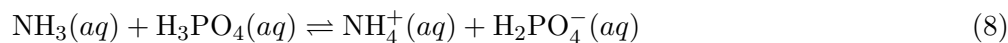
In Part D of the lab, the system is the dissolution of a salt.

$$NH_4H_2PO_4(s) \rightleftharpoons NH_4^+(aq) + H_2PO_4^-(aq) \tag{9}$$
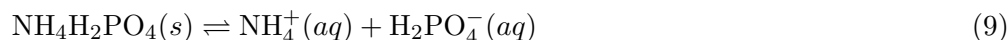
Since these systems are reactions,

$$\Delta H = \text{-}m_{water} \cdot s_{water} \cdot \Delta T_{water} \tag{10}$$

The ΔH obtained for Reaction 8 is called the "heat of neutralization", while that determined for Reaction 9 is called the "heat of solution". Technically, this acid/base reaction is not a neutralization, since the products are not a salt and water, but rather a weak acid and a weak base. Note that the terms "enthalpy" and "heat" are synonymous, and chemists use the two interchangeably. Thus, "heat of reaction" and "enthalpy of reaction" mean the same thing.

Enthalpy changes for reactions depend on the amounts of reactants used; consider the difference between blowing up a speck of dynamite and a stick of dynamite! In order to compare the energetics of different reactions, ΔH data from calorimetry is usually converted to "molar enthalpies," the ΔH that would be measured if the reaction were run on a one mole scale. Analysis of the units in the calorimetry equations above shows that ΔH is in Joules. Conversion to molar enthalpy requires determining the number of moles of a compound that have reacted. For example, if 500 J of heat were produced when 0.20 moles of compound dissolved, the molar enthalpy would be:

$$\frac{500\text{J}}{0.20\text{mol}} = 2,500\frac{\text{J}}{\text{mol}} \text{ or } 2.5\text{kJ/mol} \tag{11}$$

In Part A of this experiment, you will check the assumption that the Styrofoam cup calorimeter insulates the system (reaction of interest) and surroundings (water) well enough to make reliable heat transfer measurements. In Part B, you will identify an unknown metal by measuring its specific heat and comparing the result to values for metals of known identity. In Part C, you will measure the heat of neutralization for the reaction of phosphoric acid and ammonia. In part D, you will measure the heat of solution of ammonium phosphate.

EQUIPMENT

1 400 mL beaker

2 Styrofoam cups with lid

1 18 x 150 mm test tube

1 test tube holder

1 150 mL beaker

1 250 mL beaker

1 50 mL beaker

2 100 mL graduated cylinders

1 hot plate

1 MicroLab Interface

1 MicroLab Thermistor Instruction Sheet

1 thermistor

1 deionized water squirt bottle

REAGENTS

~**20 g** metal unknowns

~**50 mL** 1.5 M NH_3

~**50 mL** 1.5 M H_3PO_4

~**10 g** $NH_4H_2PO_4$

deionized water

SAFETY

Phosphoric acid is corrosive. It can attack the skin, cause permanent damage to the eyes, and cause burns. If contact with skin or clothing occurs, immediately rinse the affected area with water for at least 15 minutes and have your lab partner notify the teaching assistant. Do not inhale the fumes. If you inhale enough ammonia vapors to cause discomfort, get to fresh air. Have your lab partner notify the teaching assistant of the problem.

Students will have access to gloves owing to the use of concentrated acid and base solutions during the lab period.

WASTE DISPOSAL

All solutions may be disposed of down the sink drain followed by flushing with plenty of water. Do not put the metal samples in the sink. Return them to the side shelf in the appropriate containers.

PRIOR TO CLASS

Please review the following video:

Safety[1]

Please complete WebAssign prelab assignment. Check your WebAssign Account for due dates. Students who do not complete the WebAssign prelab are required to bring and hand in the prelab worksheet.

LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

Part A: Validating the Assumption about Insulation

1 Start the MicroLab Interface and calibrate the thermistor as described in the MicroLab instructions provided in the lab.

2 Set the MicroLab collection increment to 5 seconds, using the detailed instructions provided in the lab.

3 Measure about 40 mL of deionized water with a graduated cylinder, and add it to a 150 mL beaker. Heat to between 60 and 70°C. Work on steps 4 and 5 while the water is heating.

4 Weigh and record the mass of two nested Styrofoam cups and cover in Data Table A.

Table A: Validating the Assumption about Insulation

5 Measure about 60 mL of deionized water with a graduated cylinder, and add it to the cups. Reweigh the cups, lid, and water, and record this mass in Data Table A. Calculate and record the mass of the "cold water."

6 Set up your calorimeter as follows: place the nested cups in a 400 mL beaker to prevent spilling the contents. Place the lid tightly on the cup.

7 When the warm water is between 60 and 70°C, you are ready to measure temperatures. Insert the thermistor in the warm water; start MicroLab data collection. Measure the temperature of the warm water and record it in Data Table A.

8 Measure the temperature of the water in the calorimeter (cold water) by inserting the thermistor through the hole in the cup lid. When the lid is on the cup, the thermistor should not touch the cup's sides or bottom. Keep the lid tightly on the cup during measurements so all the heat exchange occurs within the cup. Record this temperature in Data Table A.

9 Uncover the calorimeter and quickly pour the warm water into it. Be careful not to let the water spatter from the cup, or you will lose accuracy. Replace the calorimeter cover. Swirl the water carefully so as not to splash or spill the water. Record the temperature of the mixture in Data Table A as soon as it becomes steady, about 30 seconds after mixing.

10 Reweigh the assembly and record the mass in Data Table A. Calculate and record the mass of the warm water you added.

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[1]https://www.youtube.com/watch?v=S_mm-PF_Iq8

Question 1: When the cold and warm water are mixed, do you expect $\Delta T_{coldwater}$ and $\Delta T_{warmwater}$ to have the same value or different values? What about $q_{coldwater}$ and $q_{warmwater}$?

Question 2: Calculate $\Delta T_{coldwater}$, $\Delta T_{warmwater}$, $q_{coldwater}$, and $q_{warmwater}$. Show your work.

$\Delta T_{cold\ water}$	°C
$\Delta T_{warm\ water}$	°C
$q_{cold\ water}$	kJ
$q_{warm\ water}$	kJ

Part B: Identifying an Unknown Metal by Specific Heat

1 Make a boiling water bath with 100 - 150 mL of water in a 250 mL beaker on the hot plate. While it heats, proceed with the following steps.

2 Record the number of the unknown metal you are using in Data Table B.

3 Weigh and record the mass of the unknown metal in Data Table B.

4 Place the metal into a test tube and place the test tube into the 250 mL beaker containing the boiling water.

5 Empty and dry the calorimeter from Part A, then add about 40 mL of water to the calorimeter.

6 Weigh and record the mass of the cups, cover and water in Data Table B. Calculate and record the mass of the water.

7 While the metal is continuing to heat, answer the following questions.

Question 3: Confer with your lab partner and instructor. In this experiment, what is the system and what are the surroundings?

Question 4: When the metal and water are mixed, do you expect ΔT_{metal} and ΔT_{water} to be the same or different?

Question 5: When the metal and water are mixed, do you expect q_{metal} and q_{water} to be the same or different?

8 Measure the temperature of the water in the calorimeter and record it in Data Table B.

9 After the metal has been in boiling water for 5 - 6 minutes, it is safe to assume the metal is at the temperature of the water. Measure this temperature and record it in Data Table B.

10 Using a test tube holder to avoid being burned, remove the test tube and carefully but quickly pour the metal into the calorimeter. Quickly replace the cover. Be careful not to let water spatter from the cup. Swirl the water gently.

11 Read the temperature of the mixture as soon as it becomes steady and record it in Data Table B.

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Table B: Identifying Unknown Metal by Specific Heat

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Question 6: Calculate the specific heat of the metal. Show your work.

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Question 7: What is the identity of the metal? Refer to the table below.

Specific Heats of Selected Metals

Metal	S_{metal}, J/g·°C	Metal	S_{metal}, J/g·°C
Al	0.901	Fe	0.449
Cu	0.384	Ni	0.444
Si	0.711	Sn	0.226
Zn	0.389	Mn	1.02

Part C: Heat of Neutralization

1 Empty and dry the calorimeter from Part B.

2 Measure exactly 50.0 mL of 1.50 M NH_3 with a graduated cylinder and add the solution to the empty, dry calorimeter.

3 Measure exactly 50.0 mL of 1.50 M H_3PO_4 into a different graduated cylinder.

4 Cover the calorimeter and insert the thermistor. Measure the initial temperature and record this value in Data Table C. The NH_3 solution should be at the same temperature as the H_3PO_4 solution, thus, one reading will serve as the initial temperature for both.

5 Lift the cover of the calorimeter, add the acid and quickly replace the cover. Swirl gently. When the temperature stops changing (shortly after mixing), record this temperature as the temperature of the mixed solution in Data Table C.

6 Weigh and record the mass of the cups, cover and solution in Data Table C. Calculate the mass of the mixed solution and the phosphoric acid solution.

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Table C: Heat of Neutralization

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Question 8: What is ΔH for this reaction? Show your work.

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Question 9a: Using volume and concentration, how many moles of NH_3 and H_3PO_4 were mixed together?

W_A

Question 9b: What is the molar value for ΔH for this reaction? Show your work.

W_A

Question 10 Calculate the amount of $NH_4H_2PO_4$ that you made in Part C in grams.

Part D: Heat of Solution

1 After thoroughly rinsing and drying your calorimeter, measure 100.0 mL of deionized water in a clean graduated cylinder and add this to the calorimeter.

2 Record the mass of the apparatus plus the water in Data Table D. Calculate the mass of water in the calorimeter.

W_A

Table D: Heat of Solution

3 Tare a clean, dry 50 mL beaker. Weigh the amount of $NH_4H_2PO_4$ you calculated in Question 10 into the 50 mL beaker, and record the exact mass you have obtained in Data Table D.

4 Cover the calorimeter, insert the thermistor and record the initial temperature of the water in Data Table D.

5 Lift the cover, dump the solid into the calorimeter and quickly replace the cover. Swirl gently. It may take a minute or two for the solid to dissolve. Continue swirling until the temperature no longer changes. Record this temperature as the temperature of the solution in Data Table D.

6 After your last measurement, choose *stop* on the screen and close the MicroLab software. Discard your solution down the sink drain and flush it down with plenty of water. Rinse all of your glassware and calorimeter with water, dry it and return it to the set-up area where you found it.

W_A

Question 11: Confer with your lab partner and teaching assistant. In this experiment, what is the system and what are the surroundings?

W_A

Question 12: How would you expect the molar change in enthalpy (ΔH) for this reaction to compare with the heat of neutralization in Part C? (If you would like to check, calculate it now. You will be asked for the value in the WebAssign postlab exercise.)

7 Before leaving, enter your results in the InLab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your teaching assistant. When all results are correct, note them and log out of WebAssign. The InLab assignment must be completed by the end of the lab period. If additional time is required, please consult with your teaching assistant.