Experiment 9: CALORIMETRY

Purpose:
Part I: Identify an unknown metal by determining its specific heat
Part II: Determine the molar heat of neutralization of an acid-base reaction

Performance Goals:
- Determine specific heat of a metal
- Identify an unknown metal by its specific heat
- Calculate heat of reaction of an acid-base reaction
- Determine heat of a reaction using the heat of solution
- Calculate change in molar enthalpy of a neutralization by using heat of reaction

Introduction:

Thermochemistry is the study of the heat released or absorbed during the course of a physical or chemical transformation. Reactions (physical or chemical) that release heat are said to be *exothermic*, and those that absorb heat are said to be *endothermic*.

A *calorimeter* is the apparatus used in the measurement of the quantity of heat transferred during a reaction. The type used in this experiment is commonly called a "coffee cup calorimeter." It consists of a reaction chamber made of double-nested Styrofoam cups, a lid, and a temperature measuring device. The reaction takes place inside the cup. It is assumed that any heat lost by the *system* (the reactants) is totally transferred to the *surroundings* (calorimeter and the solution in it). Conversely, any heat produced by the system is totally gained by the surroundings. That is, we assume no heat is lost to the universe <u>beyond</u> the walls of the cup.

The letter, q, stands for the heat transferred in a reaction. If a reaction is exothermic, q has a negative sign, and if endothermic, it has a positive sign. In an exothermic reaction, q_{system} is negative because it is <u>producing</u> heat, but $q_{surroundings}$ is positive because the surrounding is <u>absorbing</u> the heat produced by the reaction. Note that the <u>magnitudes</u> of q_{system} and of $q_{surroundings}$, however, must be the same. They differ only in the sign. Thus we can write the equation

$$q_{system} = -q_{surroundings} \qquad\qquad \text{Equation 1}$$

Note that the minus sign does **_NOT_** mean q_{system} is negative. It merely means that the two q's must have opposite signs. For example, if a reaction absorbs 4 kJ, q_{system} would be +4 kJ, and $q_{surroundings}$ would have the same value, but the opposite sign, −4 kJ (supplying the heat that is absorbed by the system): $q_{surroundings} = -(+4 \text{ kJ}) = -4 \text{ kJ}$.

In this experiment, two reactions are studied, one physical and one chemical. The first involves the transfer of heat from a hot object to water at room temperature. The second involves a neutralization reaction between HCl and NaOH.

Specific Heat of an Unknown Metal

The specific heat (s) of a pure substance is defined as the amount of heat needed to raise the temperature of one gram of the substance by one degree (either Celsius or kelvin). It makes no difference whether the rise in temperature is in Celsius or kelvin but in this experiment °C will be used. Specific heat is a characteristic of a substance and can be used as supportive evidence to determine the identity of an unknown metal. By definition this will always be a positive number.

The relationship between heat and temperature change can be expressed by the equation shown below:

$$q = m \times s \times \Delta T \qquad \qquad \text{Equation 2}$$

where q = amount of heat transferred (in J)

m = mass of the substance (in g)

s = specific heat of the substance (in $J \cdot g^{-1} \cdot °C^{-1}$)

$\Delta T = T_{final} - T_{initial}$ (in °C)

Rearrangement of Equation 2 gives us the following: $s \; = \; \dfrac{q}{m \; \Delta T}$ \qquad Equation 3

In Part I of this experiment, the specific heat of a metal will be determined by heating a pre-weighed amount of a metal sample in a test tube and then dropping the hot metal into a coffee-cup calorimeter containing a measured amount of water at room temperature. In the process the temperature of the metal will decrease and the temperature of the water will increase. Heat exchange between the metal sample and water will stop after they reach the same temperature. The amount of heat lost by the metal sample (q_{metal}) will be equal to the amount of heat gained by the water (q_{water}) and the calorimeter ($q_{calorimeter}$).

In this part of the experiment, q_{system} is the same as q_{metal}, and $q_{surroundings}$ is a combination of $q_{calorimeter}$ and q_{water}. "Surroundings" consists of the calorimeter and the water within it. Thus we have the overall equation

$$q_{metal} = - \left[q_{calorimeter} + q_{water} \right] \qquad \qquad \text{Equation 4}$$

The Styrofoam cups (the calorimeter) have so little mass that they do not absorb a significant amount of heat. This simplifies our calculations because we can assume that the water in the calorimeter absorbs all of the heat from the reaction and the tiny amount absorbed by the calorimeter is insignificant. That is, $q_{calorimeter}$ = zero. The equation can therefore be simplified:

$$q_{metal} = - q_{water} \qquad \qquad \text{Equation 5}$$

As described previously, the magnitudes of the two q's are the same but they will have different signs since one will lose heat whereas the other will gain the same amount of heat.

Applying Equation 2 to the heat transfer that occurs in the water allows us to calculate the amount of heat that is transferred: $q_{water} = s \times m \times \Delta T$

where s = specific heat of water = 4.184 $J \cdot g^{-1} \cdot °C^{-1}$. The mass ($m$)

and change in temperature (ΔT) of the water are measured. We next apply Equation 5 to determine the heat transfer for the metal from the heat transfer for the water ($q_{metal} = -q_{water}$). Using Equation 3, the specific heat of the metal can be determined.

$$s = \frac{q}{m\,\Delta T}$$

where q = q_{metal}
m = mass of the metal
ΔT = ($T_{final} - T_{initial}$) of the metal

By comparing the experimental specific heat to the specific heat values given below the identity of the unknown metal can be established.

Metal		Specific Heat $(J{\cdot}g^{-1}{\cdot}{}^{\circ}C^{-1})$
lead	(Pb)	0.13
tungsten	(W)	0.13
tin	(Sn)	0.21
copper	(Cu)	0.39
zinc	(Zn)	0.39
aluminum	(Al)	0.91

Molar Heat of Neutralization (or Molar Enthalpy of Neutralization)

The amount of heat transferred during a chemical reaction is called the *heat of reaction,* an extensive property that is proportional to the amount of the limiting reactant used. The heat of reaction to be examined in Part II of this experiment is the *heat of neutralization* (the heat transferred during the reaction between an acid and a base). The term, ***molar*** *heat of reaction*, refers to the amount of heat transferred ***per mole*** of the specified reactant. It is, by definition, an intensive property. Since neutralization is always exothermic, the molar heat of neutralization of HCl therefore refers to the amount of heat produced by one mole of HCl as it reacts with a base (NaOH in this case).

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \text{Equation 6}$$
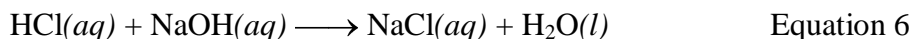
In a chemical reaction, the *reaction* is the *system.* Since this is a neutralization reaction, we will refer to the heat produced as q_{neutr}. The heat is absorbed by the calorimeter (assumed to be zero, as discussed earlier) and by the solution in the coffee cup calorimeter, which consists of HCl*(aq)* and NaOH*(aq)* at the beginning of the reaction and NaCl*(aq)* and water at the end of the reaction. We will refer to the heat absorbed by the solution as q_{soln}.

$$q_{neutr} = -\,q_{soln}$$

The value of q_{soln} will be determined by measuring the change in temperature (ΔT) of the solution inside the calorimeter during the reaction. Applying Equation 2 to the heat transfer of the solution

$q_{soln} = m \ s \ \Delta T$

where q_{soln} = amount of heat absorbed by the solution

m = mass of the solution

   = mass of HCl soln + mass of NaOH soln

s = specific heat of the solution = 4.18 J·g^{-1}·°C^{-1}

      (assume to be the same as the specific heat of water)

ΔT = change in temperature of the solution = $T_{final} - T_{initial}$

In this experiment mass of the solution will be calculated using the volume of the solution and its density (assumed to be 0.997 g·mL^{-1})

Heat of neutralization is the same value as q_{soln} but with the opposite sign. The solution is absorbing heat so q_{soln} is positive. The reaction is exothermic, so q_{neutr} should be negative.

Relationship between q and ΔH: The term, q, refers to the heat flow measured under the conditions of the experiment. If the reaction takes place in an open vessel (not in a sealed container), the pressure is equal to the atmospheric pressure and we say that the q is under constant pressure (given the symbol q_p). Under this condition, q is equal to ΔH (enthalpy change of a reaction). Note that ΔH, like q, is an extensive property, proportional to the amount of limiting reactant used. The calculation described above was for the amount of heat transferred for a particular mass of reactants. The final step in the calculations would be to determine the <u>molar</u> heat of neutralization (or *molar ΔH, the molar enthalpy change of neutralization*). It is determined by dividing q_{neutr} by the number of moles.

Equipment/Materials:

Part I: Double-nested Styrofoam cups, two temperature probes, 50-mL beaker, 250-mL beaker, 400-mL beaker, large test tube, boiling chips, unknown metal, utility clamp, ring stand, hotplate, electronic balance

Part II: Double-nested Styrofoam cups, two temperature probes, two 250-mL beaker, two 50-mL graduated cylinders, large test tube, 1.00 M HCl, 1.00 M NaOH

Procedure: *Work with one partner but perform calculations individually.*

Part I: Specific Heat of an Unknown Metal

1. Place approximately 300 mL of tap water in a 400-mL beaker. Add two boiling chips and heat to boiling.
2. An unknown metal will be assigned to you and your partner. Record the unknown code number.
3. Record the mass and appearance of the metal. If you were given a metal cylinder, you can place it directly on the balance pan. If you were given metal pellets, tare a small beaker (50-mL beaker) to zero, remove the beaker from the pan, transfer all of the metal pellets into the beaker and record the mass in your lab notebook.
4. Gently slide the metal into a large test tube. Fasten a utility clamp near the mouth of the test tube. You must be able to safely hold the test tube up by the utility clamp.

5. Attach the clamp onto a ring stand and lower the test tube into the water being heated (See Figure 9.1). The portion containing the metal should be surrounded by water. You do not have to wait for the water to boil before placing the test tube in the water. Do it as soon as you can so that the temperature of the test tube and the metal can begin equilibrating with that of the hot water.

6. Heat the water to boiling and ***continue*** **to heat for at least 10 minutes more.**

Utility Clamp

Temperature Probe

Test tube holding Unknown Metal

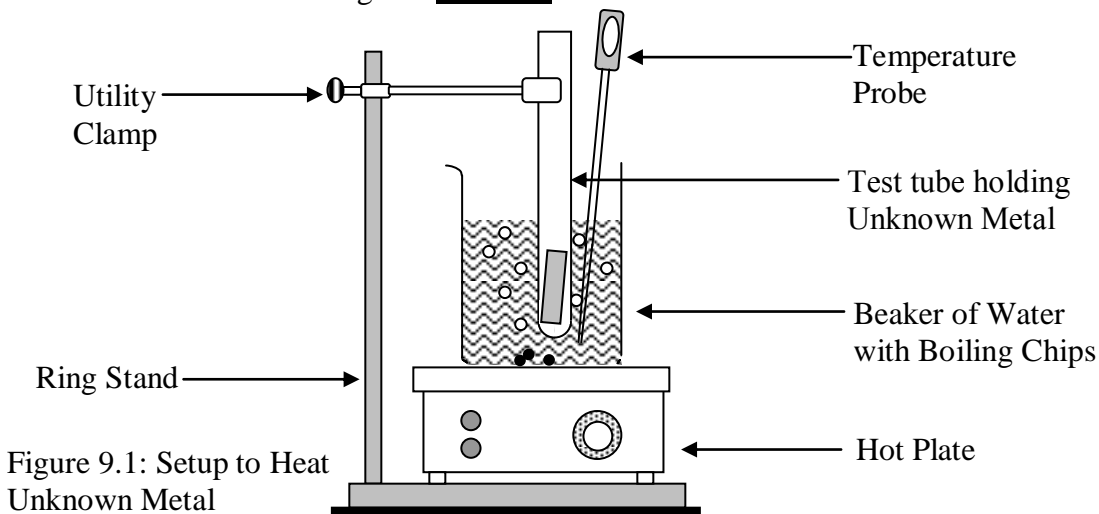Beaker of Water with Boiling Chips

Ring Stand

Hot Plate

Figure 9.1: Setup to Heat Unknown Metal

7. **Setting up the calorimeter:** Meanwhile, one of the partners should be preparing the calorimeter as follows:

    a. Obtain a calorimeter (double nested Styrofoam cups). Examine both cups to ensure there are no holes on the bottom of the cups. Check to see that they are dry.

    b. Record the mass of the calorimeter (the nested cups).

    c. Measure approximately 75 mL of deionized water and carefully add it to the calorimeter, being careful that the outside of the calorimeter does not get wet.

    d. Record the combined mass of the calorimeter and water, then place it in a 250-mL beaker to keep it safely upright, far away from the hot plate.

    e. Cover the calorimeter with the lid and insert a SECOND temperature probe through one of the holes in the lid. Do not use the same temperature probe as the one being used for the hot water. After a minute, check to see whether the temperature in the calorimeter has stabilized. Meanwhile study Step 9.
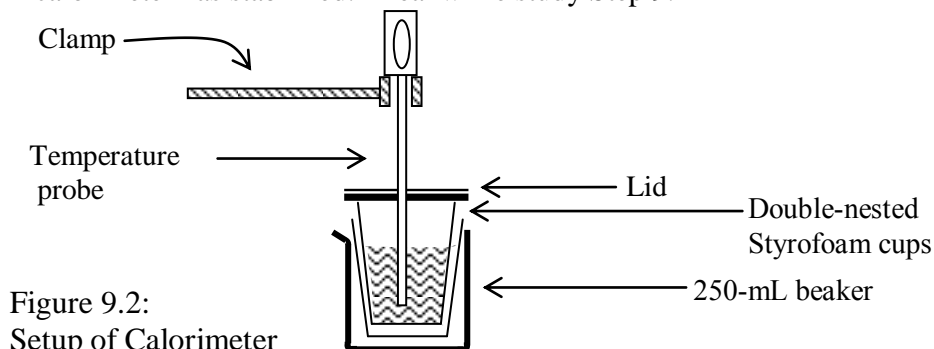
Clamp

Temperature probe

Lid

Double-nested Styrofoam cups

250-mL beaker

Figure 9.2: Setup of Calorimeter

8. Wait until the metal has been heated for at least 10 minutes, and the temperature of the water in the calorimeter has stabilized. At this point record the temperature of the boiling water in the beaker. We will assume this is the temperature of the hot metal,

and it is considered the *initial temperature of the metal:* $T_{initial}$ of metal. Next record the temperature of the water in the calorimeter (at room temperature). This is the *initial temperature of the water*, $T_{initial}$ of water.

9. Pour the heated metal into the calorimeter and quickly cover with the lid. Gently swirl the contents of the calorimeter and measure the **maximum temperature (T_{final})** reached by the water. This is the T_{final} for both the metal and the water in the calorimeter.

> TIPS to minimize experimental error:
> - Transfer the metal quickly to minimize loss of heat to the surrounding air, however, do not allow water to splash out.
> - Swirling must be thorough enough that the hot metal transfers its heat uniformly to the water as quickly as possible, however, avoid splashing the water onto the lid.

10. Take the metal out of the calorimeter and dry it thoroughly with paper towels. Dry the calorimeter with paper towels as well.
11. Repeat Steps 3 through 9 and record the data under Trial #2. Be sure to add more water to the beaker on the hot plate to make up for loss due to evaporation, and bring the water back to boiling.
12. When you are finished with both trials, dry your metal thoroughly with paper towels before returning it to your instructor. Check to make sure there are no boiling chips in the sink.
13. Complete calculations on the Calculations & Results pages and draw your conclusions as to the identity of your unknown metal.
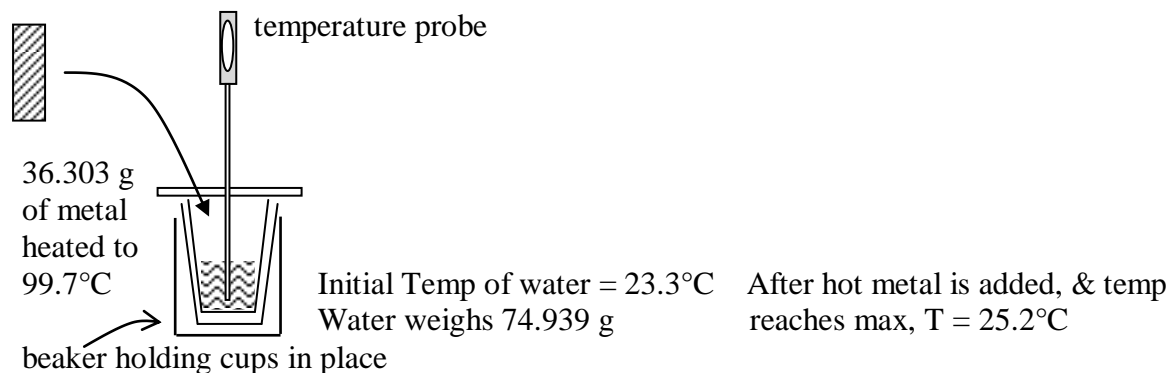
Sample Data Table for Part I: Specific Heat of an Unknown Metal

Unknown Metal Code #: ___
Appearance of Metal (shape and color):_____

	Trial #1	Trial #2
Mass of Metal (g)		
Mass of Calorimeter + Water (g)		
Mass of Empty Calorimeter (g)		
Mass of Water in Calorimeter (g)		
Initial Temp of Water (°C)		
Initial Temp of Hot Metal (°C)		
Final Temp of Water & of Metal (°C)		

Sample Calculations for Specific Heat of Unknown Metal: *Your instructor will take you through these calculations in the pre-lab. Take careful notes so that you can do the same calculations for your own set of data after the experiment.*

temperature probe

36.303 g of metal heated to 99.7°C

Initial Temp of water = 23.3°C   After hot metal is added, & temp
Water weighs 74.939 g   reaches max, T = 25.2°C

beaker holding cups in place

Mass of metal =
Mass of water =
Initial Temp of Water =
Initial Temp of Hot Metal =
Final Temp of Water & of Metal =

Calc of ΔT of water = $T_{final} - T_{initial}$ =

Calc of ΔT of metal = $T_{final} - T_{initial}$ =

Calc of q_{water} = s m ΔT =   Ans. q_{water} = +595 J (2 sig.fig.)

Calc of q_{metal} = $-$ q_{water} =   Ans. q_{metal} = $-$595 J

Calc of s_{metal} = $\dfrac{q_{metal}}{m_{metal}\Delta T_{metal}}$ =   Ans. $s = 0.22 \text{ J·g}^{-1}\text{·°C}^{-1}$

Conclusion: What is the metal in this example?

Part II: Neutralization Using 1.00 M HCl and 1.00 M NaOH

1. Take two clean and dry 250-mL beakers and label one "HCl" and the other "NaOH." Similarly, label two clean and dry 50-mL graduated cylinders.
2. Using the labeled 50-mL graduated cylinders, measure out exactly 50.0 mL of the 1.00 M HCl, and exactly 50.0 mL of 1.00 M NaOH solution. If you plan to use droppers to help you measure out the volumes precisely, label these also so you do not mix them up either.
3. Check to ensure the calorimeter, temperature probe and lid are dry.
4. Transfer the 50.0 mL HCl solution from the grad cylinder into the calorimeter, and place the calorimeter in a beaker as shown in Figure 9.2 so that the calorimeter would not topple over. Adjust the clamp so that the temperature probe is not touching the bottom or sides of the calorimeter, but extends below the liquid level.

Replace the lid as shown in the figure. Wait 5 minutes for the temperature of the system to stabilize and record it as the "initial temperature." Using a second temperature probe, record the initial temperature of the 50.0 mL of NaOH in the graduated cylinder.

5. Remove the calorimeter lid, quickly pour in the 50.0 mL of the NaOH solution, replace the cover and ***immediately*** begin to swirl the contents of the calorimeter to mix thoroughly.   Keep an eye on the temperature and record the maximum temperature as the "final temperature."

6. Thoroughly rinse the inner Styrofoam cup, temperature probes and stirrer with deionized water and gently wipe them dry before repeating steps 2 through 5 for Trial 2. (The grad cylinders and droppers do not have to be dry, but you must be careful you do not get the "HCl" and "NaOH" apparatus mixed up!

7. Complete the calculations on the Calculations & Results page.

CLEANUP: Be sure to rinse the temperature probes with water and wipe them dry. Check to see that your temperature probes are OFF before returning them to the side shelf. Do not discard the Styrofoam cups and lid. Return them to the side shelf after cleaning them.

Sample Data Table for Part II: Neutralization of HCl with NaOH

	Trial #1	Trial #2
$T_{initial}$ of HCl solution (°C)		
$T_{initial}$ NaOH solution (°C)		
Average $T_{initial}$ (°C)		
Total Volume After Mixing (mL) (Vol HCl soln + Vol NaOH soln)		
Maximum T After Mixing (T_{final}) (°C)		
ΔT (T_{final} – Average $T_{initial}$) (°C)		

Sample Calculations for Part II: Molar Heat of Neutralization of HCl and NaOH
NOTE: Numbers used here are fictitious and the ΔH values are nowhere near the correct. The # sig. fig. is consistent with what is presented HERE and not necessary what students will be actually dealing with. Do not blindly use the same # sig. fig. as shown here.

35.00 mL
1.00 M HCl

35.00 mL
1.00 M NaOH
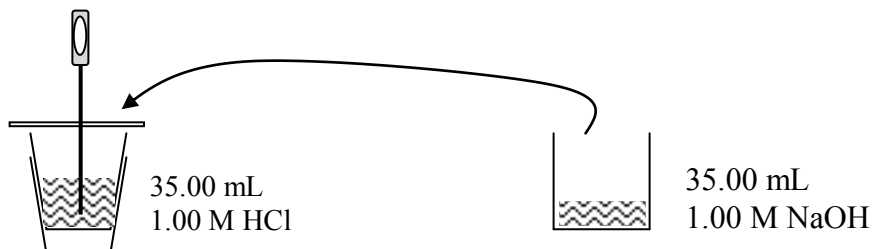
$T_{initial} = 25.2°C \longrightarrow T_{final} = 29.0°C$

As your instructor goes through the calculations in pre-lab it would be wise to take careful notes on your own paper. Do not just scribble them on this page.

The heat released in the neutralization (q_{neutr}) will heat up the total solution inside the calorimeter. What is the mass of the solution (m_{soln}) in the calorimeter?

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O\ (l)$$
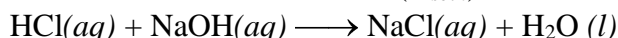
The neutralization reaction is very fast. Almost immediately the only substances in the calorimeter consist of only NaCl dissolved in water. At this concentration we can assume that the density of this solution is the same as that of water: 0.997 g/mL, and the specific heat of the solution is also the same as that of water: $4.18\ \text{J·g}^{-1}\text{·°C}^{-1}$

Since there are multiple steps in the calculations, always keep at least one extra significant figures until you reach the final answer before rounding off properly.

<u>**Total**</u> Volume of Solution After Mixing =
Mass of Solution After Mixing (from total volume and density) =
$T_{initial}$ of Reactants =
T_{final} (of Soln) =
Calc of $\Delta T_{soln} = T_{final} - T_{initial} =$
$q_{soln} = s_{soln}\ m_{soln}\ \Delta T_{soln} =$
Convert q_{soln} to kJ = Ans. ~~+1.18 kJ~~ +1.10 kJ
$q_{neutr} = -q_{soln} =$ Ans. ~~−1.18 kJ~~ −1.10 kJ
To calculate *molar heat of neutralization*, we need the # mol limiting reactant.
In this case, either HCl or NaOH can be used as the limiting reactant.
How do we determine # mol HCl? What information do we have concerning the HCl?
We know its volume and its molarity.
Volume of HCl used in neutralization =
Molarity of HCl used in neutralization =
mol HCl = Ans. 0.035 mol HCl
molar heat of neutralization = $\dfrac{\text{heat transferred in each trial}}{\text{\# mol HCl in each trial}} = \dfrac{q_{neutr}}{\text{\# mol HCl}} =$

−31
Ans. Molar heat of neutralization = Ans. ~~−34~~ kJ/mol HCl

Pre-Lab Exercise:
1. In Part I of the experiment, which do you expect to be larger, $T_{initial}$ or T_{final} of the water? Based on your answer, do you expect ΔT_{water} to be positive or negative? Explain.
2. In Part I of the experiment, would you expect q_{metal} to be positive or negative? Would you expect q_{water} to be positive or negative? Explain.
3. Consider the two parts of the experiment. What is producing the heat measured in Part I? What is producing the heat measured in Part II? Explain your answers.
4. How are the terms "heat of neutralization" and "molar heat of neutralization" different? Include in your answer an explanation why one is an extensive property and the other is an intensive property.
5. In this experiment q equals ΔH? What are the experimental conditions that allow us to equate them?
6. In Part I of the experiment, we utilize the equation $q_{metal} = s\ m\ \Delta T$. If we change the mass of the metal, what would you expect to change (q? s? m? ΔT?). Explain your answer.

Post-lab Questions:
1. Examine the initial and final temperatures in Part I. Explain how the temperatures tell you what type of thermochemical reaction was involved (endothermic or exothermic). Is the sign of your overall average of the molar ΔH_{neutr} consistent with this? Explain.
2. In Part I, we see that copper and zinc have the same specific heat (See table in the Introduction.) If you obtained an experimental value of 0.39 $J{\cdot}g^{-1}{\cdot}°C^{-1}$, how might you determine which metal you have as an unknown? Explain.
3. We assumed that no heat is lost to the surroundings beyond the nested coffee cups. In Part I, obviously there would have been some loss in heat as the hot metal is transferred to the calorimeter. How does that unavoidable heat loss affect your calculated specific heat of the metal? Would your calculated specific heat be too high or too low due this error? Explain fully.
3.4. In Part II, we assume that the density and specific heat of the solution is the same as that of water. What justifications do we have to make that assumption? Explain.
6.5. Using the molar heat of neutralization ***obtained in your experiment*** (assuming it is correct), calculate how much heat you would expect to be produced if you mixed 50.0 mL of 0.250 M HCl with by 50.0 mL of 0.250 M NaOH. Show your calculations. (Hint: How many moles of HCl are involved?)

Calculations & Results: **Name:** _____

Lab Sec: _____   **Partner's Name:** _____

Show your calculations on a separate sheet of paper and enter the results here.

Part I: Specific Heat of an Unknown Metal

Unknown Metal Code # = _____	**Trial #1**	**Trial #2**
Mass of metal =	_____	_____
Mass of water =	_____	_____
Initial Temp of Water =	_____	_____
Initial Temp of Hot Metal =	_____	_____
Final Temp of Water & of Metal =	_____	_____
ΔT of water =	_____	_____
ΔT of metal =	_____	_____
q_{water} =	_____	_____
q_{metal} =	_____	_____
s_{metal} =	_____	_____
Average s_{metal} =	_____	

Conclusion with justifications:
What is the identity of the unknown metal?

Calculations & Results: **Name:** _____

Lab Sec: _____   **Partner's Name:** _____

Show your calculations on a separate sheet of paper and enter the results here.

Part II: Molar Heat of Neutralization   Trial #1   Trial #2

Total Volume of Solution After Mixing =   _____   _____

Mass of Solution After Mixing =   _____   _____

$T_{initial}$ of Reactants =   _____   _____

T_{final} (of Soln) =   _____   _____

ΔT_{soln} =   _____   _____

q_{soln} =   _____   _____

q_{neutr} =   _____   _____

Volume of HCl used in neutralization = _____

Molarity of HCl used in neutralization =_____

mol HCl =   _____   _____

Molar Heat of Neutralization =   _____   _____

Average Molar Heat of Neutralization =   _____