I. Determination of the calorimeter constant.

The **First Law of Thermodynamics** states:

During heat exchange in an isolated system with no mechanical work, heat is neither created not destroyed.

This means that heat lost from one object equals heat gained by another object in thermal contact, if the heat exchange can be sufficiently insulated (or isolated) from the surroundings. A vessel that provides adequate heat insulation from its surroundings is called a **calorimeter**. When heat exchange occurs in a calorimeter, temperature changes are measured in order to determine specific heats of materials or objects, or heats of reaction. A perfect calorimeter absorbs no heat from the system under measurement, nor does it allow heat to escape to or enter from the surroundings. Of course no calorimeter is perfect. A typical calorimeter used in an introductory chemistry laboratory consists of two styrofoam cups nested together, with a plastic lid and a temperature probe-usually a thermometer. In order to accurately obtain calorimetric data, it is necessary to measure the heat capacity of the calorimeter. This is known as the calorimeter constant, C_{cal}. C_{cal} can be measured by placing a known mass of cold water in the calorimeter and adding a known mass of hot water and then noting the final temperature of the mixture. The heat lost by the hot water (Δq_{hw}) is equal to the heat gained by the cold water (Δq_{cw}) plus the heat gained by the calorimeter (Δq_{cal}):

$$\Delta q_{hw} = \Delta q_{cw} + \Delta q_{cal} \qquad (1)$$

The change in heat Δq for a given mass of material is given by:

$$\Delta q = s \text{ x } m \text{ x } \Delta T \qquad (2)$$

where **s** is the **specific heat** in units of (J / g-^{0}C); m is the mass in grams and ΔT is the change in temperature using Celsius degrees (or degrees K). For example, the specific heat of water (s_w) is 4.184 J / ^{0}C-g.

For an entire object (such as a calorimeter) we use the equation:

$$\Delta q = C\Delta T \qquad (3)$$

where now **C** is the **heat capacity** and has units of (J / ^{0}C), since the entire object is considered, rather than 'per gram'.

When hot water is added to cold water in a calorimeter the following applies:

heat lost by hot water = heat gained by cold water + heat gained by calorimeter

$$\Delta q_{hw} = \Delta q_{cw} + \Delta q_{cal} \qquad (4)$$

$$s_w \text{ x } m_{hw} \text{ x } (T_h - T_f) = s_w \text{ x } m_{cw} \text{ x } (T_f - T_c) + C_{cal} (T_f - T_c) \qquad (5)$$

[note: Δq_{hw} must be greater than Δq_{cw} to account for heat lost to the calorimeter]

then: $C_{cal} = (\Delta q_{hw} - \Delta q_{cw}) / (T_f - T_c)$ **in units of (J / ^{0}C)**   (6)

The following will be provided: Styrofoam coffee cups with lids, hot plates, metal beaker.

Procedure

a. Place one styrofoam cup within the other to form a calorimeter.
b. In the metal beaker on a hotplate place distilled water and heat to 60-70 ^{0}C.
c. Using the 100 mL graduated cylinder in your kit, measure 30.0 mL of distilled water at room temperature and record the exact volume to 0.1 mL. Pour into the calorimeter.
d. Record the temperature of the water in the calorimeter to 0.1 ^{0}C.
e. From the hot water in the metal beaker on the hotplate measure about 30 mL into the 100 mL graduated cylinder. Record the exact volume to 0.1 mL.
f. Just prior to pouring into the calorimeter containing the cold water, record the exact temperature of the hot water to 0.1 ^{0}C. IMMEDIATELY after measuring the temperature pour into the calorimeter.
g. Insert the thermometer through the lid, secure the lid in place, and monitor the temperature while gently swirling the water to mix quickly and thoroughly. Record the final temperature when no change is seen for approximately 20-30 seconds.
h. Repeat steps c.-g. two more times so that you have three sets of data for determining the C_{cal}.

Fill in a table similar to the one below in your laboratory notebook:

	Run #1	Run #2	Run #3
Volume of cold water V_{cw}			
Temp of cold water T_{cw}			
Volume of hot water V_{hw}			
Temp of hot water T_{hw}			
Final Temperature T_f			

Using equations 4,5 and 6 calculate the calorimeter constant, C_{cal}. Assume that 1.0 mL of water has a mass of 1.0 g. The specific heat for water is 4.184 J / ^{0}C-g. Place these calculated values as a sixth row in the table in your laboratory notebook, each under the heading for the run #. Average the three values (find the mean) showing the average deviation from the mean.
[For example three C_{cal} values of 15.6, 19.0 and 25.5 J / ^{0}C, have a mean of 20.0 $\pm$ 3.6, which is an 18% average deviation. The value 3.6 is the average of the absolute variation (i.e. without sign) of each value from 20.0: 4.4 for 15.6; 1.0 for 19.0 and 5.5 for 25.5.]

Q U E E N S
C O L L E G E

II. Determination of the specific heat of a metal.

The specific heat of a metal, s_m, can be measured by heating a sample of the metal of known mass to a higher temperature and adding it to a known mass of water in a calorimeter. The heat lost by the metal, Δq_m, is equal to the heat gained by the water, Δq_{cw}, plus the heat gained by the calorimeter, Δq_{cal}. You will use the C_{cal} which you determined in Part I here.

$$\Delta q_m = \Delta q_{cw} + \Delta q_{cal} \qquad (7)$$
$$s_m \text{ x } m_m \text{ x } (T_h - T_f) = s_w \text{ x } m_{cw} \text{ x } (T_f - T_c) + C_{cal}(T_f - T_c) \qquad (8)$$

You will run three trials on the same sample of metal. The average s_m may be useful in identifying the metal, along with any other distinguishing characteristics you many note, such as appearance or density.

Some specific heats (s_m in J / g-^{0}C) of known metals at 25^{0}C and 1.0 bar pressure.

aluminum	0.901	nickel	0.443
brass	0.380	stainless steel	0.500
bronze	0.435	steel	0.481
copper	0.386	titanium	0.544
iron	0.450	zinc	0.386
lead	0.129		

Procedure
As in Part I, you will have access to a metal beaker on a hotplate with the water heated to the range between 70 and 80 ^{0}C. Measure the temperature once stable to the nearest 0.1 ^{0}C. Be sure to use metal tongs to handle the metal cylinder when hot .

a. Dry and assemble the styrofoam cup calorimeter.
b. Weigh the metal cylinder. Record the mass to the nearest milligram. Measure the diameter and length of the metal cylinder so a volume can be calculated.
c. Place your metal sample in the hot water and be sure it is completely covered by the water.
d. Using the 100 mL graduated cylinder measure 35.0 mL of distilled water, record the exact volume to 0.1 mL and pour into the calorimeter.
e. Record the exact temperature of the water in the calorimeter to the nearest 0.1 ^{0}C.
f. Note the temperature of the hot water in the bath holding the metal to the nearest 0.1 ^{0}C.
g. WITHOUT DELAY-using the metal tongs-take the metal cylinder from the hot water bath and place in the calorimeter with the cold water. This should take no more than 3 or 4 seconds !
h. Place the top with the thermometer on the calorimeter and swirl gently to mix. Record to the nearest 0.1 ^{0}C the highest temperature achieved that is stable for 20 seconds or so.
i. Repeat steps c. to h. two more times, giving three sets of data.

Record your data in your laboratory notebook using a table similar to this one:

	Trial #1	Trial #2	Trial #3
Code:			
Mass of metal:			
Volume of cold water:			
C_{cal} from Part I :			
Temperature of cold water T_c :			
Temperature of hot metal T_h :			
Final Temperature T_f :			
s_m calculated for each trial:			
Physical description of metal.			
Volume of metal cylinder:			
Density of metal cylinder:			

Use equations (7) and (8) to calculate the value of s_m for each trial. Assume that 1.0 mL of water has a mass of 1.0 g. The specific heat for water is 4.184 J / ^{0}C-g. Average the three s_m values (find the mean) showing the average deviation from the mean.
 [For example three s_m values of 0.110, 0.135 and 0.124 J /g-^{0}C, have a mean of 0.123 $\pm$ 0.009, which is a 7.0% average deviation. The value 0.009 is the average of the absolute variation (i.e. without sign) of each value from 0.123: 0.013 for 0.110; 0.012 for 0.135 and 0.001 for 0.124.]
Can you identify the metal ?

I. Enthalpy of Reaction.

When a chemical reaction occurs, the reaction can release heat to the surroundings (exothermic reaction) or absorb heat from the surroundings (endothermic reaction). If this reaction occurs under constant pressure conditions (i.e. the reaction system is open to the atmosphere), then the heat of reaction at constant pressure (q_p) is equal to the change in enthalpy (ΔH) of the reaction:

$$q_p = \Delta H$$

When the reaction is carried out in aqueous solution in a calorimeter open to the atmosphere, the heat released (or absorbed) by the reaction is absorbed (or released) by the water and the calorimeter. In brief, an exothermic reaction carried out in water will raise the temperature of the water, with some of the heat also being absorbed by the calorimeter.

A neutralization reaction of an acid with a base is just such an exothermic reaction, in which the products are a salt (usually soluble in water) and water. When the solutions of reacting acid and base are dilute (2 M or less), we can assume that the specific heat and density of the aqueous solutions are the same as for pure water. If the solutions of acid and base are at the same temperature before mixing (T_i) then

$$\Delta H = - [m_t\, s_w + C_{cal}]\, (T_f - T_i) \qquad [1]$$

where T_f is the final temperature after mixing and m_t is the total mass of water after mixing and s_w is 4.184 J / °C g, the specific heat of water.

The measured ΔH can then be divided by the moles of acid (or base) reacted to determine the enthalpy of reaction per mole of acid (or base) reacted.

The following will be provided: Styrofoam coffee cups with lids, as used in last week's experiments. Aqueous solutions of HCl, H_2SO_4 and NaOH of appropriate molar concentration.

Procedure

a. Place one styrofoam cup within the other to form a calorimeter.
b. Using a clean, dry graduated cylinder, measure 40.0 mL of 1.0 M aqueous hydrochloric acid (HCl) and pour into a clean, dry beaker.
c. Measure 20.0 mL of 2.0 M aqueous sodium hydroxide (NaOH) and pour into the cup calorimeter.
d. Measure the temperature of both acid and base solutions, making sure to rinse and dry the thermometer tip each time to avoid reaction. Proceed when the temperatures are both the same. This is T_i.
e. Pour the acid solution into the calorimeter containing the base solution. Do this quickly and be sure all the liquid is transferred. Close the cover quickly and monitor the temperature until a

maximum is reached. Record time and temperature every 30 seconds or so. The maximum temperature reached is T_f.

f. Use these data to calculate the ΔH for the neutralization of HCl.

g. Place the waste into the proper waste containers in the hood. Rinse and dry the cup calorimeter.

h. Repeat steps b.-g. using 20.0 mL of 1.0 M aqueous sulfuric acid (instead of the aqueous hydrochloric acid).

Fill in a table similar to the one below in your laboratory notebook:

	HCl	H_2SO_4	
Volume of acid:			
Temp of acid, T_i:			
Volume of base:			
Temp of base, T_i:			
Final Temperature T_f			

Using the average C_{cal} from the previous week's experiment and equation [1] above calculate the ΔH for each acid neutralization reaction above.   Assume that 1.0 mL of acid or base solution used here has a mass of 1.0 g. The specific heat for water is 4.184 J / ^{0}C-g.

From the ΔH calculated above and the number of moles of acid neutralized in each case, calculate the molar heat of neutralization for HCl and H_2SO_4. In each case also write the balanced chemical equation for neutralization of each by aqueous NaOH.

Using Hess' Law, and the data in Appendix 4 of your text, calculate the expected molar ΔH of neutralization for each acid. Compare to your measured values. If there are any variations propose a possible explanation.

[Note: The ΔH^o_f for Na^+ (aq) + ΔH^o_f for Cl^- (aq) = ΔH^o_f for NaCl (aq)]