Lab Session 9, Experiment 8: Calorimetry, Heat of Reaction

Specific heat is an intensive property of a single phase (solid, liquid or gas) sample that describes how the temperature of the sample changes as it either absorbs or loses heat energy. Specific heat is generally a function of temperature, but, to a good approximation, it can be treated as being constant for a single phase over a moderate temperature range. The table below lists the specific heats at 25°C of liquid water and selected metal solids.

The Zeroth Law of Thermodynamics states: "If two samples of matter, initially at different temperatures (T_H and T_C, respectively), are placed in thermal contact, heat will be lost by the hotter sample (T_H) and gained by the cooler one (T_C). This exchange of heat will take place until both samples achieve the same final temperature, T_F, so that $T_H > T_F > T_C$." The First Law of Thermodynamics states: "During heat exchange (or, as we shall see, during a chemical reaction), heat is neither created nor destroyed." Thus, heat lost equals heat gained, if the heat exchange can be sufficiently insulated from the surroundings so that not very much heat escapes to the surroundings. A vessel that provides adequate heat insulation from its surroundings, and in which temperature changes are measured in order to determine specific heats (or heats of chemical reactions) is called a **calorimeter**. A perfect calorimeter absorbs no heat from the solution that it contains, nor loses any heat to the surroundings. No calorimeter is perfect, however. A typical calorimeter used in freshman chemistry labs is made of two nested Styrofoam cups, and looks like the one shown in Figure 9.1.

Substance	Specific Heat, J/(g^{o}C)
water (liquid)	4.184
aluminum (solid)	0.901
chromium (solid)	0.448
copper (solid)	0.386
iron (solid)	0.450
lead (solid)	0.129
nickel (solid)	0.443
tin (solid)	0.217
zinc (solid)	0.386

If we place m_{metal} grams of a hot metal, at a Celsius temperature T_H, into a nearly perfect calorimeter, along with m_{water} grams of water, at a lower Celsius temperature T_C, then the metal and the water will thermally equilibrate at a final intermediate Celsius temperature, T_F.

Since the heat lost by the metal is equal to the heat gained by the water within the calorimeter, the following equation holds (m is in the units g, T is in the units °C and sp ht is in the units J/g °C):

Figure 9.1

$$[(m_{metal}) \times (T_H - T_F) \times (sp\ ht_{metal})] = [(m_{water}) \times (T_F - T_C) \times (sp\ ht_{water})] .$$
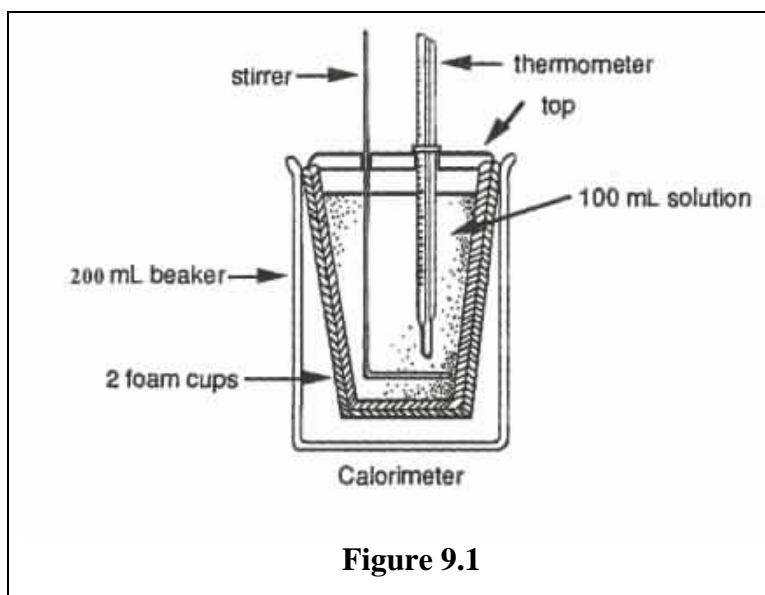
We can possibly identify an unknown metal by determining its specific heat using the preceding heat exchange formula with the specific heat of water taken to be 4.184 J/g °C. From the table above, it is obvious that we cannot distinguish between copper and zinc, or between chromium and nickel, on the basis of specific heat alone. Additional information is needed, such as color. (Copper has the characteristic "copper" color, whereas zinc is gray.) Rearranging the heat exchange formula and inserting the specific heat of water gives

$$\text{sp ht}_{metal} = \frac{(m_{water})(T_F - T_C)(4.184 \text{ J/g°C})}{(m_{metal})(T_H - T_F)} .$$

A major source of error in the preceding example is the assumption that no heat went into warming the calorimeter vessel and that no heat was lost to the surroundings. We can take this into account by defining the **heat capacity** of the calorimeter C, which has the units J/°C. By making a similar heat exchange measurement in which we mix m_H grams of hot water, initially at temperature T_H, with m_C grams of water initially at a lower temperature T_C (perhaps at or near room temperature). The value of the calorimeter's heat capacity reflects the calorimeter's efficiency. (A more efficient calorimeter has a smaller value of C.) With this correction for the calorimeter and surroundings, the heat exchange relationship becomes:

heat lost by the hot water = heat gained by the cold water

+ heat gained by the calorimeter and surroundings,

or

$$[(m_H)(T_H - T_F)(4.184 \text{ J/g °C})] = [(m_C)(T_F - T_C)(4.184 \text{ J/g °C}) + (C)(T_F - T_C)] .$$

Rearranging, we have

$$C = \frac{(m_H)(T_H - T_F)(4.184 \text{ J/g°C}) - (m_C)(T_F - T_C)(4.184 \text{ J/g°C})}{(T_F - T_C)}$$

$$= [\frac{(m_H)(T_H - T_F) - (m_C)(T_F - T_C)}{(T_F - T_C)}](4.184 \text{ J/g °C}).$$

This heat capacity is most reliable for the temperature range in which it was determined (i.e, for temperature changes that occur just above room temperature in this case). The heat which is absorbed and thereby increases the temperature of the water and the calorimeter can be generated by an exothermic chemical reaction occuring within the calorimeter. For example, if we mix equimolar amounts of an aqueous strong acid (e.g., HCl $_{(aq)}$) with an aqueous strong base (e.g., NaOH $_{(aq)}$), the neutralization reaction produces heat, which causes the temperature in the calorimeter to increase.

If we mix 50.0 mL of a 2.00 M aqueous HCl solution with 50.0 mL of a 2.00 M aqueous NaOH solution, the neutralization reaction HCl $_{(aq)}$ + NaOH $_{(aq)}$ → H_2O $_{(aq)}$ + NaCl $_{(aq)}$ will produce a measurable change in temperature. After complete reaction, the calorimeter will contain a dilute solution of sodium chloride. We can assume that the specific heat is still that of water, namely

4.184 J/g °C, without introducing much error. We can also assume that the density of the dilute salt solution is that of water, 1.00 g/mL. The heat exchange equation in this case is:

heat given off by the reaction = heat gained by the water

+ heat gained by the calorimeter and surroundings.

If the calorimeter, the HCl solution, and the NaOH solution all start at the same initial temperature T_I and warm to a final temperature T_F, then

heat given off by the reaction = $(m_{water})(T_F − T_I)(4.184 \text{ J/g °C}) + (C) (T_F − T_I)$

$$= [(V_{water} \text{ in mL})(1.00 \text{ g/mL})(4.184 \text{ J/g °C}) + (C)](T_F − T_I).$$

(**Note:** $V_{water} = 100 \text{ mL}$)

At constant pressure, the heat given off by the reaction is equal to the change in enthalpy (ΔH) for the reaction. Since the reaction involves $(2.00 \dfrac{\text{mol}}{\text{L}})\left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}}\right)(50.0 \text{ mL}) = 0.100 \text{ mol of HCl} = 0.100 \text{ mol}$ of NaOH, we can calculate the change in enthalpy for the acid/base reaction as follows (the minus sign is inserted to indicate that the reaction is exothermic):

$$\Delta H = \left(\dfrac{-(\text{heat}) \text{ J}}{0.100 \text{ mol}}\right)\left(\dfrac{1 \text{ kJ}}{10^3 \text{ J}}\right) = \left(\dfrac{-(\text{heat})}{100}\right) \text{in kJ/mol.}$$

8A Experiment: Determination of Calorimeter Constant

1. Obtain or assemble a calorimeter as shown in Figure 9. The experiment will require two thermometers, one for the calorimeter and one for the heated water.

2. Using a graduated cylinder, measure 50.0 mL of water and pour it into the calorimeter. Measure an additional 50.0 mL of water and pout it into a clean, previously dried beaker.

3. One lab partner should stir the calorimeter contents for at least 5 minutes and then record the temperature inside the calorimeter as T_C.

4. Meanwhile, the other lab partner should heat (bunsen burner) and stir the water in the beaker until it reaches a temperature of 55-60 $^\circ$C. After removing the burner, stir and record the exact temperature of the water in the beaker as T_H.

5. At that point, pour the hot water into the calorimeter, replace the top and stir the contents well while recording the temperature at 15 second intervals. The highest temperature should occur within 2 minutes. Record this maximum temperature as T_F.

6. Calculate the heat capacity C of the calorimeter in J/$^\circ$C using the formula given in the preceding section with $m_H = m_C = (50.0 \text{ mL})(1.00 \text{ g/mL}) = 50.0 \text{ g}$.

7. Repeat steps 1 through 6 in order to make a second determination of C. Reverse the thermometers for the second determination of C.

First Determination of C		Second Determination of C	
$T_C =$	°C	$T_C =$	°C
$T_H =$	°C	$T_H =$	°C
Temperature inside calorimeter at 15 s intervals:		Temperature inside calorimeter at 15 s intervals:	
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
$T_F =$	°C	$T_F =$	°C
$C =$	J/°C	$C =$	J/°C
		Average $C =$	J/°C

8B Experiment: Determination of Reaction Enthalpy

1. Dry the calorimeter and reassemble it.

2. Using a clean, dry graduated cylinder, measure 50.0 mL of a 2.0 M aqueous NaOH solution and pour it into the calorimeter. (*Caution*: NaOH is corrosive and, if spilled on the skin, should be washed away immediately with copious amounts of water.)

3. Using a clean, dry graduated cylinder, measure 50.0 mL of a 2.0 M aqueous HCl solution and pour it into a clean, dry beaker. (*Caution*: HCl is corrosive and, if spilled on the skin, should be washed away immediately with copious amounts of water.)

4. Stir the two solutions (the NaOH (aq) in the calorimeter, and the HCl(aq) in the beaker) until they exhibit the same temperature. Record this temperature as T_I.

5. Pour the HCl solution into the calorimeter, replace the top, and stir while recording the temperature at 15 second intervals.

6. Record the highest temperature reached as T_F.

7. Use these temperatures and the value of *C* determined for the calorimeter in the equations presented in the previous section to calculate the heat evolved and ΔH of the reaction. (# of moles = (0.0500 L)(2.0 mol/L) = 0.10 mol. ΔH = heat/moles.)

8. Repeat steps 1 through 7 with the thermometers reversed in order to make a second determination of the heat evolved and of ΔH. (ΔH should equal – 55.8 kJ/mol.)

First Determination of ΔH		Second Determination of ΔH	
T_I =	°C	T_I =	°C
Temperature inside calorimeter at 15 s intervals:		Temperature inside calorimeter at 15 s intervals:	
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
T_F =	°C	T_F =	°C
heat =	J	heat =	J
ΔH =	kJ/mol	ΔH =	kJ/mol
		Average ΔH =	kJ/mol
% error = [(|ΔH| - |55.8|)/55.8] x 100 =			%

8C Exercises

1. Suppose that one were to mix 30.0 g of aluminum pellets, originally at 97.0 ^{o}C, with 100 grams of water, originally at 23.0 ^{o}C, in a perfect calorimeter. What will be the equilibrium temperature T_F in the calorimeter? T_F = _____ ^{o}C.

2. Repeat the calculation of Exercise 1, but in the calorimeter you used in lab rather than in a perfect calorimeter. T_F = _____ ^{o}C.

3. When 100 g of an unknown metal at 98.0 ^{o}C were mixed in a perfect calorimeter with 50.0 g of water at 22.0 ^{o}C, the final temperature T_F was observed to be 26.4 ^{o}C. Presuming that the metal is one of those listed in the table of specific heats given above, which one is it?
Unknown metal = _____.

Name_____

Partner_____Section #_____

8A Experiment: Determination of Calorimeter Constant

First Determination of *C*		Second Determination of *C*	
$T_C =$	°C	$T_C =$	°C
$T_H =$	°C	$T_H =$	°C
Temperature inside calorimeter at 15 s intervals:		Temperature inside calorimeter at 15 s intervals:	
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
$T_F =$	°C	$T_F =$	°C
C =	J/°C	*C* =	J/°C
		Average *C* =	J/°C

8B Experiment: Determination of Reaction Enthalpy

First Determination of ΔH		Second Determination of ΔH	
$T_I =$	°C	$T_I =$	°C
Temperature inside calorimeter at 15 s intervals:		Temperature inside calorimeter at 15 s intervals:	
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
°C	°C	°C	°C
$T_F =$	°C	$T_F =$	°C
heat =	J	heat =	J
ΔH =	kJ/mol	ΔH =	kJ/mol
		Average ΔH =	kJ/mol
% error = [(|ΔH| - |55.8|)/55.8] x 100 =			%

8C Exercises

1. T_F = _____°C.   2. T_F = _____°C.

3. Unknown metal = _____ .