EXPERIMENT **3**

"...BUT A HOT TEMPER LEAPS O'ER A COLD DECREE"

ENTHALPY OF VARIOUS REACTIONS

Techniques

- calorimetry
- graphing

MSDS available for

- Copper metal, Cu
- Zinc metal, Zn
- Aluminum metal, Al
- 3 unknown salts
- sodium hydroxide, NaOH
- nitric acid, HNO_3
- hydrochloric acid, HCl (aq)

Principles

- calorimetry
- enthalpy of different reactions
- Hess' Law
- graphical extrapolation

Recommended Advanced Reading

- **Chapter 7 in Petrucci,Herring,Madura, Bissonnette's General Chemistry, 10th Ed.**

INTRODUCTION

The beginning

In this experiment, you will perform a number of different experiments to calculate the enthalpies of various types of reactions. In today's session you will work with your partner to:

- determine the specific and approximate molar mass of a metal
- determine the enthalpy of neutralization of a strong acid and strong base
- determine the enthalpy of solution of an unknown salt

This is a general overview of what you will be accomplishing in this experiment.

EXPERIMENT 3: *Enthalpy of Various Reactions*

Introduction

> "*Currently, a new polymer PEG, polyethylene glycol, is being used to treat certain fabrics. These fabrics, once coated, can generate or absorb heat, depending on air temperature. The day of air-conditioned clothing may not be that far in the future!*"

Heat of Formation

The heat of formation of a substance, ΔH_f, is defined as the change in enthalpy when one mole of the substance is formed from its elements in their standard states. The standard state is usually defined at a pressure of one atmosphere and a temperature of 25 °C. The enthalpy of any element that is in its standard state and is in its most stable form is arbitrarily given a value of zero. Thus, graphite, which is the most stable form of carbon, has an enthalpy of zero at 25 °C and 1 atmosphere, whereas diamond, another form of carbon but not the most stable at 25 °C and 1 atmosphere, does not have a zero value for enthalpy in the standard state. The heat of formation of most simple compounds can be found in the literature. Most of these have been measured experimentally. For example, the enthalpy of formation of liquid water at 25 °C can be found from the reaction,

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l) \quad \Delta H_f = -68.3 \text{ kcal} = -285.8 \text{ kJ} \qquad [1]$$

The heat of formation of liquid water is -68.3 kcal or -85.8 kJ. One calorie is defined as 4.184 Joule. The negative sign in front of the value indicates that heat is released or that the reaction is ***exothermic***. If the value of the enthalpy is positive, the reaction is ***endothermic***.

Hess' Law can be used to determine the enthalpy of a more complex reaction. The enthalpies of certain reactions cannot be measured in the lab directly. However, it is possible to measure the enthalpies of other reactions which, when added chemically together, give the desired chemical reaction. In such cases, the enthalpies of these reactions can also be added together.

Calorimetry

An apparatus called a "calorimeter" is used to measure the quantity of thermal energy gained or lost in a chemical change. A simple calorimeter can be constructed using two nested Styrofoam cups with lids and a thermometer. A more complex type of calorimeter is the bomb calorimeter, which measures thermal energy changes under constant volume conditions. Since we will be working under atmospheric pressure, we will use the first type of calorimeter, also called a ***"coffee cup" calorimeter***. Although not strictly true, we may assume that in this calorimeter, no heat is lost to the surroundings or the calorimeter itself.

Measurement of Thermal Energy

How can thermal energy be measured? One way is to measure a quantity called the specific heat capacity. The specific heat of a substance is the amount of thermal energy required to heat one gram of that substance by one degree. The specific heat capacity of a substance is an intensive property, meaning that it does not depend on the amount of substance present. The specific heat capacity of a drop of water and a pan of water are the same. When we multiply the mass of an object by its specific heat capacity, it is possible to calculate the heat capacity of that object. Heat capacity is an extensive property, meaning that it is dependent on the quantity of substance present. The heat capacity of a drop of water is much, much less than that of a lake. The specific heat capacity of water is unusually high compared to many other substances. This fact has an important impact on us. Cities located near huge bodies of water tend to have more moderate climates. Such cities are cooler in the summer as large water bodies take a long time to absorb the heat of the summer sun, and these cities are warmer in the winter, as the water slowly releases the heat absorbed during the summer. Since our bodies are composed largely of water, we are able to maintain a fairly constant body temperature, in spite of outside temperature fluctuations.

We can determine the specific heat capacity of a metal that does not react with water by heating the metal and then transferring it to cold water. The change in the temperature of the water gives a measure of the heat capacity of the metal. In reality, the specific heat capacity of a substance does vary with temperature, but in this experiment, the temperature change is small, and we may assume the specific heat capacity to be a constant in this temperature range.

Specific Heat Capacity of a Metal

In general, we may state that the energy required to change the temperature of a substance can be determined using the following equation:

$$E = m \times c \times \Delta T \qquad [2]$$

where c represents the specific heat capacity of the substance, m represents the mass of the substance and ΔT represents the change in temperature of the substance. When a hot metal is added to cold water, the temperature of the metal decreases and the temperature of the water rises. If there is no heat loss to the surroundings or the calorimeter, then the heat lost by the metal must be equal to the heat gained by the water.

$$-E\ (\text{metal}) = E\ (\text{water}) \qquad [3]$$

Equation [3] follows the convention that when the system loses heat, the sign is negative and when the system gains heat, the sign is positive. If we now substitute Equation [2] into Equation [3],

$$-c_{met} \times m_{met} \times \Delta T_{met} = c_{wat} \times m_{wat} \times \Delta T_{wat} \qquad [4]$$

In a calorimeter, since no heat is lost to the surroundings, the heat gain of the water must equal the heat loss of the metal. Do not forget, however, that $\Delta T = T_f - T_i$, so the sign is important! The specific heat capacity of water is 4.18 J/g°C.

It is also possible to estimate the molar mass of a metal once its specific heat capacity is known using the equation,

$$c_{met} \times MM_{met} \approx 25\ \text{J/mol°C} \qquad [5]$$

where MM_{met} is the molar mass of the metal. This approximation was made by Dulong and Petit in 1819, who proposed that one mole of all metals had roughly the same capacity to absorb heat.

Enthalpy of Neutralization

In the neutralization reaction, the same principle is used. The heat evolved in the reaction must be equal to the heat absorbed by the solution but opposite in sign. Thus,

$$Q_N = -m_{tot} \times c_{soln} \times \Delta T \qquad [6]$$

where Q_N is the total heat energy of neutralization, m_{tot} is the total mass of the solution, c_{soln} is the heat capacity of the solution (which we assume to be the same as that of water), and ΔT is the temperature change. Once the amount of heat released in the reaction is known, the enthalpy of the reaction per mole of substance, X, is

$$\Delta H_N = \frac{Q_N}{\text{Number of moles of X}} \qquad [7]$$

Enthalpy of Solution

The dissolution of a salt may be exothermic or endothermic depending on two main factors. The first factor is the ***lattice energy*** of the salt. The lattice energy is the energy required to vaporize one mole of the salt to form gaseous ions and this quantity is endothermic. The second factor, the ***hydration energy***, is the energy released when one mole of gaseous ions is solvated by water to form aqueous ions and is exothermic. Both these quantities are difficult to measure in the lab. However, their sum, the ***enthalpy of solution***, can be measured without much difficulty. The enthalpy of solution can be expressed as

$$\Delta H_s = (\text{- heat loss of } H_2O) + (\text{- heat loss of salt}) \qquad [8]$$

For a particular salt, if the enthalpy of dissolution is negative, the hydration energy is greater than the lattice energy. If the enthalpy of dissolution is positive, the reverse is true.

In the lab, we will calculate the enthalpy of solution using the equation below:

$$\Delta H_s = \frac{Q_s}{n_{salt}} = \frac{-(m_{solution})(c_{solution})(\Delta T_{solution})}{n_{salt}} \qquad [9]$$

where c is the specific heat capacity, m is the mass, ΔT is the temperature difference and n is the number of moles.

Concept of the Experiment

In this experiment, there are three main parts. In the first part, you will determine the specific heat capacity of a metal and approximate its molar mass from the specific heat capacity. In the second part of the experiment, you will determine the enthalpy of neutralization of two strong acids with a strong base and compare the enthalpy of neutralization of the two strong acids. In order to ensure complete neutralization, the concentration of the acid is slightly higher than that of the base. In the third part of the experiment, you will determine the enthalpy of solution of an unknown salt and decide which of the salts you were given.

(TTD) Things to Do

- Complete the prelab exercises before coming to the laboratory.
- Determine the specific heat capacity of the metal assigned to you.
- Approximate its molar mass.
- Determine the enthalpy of neutralization of a strong base with two strong acids and compare their enthalpies of neutralization.
- Determine the enthalpy of solution of an unknown salt and attempt to identify it.
- Use safe laboratory procedures at all times.

Safety Precautions

1. **Wear approved eye protection at all times**.
2. The acid/base solutions supplied are relatively concentrated. Acids and bases are **corrosive**. Be careful!!
3. **Please** be careful with the thermometers.

PROCEDURE

Equipment and chemicals needed

Chemicals

metal sample
1.1 M HCl
1.1 M HNO_3
1.0 M NaOH
unknown salt

Equipment

2 polystyrene cups with 2 covers
1 test tube
1 precision thermometer
analytical balance
wristwatch with seconds hand
hotplate
250 and 400 mL beaker
2 - 50 mL graduated cylinders
coloured pencils, graph paper

Enthalpy of Various Reactions

Starting the experiment

Specific Heat Capacity of a Metal

1. Prepare a water bath by filling a 400 mL beaker two-thirds with water.

2. Begin heating the water bath on a hot plate.

3. Ask your demonstrator to assign you a metal. Refer to Table 1 for the mass of that particular metal that you require.

4. Measure approximately the required amount and record the exact mass of the metal using an analytical balance.

5. Transfer the metal to a clean, dry test tube. Place the test tube in the water bath. Ensure that the water level is above the level of the metal in the test tube. (The metal should not be allowed to come into contact with water).

6. Allow the water to boil for at least 5 minutes to allow the metal to come to thermal equilibrium with the water. While you are waiting, continue to the next step.

7. Obtain 2 clean, dry foam cups and nest them one inside another. Ensure that there are no holes or tears in the cups. Obtain 2 pierced lids as well. The combination of the cups and the lids forms your calorimeter.

8. Determine and record the mass of your empty calorimeter using an analytical balance.

9. Measure approximately 20 mL of distilled water and transfer it to your calorimeter. Note the exact volume.

10. Measure and record the mass of the calorimeter and water using an analytical balance.

11. Place the calorimeter into a 250 mL beaker (this provides support to the calorimeter and prevents it from tipping).

12. CAREFULLY insert the thermometer probe (Caution! It is **heavier** than the cups!) into the hole pierced in the lids. Do not pierce the bottom of the cups with the probe!

13. Start the timer and record time and the temperature of the water in the calorimeter every 30 s for 3 minutes.

14. Record the temperature of the boiling water.

15. Open the calorimeter. Making careful note of the time (REMEMBER: You started the time in Step 13!), remove the test tube from the water bath and transfer the metal quickly and quantitatively into your calorimeter. As fast as possible, replace the lid on the calorimeter. Do NOT allow any water to splash out <u>or</u> any metal to be lost. THIS IS YOUR TIME OF MIXING!

16. Monitor and record the temperature and time every 20 seconds for 4 minutes while swirling the contents of the calorimeter. If the temperature has not stabilized after 4 minutes, continue recording until it stabilizes or you reach 10 minutes.

17. Repeat Steps 4-16 with another sample of the same metal.

Moving on!

Enthalpy of Neutralization

18. Measure 50.0 mL of 1.1 M acid using a clean, dry graduated cylinder and record the exact volume and concentration.

19. Using a different clean and dry graduated cylinder, measure 50.0 mL of NaOH solution. Record the exact concentration of the solution and the exact volume.

20. Transfer the NaOH solution to your clean and dry calorimeter.

21. Start the timer and monitor and record the temperature of the NaOH solution every 30 s for 3 minutes. You may assume the initial temperature of the acid is the same as that of the NaOH.

22. Open the calorimeter. Making careful note of the time, transfer all the acid to the calorimeter and close it as quickly as possible. Do not allow any solution to spill. THIS IS YOUR TIME OF MIXING!

23. Record the temperature every 20 seconds for 4 minutes while swirling the contents of the calorimeter. If the temperature has not stabilized after 4 minutes, continue recording until it stabilizes or you reach 10 minutes.

24. Determine the mass of the calorimeter, lids and solution using an analytical balance.

25. Repeat Steps 18-24.

26. Repeat Steps 18-25 using a second acid AFTER you have completed the next part and IF there is time.

Almost there!

Enthalpy of Solution

27. Ask your demonstrator to assign you a salt and record its unknown number/letter.

28. Depending on which salt was assigned to you, measure a mass as close as possible to the mass of that salt specified in Table 2 at the end of the experiment and record its exact mass using an analytical balance.

29. Measure and record the mass of your empty calorimeter using an analytical balance.

30. Measure about 20 mL of distilled water using a graduated cylinder and transfer it to your calorimeter.

31. Measure and record the mass of your calorimeter and water using an analytical balance.

32. Start the timer and record the temperature of the water every 30 s for 3 minutes.

33. Open the calorimeter. Making careful note of the time, transfer ALL of the salt to the water and close the calorimeter as quickly as possible. AVOID spilling the salt or allowing it to stick to the sides of the calorimeter. THIS IS YOUR TIME OF MIXING!

34. Swirling constantly, record the temperature every 20 seconds for 5 minutes. If the temperature has not stabilized after 5 minutes, continue recording until it stabilizes or you reach 15 minutes.

Finishing the Experiment

35. Repeat Steps 28-34 with another sample of the same salt.

Cleaning Up!

36. Rinse the calorimeters and the thermometers with distilled water and return them to your demonstrator. All solutions can be poured down the drain and flushed with plenty of water.

37. Remember to get your raw data, written in PEN, signed by your TA and to attach this raw data to your report in order to receive a grade!

Graphs

In all 3 parts, graph the Temperature as a function of the Time (the time is a continuous axis). Make a vertical line at the time of mixing. Extrapolate back from the temperature after the time of mixing to the time of mixing. The vertical distance from the initial temperature to the extrapolated temperature is the change in temperature, ΔT. Make sure that ALL temperatures measured appear on the appropriate graphs!

Calculations

Part 1. Enthalpy of a Metal

1. From your graph, calculate the change in temperature of the water, ΔT_{water}.

2. Using the specific heat capacity of water and the mass of water, calculate the energy gained by the water.

3. Calculate the change in temperature of the metal, ΔT_{metal}.

4. Determine the specific heat capacity of the metal, using the energy gained by the water and the mass of the metal.

5. Approximate the molar mass of the metal using its calculated specific heat capacity.

6. Since you know the identity of the metal, calculate a percent error with respect to the known specific heat capacity AND known molar mass of the metal.

Part 2. Enthalpy of Neutralization

7. Determine the change in the temperature of the solution, ΔT_{soln}.

8. Calculate the volume of the final solution.

9. Calculate the mass of the final solution, assuming the final solution to have a density of approximately 1.0 g/mL. How does this compare to your measured mass? Which is more accurate?

10. Calculate the energy released, assuming that the specific heat of the final solution is the same as that of water, 4.184 J/g °C.

11. Calculate the no. of moles of the limiting reagent (OH^- (aq)).

12. Calculate the number of moles of water formed in the neutralization reaction.

13. Determine the heat of neutralization per mole of water.

14. Compare the heats of neutralization per mole of water for the two strong acids.

15. Calculate percent errors for the experimental values of the heat of neutralization with respect to literature values.

Part 3. Enthalpy of Dissolution of a Salt

16. Determine the change in temperature of the solution, ΔT_{soln}.

17. Calculate the energy released/absorbed by the solution, using its specific heat and mass.

18. Calculate the enthalpy of dissolution, ΔH_s, per mole of salt.

19. Attempt to find a literature value for the enthalpy of dissolution of the salt (but make SURE you are looking for the correct quantity!). If you find a literature value, calculate the percent error.

Points to Ponder

- Is your specific heat capacity for the metal reasonable? How close is the molar mass? Error values?

- How do the enthalpies of the two strong acids compare? Can you obtain literature values for these enthalpies? What should you REALLY be looking for? (consider net ionic equations for the neutralization reaction..)

- Were you able to determine the identity of your unknown salt? How does the literature value of the enthalpy of solution compare to your experimental value?

- What are the sources of error inherent in the experiment? How does each source of error contribute to the result (ie. does it increase or decrease the value of the enthalpy?)

Lab Report

- *Refer to page iii in the FYI section and the lab report section in experiment 1.*
- All graphs should have titles, labelled axes, and clear scales. The graph should occupy as much of the page as possible!
- Complete all the calculations, as outlined in the procedural section, and **don't forget to include significant figures!!**

Table 1. Mass of Metal Required for Part 1 of the Experiment

Metal	Mass Required
-	g
Copper, Cu	10-15
Zinc, Zn	10-15

Table 2. Unknown Salts for Part 3 of the Experiment providing Molar Masses, Masses Required and Specific Heat Capacities of the Resulting Solutions Formed

Substance	Molar Mass	Mass Required	Specific Heat Capacity Of Solution of Substance in water*
-	g/mol	g	J/g°C
Water	18.0	20	4.184
Unknown Salt A	166.0	2.5	3.662
Unknown Salt B	101.11	1.5	3.877
Unknown Salt C	74.55	1.5	3.815

*The values for the specific heat capacities of the salt solutions were obtained from the following source:

Randall, Merle, Rossini, Frederick D., *The Journal of the American Chemical Society*, **Vol. 51**(2), February 1929, Table VII, pp334-335.