EXPERIMENTAL PHYSICAL

AND

INORGANIC CHEMISTRY (CHM 200B)

COURSE MATERIAL

**EXPERIMENT ONE**

**GRAVIMETRIC AND VOLUMETRIC ANALYSIS**

**INTRODUCTION**

The techniques of classical chemical analysis can be divided into two broad categories (i) gravimetric analysis and (ii) volumetric analysis .The purpose of this experiment is to employ both methods of analysis to determine the concentration of H2SO4 in solution that have been prepared by dilution from a sulphuric acid solution of define, but unknown concentration. From the dilution the concentrations of the unknown H2SO4 solution may then be calculated.

In **gravimetric analysis**, the element to be determined is isolated in a solid compound of known identity and definite composition. From the mass of this compound, the analyst can determine the mass of the element that was present in the sample. On the other hand, when the goal is to determine the amount of compound present in the original sample (rather than the amount of an individual element), either one of the ions or one of the elements is isolated in a compound to be weighed. In this experiment, the amount of sulphuric acid is determined gravimetrically by producing and weighing BaSO4(s), by reaction with BaCl2 (aq).

H2SO4 (aq) + BaCl2 (aq) BaSO4(s) + 2HCl(aq)

BaSO4 is suitable for this gravimetric determination because it is precipitated readily and completely from the solution being analyzed. Furthermore, the resulting precipitate is pure and easily filtered, it is a solid of known and definite composition, and its molar mass are sufficiently large that an appreciable and easily weighed mass of precipitate will be produced.

In **volumetric analysis**, the amount of the species present in the sample is determined by the technique of titration. The sample is present in a solution of a known volume. To this solution of unknown concentration is added another solution, called **titrant**, of known concentration. The **titrant** is added in such a way that the volume added at each point is readily determined. The solution in the titrant solution is a substance that reacts quickly and completely with the species to be the equivalence determined. It is also helpful if an easily observable change occurs at **equivalent point** of the titration, the point at which the amount of titrant solute is chemically equivalent to the amount of the species being determined. If such a change does not occur, often an **indicator** is added to the solution being titrated. As a result of this addition, a colour change occurs in the reaction mixture at a point in the titration very near to (or ideally at) the equivalence point. This point of colour change is known as the **end point**. In this experiment, the amount of H2SO4 is determined volumetrically by its titration with sodium hydroxide solution.

H2SO4(aq) + 2NaOH(aq) Na2SO4(aq) + 2H2O

Since no perceptible change occurs at the equivalence point of this reaction (2moles of NaOH have been added for every mole of H2SO4 originally present), phenolphthalein is used as an indicator. Phenolphthalein is colourless in acidic solution and pink in alkaline solution.

**PROCEDURE**

**A Dilution of Concentrated H2SO4**

1. Obtain 25mL of 6M H2SO4  in a 100ml or smaller graduated beaker. Label this as the **initial solution.** The beaker should be scrupulously clean to avoid contamination. After use carefully rinse the beaker with water and discard the rinsings.
2. Pour approximately 50ml of distilled water in a clean 100ml volumetric flask. Pipet exactly 10.00ml of 6M H2SO4 into the flask. (Be sure to rinse the pipet with a small volume of the sulphuric acid solution first. If you are unsure of the proper, safe procedure for pipeting. **Consult your instructor before beginning).** Add distilled water to the calibration mark of the volumetric flask. Stopper securely and invert ten times to ensure thorough mixing and uniform concentration throughout the solution. This solution will be referred to as the **stock solution** (it has a concentration of approximately 0.6M) it can be transferred to a clean and dry Erlenmeyer flask and stoppered for storage and labelled stock solution.(Retain this stock solution until you have completed the experiment , so that you can make up more final solution if needed.)
3. Rinse the volumetric flask with several portion of distilled water. Discard the rinse water.
4. Pipet 25.00ml of the stock solution into the 100ml volumetric flask. This must be clean but not necessarily dry; you will be adding distilled water to its contents. Add distilled water, swirling it in order to mix thoroughly after each addition, to fill the flask to the calibration mask. Stopper securely and invert ten times to ensure thorough mixing. This **final solution** has a concentration of approximately 0.15M. It should be stored in a stoppered, clean, and dry 125ml Erlynmeyer flask (labelled “final solution ) for further use. **(Careful! pipeting from a volumetric flask can be hazardous.)**

**B. GRAVIMETRIC DETERMINATION OF SULFATE ION**

1. Obtain approximately 12ml of 0.2 M BaCl2(aq) in a clean, dry, stoppered 125ml Erlenmeyer flask.

2. Obtain a piece of filter paper and determine its mass to the nearest mg (+0.001g). With pencil (not ink!) write an identifying mark (1 or 2) on the outside edge of the filter paper. Fold the filter paper in quarters, make a cone, and place it in a funnel. Moisten it will distilled water so that it adheres to the walls o the funnel.

3. Using a 10mL graduated cylinder, transfer 5.0mL of the 0.2M BaCl2 obtained in step one into a 50ml beaker. This provides a slight excess of barium ion. On a hot plate warm this solution to neaKr boiling (for about 15 minutes). Do not allow it to boil or heat to dryness.

4. While the above solution is heating, pipet 5.00ml of the **final solution** of H2SO4 into a 50ml beaker. Add 5ml of 1.0ml of HCl (use a graduate cylinder) to this solution. This added acid will help to form large, filterable particle of precipitate. Heat this solution to near boiling point (about 10 minute on a hot plate). Do not heat to dryness.

5. While both solution (Steps 3 and 4) are still hot, slowly add the BaCl2(aq) into the beaker of H2SO4(aq) with vigorous stirring. Add slowly so that large particles of precipitate will form. Rinse the stirring Rod with your wash bottle before removing it from the beaker.

6. To further promote the formation of large particles of precipitate, you should warm the mixture in the beaker to near boiling on a hot plate and keep it at this temperature for 20 minutes. Do not heat to dryness. Stir occasionally, then allow it to cool slowly. This digestion procedure dissolves the smaller particles of solid, which later re-precipitate on the remaining particles when the mixture cools.

7. Use the stirring rod to direct the liquid, and pour the mixture from the beaker onto the filter paper in the funnel. Wash the precipitate from the beaker wit 5ml aliquots of distilled water. Make sure to also wash off the stirring rod so that all solid is quantitatively transferred (if some of the fine precipitate passes through the filter paper , re-filter the filtrate through the same filter paper. Make sure to quantitatively transfer all the filtrate to the filter to the funnel). Carefully transfer the wet filter paper from the funnel onto a clean dry filter paper towel, and place it in your locker to dry until d next laboratory period. Be very careful with this transfer, since wet filter paper may tear. If a drying oven is available, place the wet filter on a large watch glass and dry in a 110oC oven for 1 to 2 hours.

8. If time allows, repeat steps 2 through 7 for a second determination.

9. Rinse all glass wear that has been used for BaCl2(aq) with small portion of H2O. Discard these rinsing in the manner indicate for solutions in the disposal section

10. During the next laboratory period, determine the mass of the filter paper and BaSO4(s) to nearest mg. Subtract the recorded mass of the filter paper to determine the mass of the precipitate.

C. **Volumetric Determination of Acid Concentration**

1. Obtain a clean 5ml portion of standardized 0.100 M NaOH solution. Make sure to run some of this rinse solution through the burette tip.

2. Fill the burette with 0.100M NaOH. Do not fill the burette to the 0.00ml mark. Instead, fill the burette nearly to this mark, making sure that the tip is filled, and read the liquid level (to one beyond the finest graduation, estimate the last digit).

3. Using a suction device and careful, safe procedure pipet 10.00ml of the final solution into a clean 250 ml Erlenmeyer flask. Add two or three drop of phenolphthalein indicator solution.

4. Titrate this sample of the final solution with 0.100 M NaOH(aq) until a faint pink colour persist for over 15 seconds. Swirl the solution in the flask as you titrate. Wash down the wall of the flask with distilled water from your wash bottle to ensure splattered acid or base is returned to the titration mixture. A half drop of 0.100M NaOH(aq) can be added by hanging a partial drop on the burette tip, touching this drop to the inside of the flask, and washing the drop into the solution of distilled water. Record the volume (to + or – 0.01ml) of the base used.

5. Repeat step 2 through 4 with a second portion of the final solution, until the volume of titrant used in successive titration agrees within 1%.

**Results**

Calculate the concentration of the H2SO4 in mol/dm3 as determined by the gravimetric and volumetric analysis.

**Questions**

1. In this experiment you were asked to make several quantitative transfers. What is quantitative transfer and what is its purpose?
2. The gravimetric determination constantly yields a higher (H2SO4) of the initial solution than does the volumetric determination. Which concentration is more accurate? Explain why. Explain how you would modify the less accurate procedure to obtain more accurate results.
3. A 10.00ml sample of 0.500 M H2SO4 is pipette into a 250ml volumetric flask and diluted with water to the calibration mark. What is the concentration of the diluted solution?

**PRELAB EXERCISE**

1. What do you understand by Titrant and Titrand?
2. In the experiment above, specify the titrant and titrand used.
3. State five (5) experimental precautions that you must observe in the experiment above.

**EXPERIMENT TWO**

**THERMOCHEMISTRY**: **THE HEAT OF REACTION**

**INTRODUCTION**

Chemical thermodynamics deals with energy changes that accompany chemical reactions. Such energy changes are among the factors that determine the following.

1. How fast a chemical reaction takes place- i.e the problem of chemical kinetics?

2. How complete the reaction will be- i.e the position of chemical equilibrium?

Thermochemistry involves the energy changes that are manifested as the enthalpy change ∆H of reaction, is the heat given off or absorbed by the reaction at constant pressure. A reaction in which heat is lost by the reactant to the surrounding has negative ∆H and is said to be exothermic; one in which heat is absorbed as a positive ∆H and is said to be endothermic.

The general term, enthalpy of reaction, may be classified into more categories:

1. The enthalpy of formation is the quantity of heat involve in formation of 1 mole of the substance in its standard state directly from its constituent element s in their standard state.

2. The enthalpy of combustion is the quantity of heat evolved per mole of a combustible substance, such as carbon or methane, undergoing a reaction with excess oxygen.

3. The enthalpy of solution, vaporization, fusion and sublimation are concern with changes in state or solvation of molecule or ion.

4. The enthalpy of neutralization is the heat evolved when 1 mole of water is produced by the reaction of an acids and base.

In this experiment, we shall measure the enthalpies of neutralization of HCl solution with NaOH solution, the enthalpy of solution of NaOH(s), and the enthalpy of neutralization of (s) with HCl solution. Comparison of calculated results for different part of the experiment should permit you to verify the generalization known as Hess’s law of constant heat summation, which states that a process proceeds through one or several steps, the enthalpy change for the overall process can be calculated by summing the enthalpy changes for the individual steps

Heat measurements are performed by carrying out the reaction in the calorimeter, in which temperature change and mass of solution are measured. The purpose of the calorimeter is to prevent the gain of heat from the surrounding or lose of heat to the surroundings. As a chemical reaction proceeds, heat is given off by the reaction and this same is gained by the solution. Thus the temperature of the solution increases. If we assume heat gain or lost by the calorimeter is insignificant, the heat of the reaction qrxn is the negative of the heat that is gained by the solution, qsolution. The heat gain by the solution is calculated with the equation qsolution = mc ∆ t, where m and ∆t` are the mass and temperature change of the solution. The specific heat capacity c, is the quantity of heat required to raise the temperature of one gram of material (in this case, the material is the solution) by one degree Celsius (j/g/0C). The specific heat is given for different parts of this experiment. The heat given off by the reaction and gain by the solution is measured in unit of joules. The change in the enthalpy, ∆H, of a reaction is the heat evolved per mole of reactant. The ∆H is determined by dividing the qrxn by the number of moles of reactant or product. In this experiment, the number of water produced is equal to the number of moles of each reactant. The assumption that no heat is gain by the calorimeter when the reaction occurs is strictly true. However, not including the heat gain by the calorimeter introduces a typical error of 2% or less. This amount of error is well within the experimental error associated with the measurement of the temperature change in the experiment.

**PROCEDURE**

1. **The Enthalpy of Neutralization of HCl(aq) and NaOH(aq)**

Place 50.0ml of 1.0 HCl in one calorimeter and 50.0ml of 1.0 M NaOH in another calorimeter. With the lids and thermometers in the place, read the temperature (±0.10C) for 3 minute at 1-minute intervals; quickly mix the NaOH thoroughly into the HCl solution, and continue the reading for 4 min at 1-minute interval. Extrapolate the temperatures to the time of each solution as in part A, and calculate the enthalpy of neutralization per mole of water produced (the density of the 0.5 M NaCl produced is 1.02g/ml, and its specific heat is 4.0j/g/0C).

1. **The Enthalpy of solution of NaOH(s)**

Carefully weigh about 2.0g of **NaOH(s).** Because of the hygroscopic nature, weigh this by difference, in a stopped 50 or 125ml Erlenmeyer flask used as a weighing bottle. Your instruction will tell you the approximate number of **NaOH(s)** pellets required to assist in estimating the mass needed. Be sure to be clean up any spilled **NaOH(s).** This solid absorb water from the air and forms a slipper solution that is also corrosive] place 50.0ml of distilled water in your calorimeter. With the lids and thermometer in place read the temperature (0.10C) for 3 minute at 1-minute intervals; then add the **NaOH** as quickly as possible. At the same time continue the temperature reading at 1minute interval for at least 9 minute total (at least three readings after the maximum temperature reading is attained). Because of the time required for solution and complete mixing, the proper estimate for complete solution at a time of mixing is more difficult make your best estimate based on extrapolations of temperatures before and after mixing as explained in the section on the determination of temperature. Calculate The heat of solution per moles of **NaOH(s)** to form a 1.0 M **NaOH** solution (note you have about 52g of solution. the specific heat of 1.0 M **NaOH** is 3.90j/g/deg).

**C The Enthalpy of Reaction of HCl(aq) and NaOH**

Carefully weigh about 2.0g of slightly less of **NaOH(s). Use a stopped Erlenmeyer flask** as in part B. Measure about 55.0ml of 1.0 M HCl (which provides a small excess of HCl to react with all the **NaOH** used) in a 100ml graduated cylinder, and dilute this to 100.0ml, as precisely as u can. Transfer this completely to your calorimeter and with lid and thermometer in place, take temperature reading once each minute for 3 minute. Then add **NaOH(s),** replace the lid and thermometer , gently swirl the mixture and stir it carefully with the thermometer to dissolve the **NaOH** as quickly as possible, and at the same time continue the temperature readings for 9 minute total 1-minute intervals (at least 3 reading after the maximum temperature).

**PRELAB EXERCISE**

1. What do you understand by Enthalpy, Entropy and Free Gibb’s energy?
2. State the relationship between free Gibb’s energy, Enthalpy and Entropy

**EXPERIMENT THREE**

**KINETIC STUDY OF THE REACTION BETWEEN IRON (III) AND IODIDE IONS**

**INTRODUCTION**

To write the rate expression for a reaction, we must determine, experimentally, how the rate is related to the concentration of each reactant. You can do this easily by varying the initial concentration of one reactant at a time while the concentrations of the other reactants are held constant, observing the effect of each such change on the rate. However, because the tare will probably change as the as the reactant under study is being used up, you will need to determine the concentrations of all the reactants at the time a rate measurement is made. An elegant solution to the problem is to limit each rate measurement to the initial1 percent or so of the reaction, so that the reactant concentrations do not have time to change appreciably during the monitoring period. Therefore you will need to know only the initial concentrations of the reactants in the mixture and not how they change with time. This procedure, called the **initial rate method,** will be used in this experiment.

**The Rate Law**

Consider the hypothetical reaction represented by Equation 3.1

2A + B A2B

The rate may be related to either the change in product concentration per unit time or the change in reactant concentration per unit time, according to equation 3.2.

rate = - 1 *d*[A] = *d*[B] = *d*[A2B]

2*dt dt dt*

The rate expression or rate law has the general form shown in Equation 3.3

rate = *k*[A]a[b]b

Where, *k* is the constant for the reaction, *a* and *b* represent the order of the reaction with respect to A and B. it should be emphasized that *a* and *b* are determined experimentally and are not deduced from the stoichiometry of the reaction. The order with respect to any reactant may be positive or negative, integral or fractional, or even zero.

**Reversible Reactions**

The top curve of figure 1 shows how a system initially containing the only A and B behaves. The rate of the forward reaction is large at the start but decreases, as predicted from equation 3, as the reactants are converted to A2B. if the reaction is reversible, as assumed in equation figure 1, the rate of the reverse reaction is zero at the start, when no A2B is present, but increases with time as A2B is formed by the forward reaction. Eventually, of course, the forward and reverse rates become equal, and the system is then at equilibrium.

We assumed in equation 1.3 that the rate of formation of product is related to the forward reaction rate, according to the expression shown in Equation 3.4

*d*[A2B] = rate(forward)

*dt*

However, if the reaction is reversible, the expression shown in Equation 1.5 applies. The addition of the rate(reverse) term greatly complicates the calculations, and we therefore try to work under conditions where the reverse rate can be set equal to zero. An obvious advantage of the initial rate method is that the reverse rate is negligible under these conditions and, therefore, the reverse reaction can be ignored.

*d*[A2B] = rate(forward) – rate(reverse)

*dt*

**The Iron (III) Ion-Iodide Ion System**

In this experiment, you will study the oxidation of I- by Fe3+ ions, as shown in Equation 3.6. Note that the triiodide ion, I­3- is simply an iodine molecule complexed with an iodide ion. This complexation greatly increases the solubility of the iodine species in water.

2Fe3+ + 3I- 2Fe2+ + I3-

The expected rate expression for the reaction of Fe3+ and I- is given in equation 3.7

rate = - 1 *d*[Fe3+] = *d*[I3-] = *k*[Fe3+]a[I3-]

2*dt dt*

Parts A and B of the experiment are concerned with evaluating the exponents a and b, respectively, in the rate expression. Part C is concerned with the effects of temperature and of other ions in the reaction rate.

You will determine the initial rate by measuring the time, in seconds, required for part (about 4 x 10-5 mole) of the Fe3+ to be reduced to Fe2+. You will know that this has occurred because of the presence of starch and a small, constant amount of S2O32- in each mixture. The thiosulphate will react with the triiodide ion produced in the reduction of Fe3+ ion as shown in equation 3.8.

I3 + 2 S2O32- 3I- + S2O62-

As soon as the S2O32- has been consumed, any additional I3- formed by the reaction between iron (III) and iodide ions will react with the starch to give a characteristic blue color. When the blue color first appears, the decrease in the concentration of Fe3+ from its initial value is just equal to the initial concentration of S2O32- in the mixture. Thus the initial rate of disappearance of iron (iii) ions, ½*d*[Fe3+]/*dt*, is equal to ½[S2O32-]/Δ*t*, where [S2O32-] is the initial concentration of S2O32- and Δ*t* is the time in seconds between mixing and the appearance of the blue colour. In order to obtain reasonable reaction times, you will need to use initial rate intervals that allow the Fe3+ concentration to decrease slightly (about 4 to 10 percent) from its initial value. To compensate for this change, the average Fe3+ concentration during this time interval should be used in place of the initial concentration when plotting your data.

In Part C, the effects of other ions and of temperature will be studied. Ions other than iron (iii) or iodide may affect the rate by varying the ionic strength, serving as catalysts, or serving as inhibitors. Changing the ionic strength affects the activity of the ions reacting and, therefore, changes the rate. This effect will not be studied. Catalysts provide a new and easier path for the reaction and thereby increase the rate. Inhibitors decrease the rate by lowering the concentration or the activities of some species, which is important in the reaction mechanism.

The effect of temperature on reaction rate is treated in your text theoretically. Therefore, we will deal with the subject only briefly here. The specific rate is constant, *k*, is related to the Kelvin temperature *T* by the expression shown in equation 3.9, where *Ea* the activation energy for the reaction. The activation energy represents the minimum energy required for the reactants to pass over an energy barrier to from products, as shown in figure 3.2. Because the reactant particles have a statistical distribution of energies, at a given temperature only a fraction of the particles will have sufficient energy to react upon colliding. If the absolute temperature is increased, however, the fraction of the particles having the energy needed to react upon colliding also increases, resulting in a greater rate or a larger value for the specific rate constant.

*k =* A*e-E­a/RT*

Energy to reach reactive state

Activation

energy

Energy of products

Energy of reactants

**Fig 1.2:** Schematic representation of the energy barrier for a chemical reaction.

If A is a constant in Equation 1.9, then expressions for *k* as a function of *T* may be derived (see Equations 3.10 and 3.11).

In *k* = - *Ea* + constant

*R*

Δln *k* = - *Ea* Δ (1/T)

*R*

A plot of ln *k* (or 2.303log *k*) versus 1/T should therefore be linear, with a slope equal to – *Ea /* *R.*

Many solutions must be used in preparing each reaction mixture to be studied. The thiosulfate solution is somewhat unstable and is best prepared on the day it is to be used. The rate of reaction is quite sensitive to changes of temperature. All of these factors can affect the accuracy of the results obtained in this experiment.

**PREPARATION AND STANDARDIZATION OF THE THIOSULFATE SOLUTION**

Weigh out 2.4 g of Na2S2O3.5H2O and dissolve it in approximately 2 L of distilled water. Mix well. Rinse a burette with two small volumes of distilled water, followed by two small volumes of your thiosulphate solution. Then fill the burette with the solution. Record the initial burette reading.

Record the molarity of the standard potassium iodate (KIO3) solution provided for your use. Rinse a pipet with two small volumes of distilled water, followed by two small volumes of standard KIO3 solution. Then use the pipet to deliver 1.00 mL of the standard iodate solution into a clean, 250 mL of distilled water and 20 mL of 0.04 M potassium iodide (KI) to the Erlenmeyer flask. Add 20 mL of distilled water and 20 mL of 0.04 M potassium iodide (KI) to the flask. Swirl the flash to mix the solution; continue swirling the flask while adding 2 mL of 0.5 M H2SO4. The mixture in the Erlenmeyer flask should take on the deep red-brown color characteristic of I3- ions.

Titrate the I3- ions with S2O32-, adding 1mL increments of thiosulfate initially, but reducing the incremental size as the colour of the titration mixture turns from brown to yellow. Then add 5 mL of 0.2% starch solution. Consult your instruction if the titration mixture does not develop a blue colour after starch has been added and the flask has been swirled. Use your wash bottle to rinse all splattered drops from the walls of the flask into the titration mixture. Resume the addition of thiosulphate, adding titrant by drops until the blue colour of the starch-iodine complex disappears completely. Usually, only a few additional drops are required. Record the final reading of the thiosulphate burette and calculate the molarity of your thiosulphate solution. Repeat the procedure. Report the molarity obtained in each trial and the average molarity.

Give the thiosulfate solution to that is setting up the solution stations. Report the concentration of the thiosulfate solution to the class. When the work stations and water baths are set up, individual students or pair of students should proceed to the determination of the orders of the reaction and the value of the activation energy.

**MAINTAINING CONSTANT TEMPERATURE**

It is inevitable that water that has been cooled below room temperature (by the addition of small amounts of ice that melt completely) will absorb heat from the air and begin to warm up. It is also inevitable that water that has been heated a bit above room temperature will begin to lose heat to the surroundings once heating has stopped. Heat transfer with the surroundings can be minimized by insulating the water baths. However, because the reaction rate is very temperature sensitive, use constant bath temperatures. Team members should be assigned to check the bath temperature regularly and should also be prepared to add ice or hot water to the baths as necessary.

**ASSEMBLING THE WORK STATIONS**

The number of work stations needed on the size of the class. There should at least one station for every six pairs of students. Refilling is easy if automatic burets are used. If these are not available, be sure there is a good supply of each reagent left at the station so that burets can be refilled as necessary. The starch solution should be dispensed from a graduated cylinder; all other solutions can be dispensed from burets. The solutions needed are identified in Table 1.1

**Table 1.1 Reaction Mixtures**

**Container 1 Container 2**

0.04 M 0.15 M 0.04 M 0.004 M

Trial# Starch H2­O Fe3+ HNO3 H2O KI S2O32-

mL mL mL mL mL mL mL

1 5.00 20.00 10.00 10.00 30.00 15.00 10.00

2 5.00 20.00 15.00 15.00 20.00 15.00 10.00

3 5.00 20.00 20.00 20.00 10.00 15.00 10.00 4 5.00 20.00 25.00 25.00 0.00 15.00 10.00

5 5.00 23.00 10.00 10.00 30.00 12.00 10.00 6 5.00 17.00 10.00 10.00 30.00 18.00 10.00

7 5.00 14.00 10.00 10.00 30.00 21.00 10.00

**OBTAINING DATA ON THE KINETICS OF THE REACTION**

**Part A. Reaction Order with Respect to Fe3+**

Prepare the mixture for Trial #1 by adding the solution specified in Table 1.1 to appropriate containers. Briefly swirl the contents of each container and place the containers in a constant temperature water bath set at room temperature. Allow a few minutes for the mixtures to reach temperature equilibrium. Meanwhile, prepare the solutions for Trial #2 in a second set of containers and place these also in the water bath. By the time you do that, the solution for Trial #1 should be at bath temperature.

Measure and record the temperature of the Trial #1 solutions. Then simultaneously start the timer and rapidly add the contents of container 1 to container 2. You may temporary remove the solutions from the water bath when you are doing this. Swirl the solutions until they are well mixed, then return container 2 to the bath. Stop the timer at the first appearance of the blue colour. Record the time, *t*, and the temperature (to within 0.1oC). Clean and dry the containers, place the solutions for Trial #3 in them, and return the containers to the water. Measure the temperature of the solutions for Trial #2, mix the solutions, and time the reaction as before. Continue in this manner through Trial #4.

**PART B. REACTION ORDER WITH RESPECT TO I-**

Repeat the procedures specified in Part A, but use the various reaction mixtures given in Table 1.1 for Trials #5, 6, and 7.

**PART C. EFFECT OF TEMPERATURE AND OF FE3+ IONS**

Perform Trials #8, 9, and 10 by preparing reaction mixtures as in Trial #1 and measuring the reaction times in water baths at various temperatures. Trial #8 should be performed at room temperature about 5oC below room temperature.

If time permits, prepare a solution of 0.002 M in Fe2+ by dissolving Fe(NH4)2(SO4)2 in 0.15 M HNO3. Perform Trials #11, 12, and 13 by repeating Trials #8, 9, and 10, substituting the Fe2+ for the HNO3 solution.

**CALCULATIONS**

Using the experimental reaction times and the known concentrations of the reagents, calculate the initial rate, ½[S2O32-]/Δ*t*, for each experiment.

Calculate the initial concentrations of Fe3+ and I- present in each experiment. Approximate [Fe3+]*av* for each experiment by using the specified multiplication factor for each experiment, the initial rate, log [Fe3+], and log(rate).

Using the data for Trials #1 through 4, plot log(rate) versus log [Fe3+]. Draw the best straight line through the experimental points, and calculate its slope. This is equal to *a*, the reaction order for Fe3+.

Using the data for Trials #1, 5, 6, and 7, plot log(rate) versus log[I-]. Draw the best straight line and calculate its slope. This is equal to *b,* the reaction I-.

Round off *a* and *b* to integers and write the resulting rate expression. Calculate the initial rates for Trials #9, 10, and 11. Substitute the measured rates, [Fe3+]av and [I-]I in the rate expression to obtain the specific rate constant, *k,* at each of the three temperatures. Prepare a table showing *k,* In*k, T* and 1/*T*. Plot In*k* versus 1/*T*. Measure the slope and from it calculate the activation energy, *Ea*.

Repeat the process for Trials #11, 12, and 13. Comment briefly on the effect of added Fe2+ on the reaction rate and on the value of the activation energy.

**DISPOSAL OF REAGENTS**

The acidic solutions (HNO3 and Fe(NO3)3) should be neutralized with dilute NaOH solution. The neutralized chemicals may be diluted and poured down the drain. All other solutions may also be diluted and poured down the drain.

**QUESTIONS**

1. For reactions in aqueous solution, would it be easy or difficult to determine the order with respect to H2O? Explain.
2. Why is it necessary to convert [Fe3+]I to [Fe3+]*av*? Why is it unnecessary to convert [I-]*I* to [I-]*av*?
3. What is the effect of a catalyst on the value of the reaction’s activation energy?

**PRE-LAB EXERCISES FOR EXPERIMENT**

These exercises are to be performed after you have read the experiment but before you come to the laboratory to perform it.

1. The reaction between bromide ions occurs according to the equation shown below.

BrO3- *(aq)*  + 5Br- *(aq)* + 6H+ *(aq)* 3Br2*(l)* + 3H2O*(l)*

The following table shows the results of four experiments done on this system. Use these data to determine the order of the reaction with respect to each reactant, the overall order of reaction, and the value of the rate reaction.

**Measured initial rate**

**Trial # [BrO3‑]*I* [Br-]*I* [H+]*I* - Δ[BrO3-]/ Δ*t*, (mol/L.s)**

1 0.10 0.10 0.10 7.9 x 10-4

2 0.20 0.10 0.10 1.7 x 10-3

3 0.30 0.20 0.10 3.1 x 10-3

4 0.10 0.10 0.20 3.2 x 10-3

1. Methane gas reacts with diatomic sulfur in the gas phase producing carbon disulphide and hydrogen sulfide. The rate constant for this reaction is 1.1 L/mol.s at 550oC. It is 6.4 L/mol.s at 625oC. Use these data to determine the value of the activation energy for the reaction. When *k* is measured at only two temperatures, Equation 1.11 may be written as shown below.

In *k2* - In *k1* = - *Ea* 1 1

*R T2 T1*

**EXPERIMENT FOUR**

**THE SYNTHESIS OF COBALT OXALATE HYDRATE**

Compounds that contain water may have it present either in a variable or in a definite mass percentage. If the water content is variable, the substance may be merely wet; or the water may occupy channels, as in a Zeolite; or a mixture of hydrates may be present. If the substance has definite, nonvariable water content, it is called a hydrate, and the water molecules are found to occupy definite sites in the crystal. A few common hydrates and their formulas are borax (Na2B4O7. 10H2O), plaster of Paris (CaSO4.1/2 H2O), Epsom salt (MgSO4.7H2O) and blue copper sulphate pentahydrate(CuSO4.5H2O).

Under appropriate conditions, most hydrated salts can be dehydrated to form either a lower hydrate or the anhydrous salt. For example, when the mineral gypsum is heated no hotter than about 1600C, it dehydrates to form plaster of Paris as shown below

CaSO4.2H2O↔ CaSO4.1/2H2O + 3/2H2O

This reaction is reversible and the setting of plaster of Paris may be attributed to its rehydration to form crystalline gypsum. The equilibrium between the hydrated and the anhydrous forms of the salt is influenced both by the temperature of the system and by the relative humidity. Salts that can be reversibly hydrated are frequently used to control the amount of the moisture in the air. Anhydrous salts that are commonly used as desiccants (drying agents) include CaSO4, CaCl2, and Mg(ClO4)2.

**CALCULATION OF PERCENTAGE YIELD**

If stoichiometric quantities of chemicals are mixed together when a compound is being synthesized, then all reactants will be used up at the same time. No excess unreacted starting material will remain at the completion of the reaction. On the other, if the reactants are mixed in a nonstoichiometric ratio, then one reactant will be used up before the others. Because no more product can be formed when the supply of one of the reactants has been exhausted, the first reactant to be consumed limits the amount of product that can be formed and is designated as the ***limiting reactant or limiting reagent*.**

The amount of product formed when the limiting reagent has been completely consumed is called the ***theoretical yield of the reaction*.** In practice, the actual yield of the product is frequently lower than this theoretical maximum (because side reactions occur, or product is lost in collection or because the product is unstable). The percent yield of the reaction is a measure of the success of the reaction. It is defined below

**Percent yield= actual yield/theoretical yield × 100**

**EXPERIMENTAL**

(A) Place 100ml of distilled water in a 250ml beaker. Add 1.26g of oxalic acid dihydrate (H2C2O4.2H2O) and 1ml of concentrated ammonia. Stir the mixture until the solid has dissolved completely.

Dissolve 2.34g of Cobalt Chloride hexahydrate (CoCl2.6H2O) in 100ml of water in conical flask. While stirring the oxalic acid solution constantly, add the cobalt chloride solution drop by drop. Let the mixture cool in an ice bath. A precipitate will form slowly.

After the precipitate has had a chance to settle, collect it by gravity filtration. Wash the collected solid sparingly with cold water. Allow the water to drain from the collected solid. Then transfer the filter paper and precipitate to a paper towel so that excess moisture can be absorbed. Before you leave the lab, place your precipitate (still in its filter paper cone) in a beaker and leave it in your desk to air dry for at least three days.

After your precipitate has dried thoroughly, weigh it on the analytical balance. Report your yield of product.

**PRE-LAB EXERCISES**

1).The equation below refers to the reaction of ammonium chloride and barium hydroxide octahydrate.

2NH4Cl (s) + Ba(OH)2.8H2O (s) → 2NH3 (g) + BaCl2 (aq) + 10H2O (l)

In a particular experiment, 150g of ammonium chloride were reacted with 290g of barium hydroxide octahydrate, producing 157.2g of water.

1. Find the limiting reagent in this situation
2. Calculate the theoretical yield of water
3. Calculate the percent yield of water

What mass of anhydrous barium hydroxide contains the same number of moles of Ba2+ ions as 31.5g of Barium hydroxide octahydrate?

**EXPERIMENT FIVE**

**DETERMINATION OF PERCENTAGE METAL IN COORDINATION COMPOUNDS**

**PREPARATION OF REAGENTS.**

**Preparation of standard solution of 0.01M zinc sulphate heptahydrate (ZnSO4.7H20).**

0.72g of Zinc sulphate heptahydrate was weighed and dissolved in distilled water in a 250ml standard flask. The flask was then thoroughly shaken to allow complete dissolution. The solution was made up to the mark with distilled water.

**Preparation of 0.01M EDTA solution.**

The dissolution of EDTA was dried in an oven at 80°C for 3hours. 3.78g of EDTA was weighed and transferred into a one litre standard flask with a short neck funnel at its mouth. The EDTA was washed into the flask with distilled water. This solution was made up to the mark with distilled water.

**Standardization of the solution.**

20ml of 0.01M ZnSO4 Analar solution was pipetted into a conical flask and few drops of Erichrome black T indicator was added to it to give a purple color. 2ml of ammonia/ammonium chloride buffer was also added and then this was titrated against the EDTA solution. The color change was from purple to blue.

Volume of ZnSO4.7H2O solution (0.01M) used= 25.00ml

EDTA4-(aq)+Zn2+(aq) →[Zn(EDTA)]2-

Mole ratio: 1 : 1

Table of readings

|  |  |  |  |
| --- | --- | --- | --- |
| Burette reading | 1st(ml) | 2nd(ml) | 3rd(ml) |
| Final reading |  |  |  |
| Initial reading |  |  |  |
| Volume of EDTA used |  |  |  |

Average volume of EDTA used=

Molarity of the ZnSO4.7H2O solution= 0.01M

MZnSO4×V znso4 = mole ratio

MEDTA × VEDTA

MEDTA = MZnso4 × Vznso4  × 1 =

VEDTA  × 1

MEDTA =

The molarity of the EDTA =

**Preparation of Erichrome Black T indicator.**

0.2g of Eriochrome Black T was dissolved in 15ml of Triethanolamine and 5ml of absolute ethanol was added to aid free flow.

**Preparation of 1:1 Nitric / Perchloric acid.**

20ml of 0.1M Nitric acid was added to 20ml of 0.1ml perchloric acid drop wisely and mixed thoroughly. The vessel should be placed in ice cold water to cool the reaction vessel and prevent splashing of the acids on the skin.

**Preparation of Ammonia/ammonium chloride buffer solution**

142ml of ammonium hydroxide was added to 17.5g of ammonium chloride in a 250ml standard flask. The solution was made up to the mark with distilled water.

**Preparation of Murexide indicator.**

50g of sodium chloride was added to 0.1g of Murexide in a brown bottle. The mixture was then agitated thoroughly.

**METAL ANALYSIS OF THE COMPLEX.**

The percentage composition of the metal constituents of the complex was determined by complexometric titration using EDTA. This was done by making standard solutions of known amount of the complex and then titrating them against a standardized EDTA solution.

**Digestion of the Cobalt complex.**

A known amount (about 0.02- 0.08g) of each of the Cobalt complex was weighed accurately into a pyrex beaker and a few drops of 1:1 Nitric/perchloric acid mixture was added to it. It was then placed on a hot plate till it was dry. A few drops of distilled water was added and allowed to dry. About 5ml of distilled water was added to dissolve it and then made up to the mark in a 100ml standard flask with distilled water.

**Titration of the digested Cobalt complex solutions.**

The standard solution of the digested compound was titrated against standardized EDTA.

**Determination of the percentage Cobalt in Cobalt Oxalate complex**

Direct EDTA titration was used in the estimation of the Cobalt content in Cobalt Oxalate complex. 20ml of the digested Cobalt complex solution was pipetted into a 100ml conical flask. Few drops of Ammonia/ ammonium chloride buffer (pH=10) changed the color to blue and on addition of a few grams of Murexide indicator , it gave a yellow color which on titration with EDTA gave an end point color change of violet . The calculation of the percentage metal in Cobalt Oxalate complex should follow this table:

**Table of readings**

|  |  |  |  |
| --- | --- | --- | --- |
| **Burette reading** | **1st(ml)** | **2nd(ml)** | **3rd(ml)** |
| **Final reading** |  |  |  |
| **Initial reading** |  |  |  |
| **Volume of EDTA used** |  |  |  |

Volume of Co2+ solution used = 20ml

Average volume of EDTA used =

Equation for the reaction

Co2+  + EDTA4- → [Co (EDTA)] 2-

1 mole of EDTA4- = 1mole of Co2+

Number of moles of EDTA = MEDTA× VEDTA

1000

Number of moles of Co2+ =

Weight of Co2+ in 100ml solution = Number of moles of Co2+× molar mass of Co × 100

20

Weight of Cu2+ in solution =

% Co = weight of Co2+ in solution × 100

Weight of the Cobalt Oxalate

This procedure of metal analysis was used in calculating the percentage metal for the complex. The value obtained were then compared with the calculated percentage metal in 1:1, 1:2, 1:3 and 1:4 metals to ligand complexes.

**PRE-LAB EXERCISE**

1) What are coordination compounds and ligands?

2) Briefly explain the concept of Chelating agent and give examples.

3) Write **five (5)** coordination compounds and give their coordination numbers.

4) Show the structure of the coordination compounds above and their binding sites.

**EXPERIMENT SIX**

**pH TITRATION**

**WEAK ACIDS**

A weak acid differs from a strong acid in being only partially ionized in aqueous solution. In such solutions, a dynamic equilibrium exists between the molecular and ionized forms of the acid as shown below

HA + H2O ↔ H3O+ + A-

The equilibrium expression for this reaction is shown in the equation below, where ka is the acid dissociation constant for the weak acid

Ka = [H3O][A-]/[HA]

When the weak acid, HA, is titrated with sodium hydroxide, the concentration of HA progressively decreases, whereas the concentration of A- progressively increases, because the acid reacts with the base to form the strong electrolyte NaA

HA(aq) + Na+(aq)+OH+(aq) → H2O + Na+(aq) +A-(aq)

In order for the titration to be successful, the reaction shown below must go to completion. This condition will be met if the acid’s ka value is several orders of magnitude larger than kw, the ion product for water

Kw = [H3O+][OH-]

To see how the values of ka and kw are involved in determining whether the titration reaction will go to completion, begin by assuming the reaction shown above results in an equilibrium situation

HA + OH-↔ H2O + A-

Next, set up an equilibrium corresponding to the above equation. Then multiply both the numerator and denominator by [H3O+]

K= [A-]/[HA][OH-] × [H3O+]/[H3O+] =ka/kw

The value of kw is 1.0×10-14 at 250C. For a typical weak acid (ka= 1×10-5)., k for the titration reaction will have a value on the order of 109, certainly high enough to ensure that the reaction does indeed go to completion.

**PROCEDURE**

**Option A**

Prepare your pH meter for use. Connect the electrodes according to the instructions and leave them suspended with their tips immersed in water. Connect the line cord and turn on the instrument to allow a brief warm-up period.

Place approximately 100mL of your cola drink in a conical flask. Mark the liquid level with a label and cover the mouth of the flask with a watch glass. Simmer the sample for 20minutes to expel the carbon dioxide from the sample. After you have stopped heating and the sample has cooled down to room temperature, add distilled water, if necessary, to restore the liquid level to its preheating height.

Rinse a burette once with distilled water and three times with small amounts of a solution of 0.01 M NaOH. Then fill the burette with NaOH and mount it in the burette clamp. Standardise the NaOH solution by titrating it against accurately weighed 0.06g samples of KHP. Record the standardizations data on a Report sheet. Refill the burette as necessary for the standardizations and the titration of the cola sample.

Rinse a 10mL pipette once with distilled water and three times with small amounts of the decarbonated cola drink. Use the pipette twice to transfer 20mL of the decarbonated cola drink into a 50mL beaker. Save the remainder of your decarbonated cola sample for analysis.

Calibrate the pH meter using pH 7.0 buffer. Place a stirring bar in your cola sample. Place the flask containing the sample on a magnetic stirrer. Immerse the tips of the electrodes in the decarbonated cola. Adjust the speed of the stirrer so that good mixing is achieved without endangering the electrode tips by a flying stirring bar. Read and record the initial pH and burette readings after each addition of base. As each equivalence point is approached, decrease the size of the base increments until, finally, single drops are being added. Continue the titration until well past the second equivalence point.

**Analysis of Data**

Prepare a plot of pH versus volume of base added. Use your plot to locate the first equivalence. Determine the concentration of Phosphoric acid in the drink, using the assumption that the only reaction that has occurred is

H3PO4  + OH- → H2O + H2PO4-

Find the pH at the halfway point for the first portion of the curve to find a value of Ka1 for Phosphoric acid. Compare this value with the literature value.

Now calculate an independent value of Ka1 by combining the initial pH of the drink with the concentration of Phosphoric acid. Compare this value of Ka1 with the literature value. Find the percent ionization of the phosphoric acid in the drink prior to the addition of the base.

Evaluate Ka2 by finding the pH halfway between the first and second equivalence points. Compare this value with the literature value. Calculate the initial percent ionization of H2PO4- in your sample.

Calculate an independent value for the concentration of Phosphoric acid in the drink, based on the assumption that the only reaction that took place between the first and second equivalence point is H2PO4- + OH- → H2O + HPO42-.

**Option B**

Prepare your pH meter for use as you did in experiment 22. Connect the electrodes according to the instructions and leave them suspended with their tips immersed in water. Connect the line cord and turn on the instrument to allow a brief warm up period.

Calculate and weigh the mass of citric acid required to prepare 100.00mL of a 0.10M solution. Dissolve the solid in approximately 50mL of water. Transfer this solution to a 100mL volumetric flask. Rinse the beakers used for and add these risings to the volumetric flask; cap the flask and invert it several times to ensure adequate mixing of the citric acid solution.

Rinse a burette once with distilled water and three times with small amounts of a solution of 0.1 M NaOH. Then fill the burette with NaOH and mount it in the burette clamp. Standardize the NaOH solution by titrating it against accurately weighed 0.6g samples of KHP (see Experiment 8 for details on performing standardizations of base via titration of KHP). Record the standardizations and titration of the citric acid solution.

Rinse a 10-mL pipet once with distilled water and three times with small amounts of citric acid solution. Use the pipette twice to transfer 20.00mL of the citric acid solution into a 100-mL beaker.

Calibrate, the pH meter using the pH 7.0 buffer. (Increased accuracy is possible if a pH of 4.0 buffer is used as well to confirm the linearity of the pH measurements)

Place a stirring bar in your citric acid solution. Place the flask containing the sample on a magnetic stirrer. Immerse the tips of the electrodes in the citric acid solution. Adjust the speed of the stirrer so that good mixing is achieved without endangering the electrode tips by a flying stirring bar. Read and record the initial pH. Begin the titration by adding 1-t0-2-mL increments of the standardized NaOH. Record the pH and burette readings after each addition of base. As each equivalence point is approached, decrease the size of the base increments until the volume of NaOH added is at least four times the volume of citric acid solution being titrated.

**Analysis of Data**

Prepare a plot of pH versus volume of base added. Compare this plot to the one in Figure 23.2 and discuss possible reasons for the differences in their appearance. Use your plot to locate the first equivalent point. Determine the number of moles of sodium hydroxide needed to reach this point in the titration; compare it to the number of moles of citric acid titrated. Find the pH at the halfway point in the titration and use it to approximate an average *Ka* for citric acid.

**Questions (Option A)**

1. Makers of a popular carbonated beverage claim that none of their colas contain more than 30mg of Phosphorus per 6-oz. serving. How does this figure compare with your calculation of the percent of Phosphoric acid in the drink you analyses?
2. What is the equivalent mass of Phosphoric acid (i.e., the mass, in grams, of Phosphoric acid that reacts with one mole of hydroxide ions)?
3. Can equation 23.7 be used to evaluate K*a1* for phosphorus acid? Explain your answer briefly.

**Option B**

1. Which acid would have titration curves more similar to that of arsenic acid than to that of citric acid?

Oxalic acid K*a1* = 5.9 x 10-2

K*a2* = 6.4 x 10-5

Succinic acid K*a1* = 6.9 x 10-5

K*a2* = 2.6 x 10-6

1. Describe a method for determining the molar mass of an unknown acid by pH titration. What complication might arise if the acid had values of K*a1* that fell within a narrow range?

**EXPERIMENT SEVEN**

**ELECTROCHEMICAL CELLS**

An electrochemical cell is constructed from two half-cells. One half cell contains both the oxidised and the reduced form of the oxidising agent. The other half-cell contain the corresponding forms of the reducing agent .the half-cell are connected by the means of a salt bridge through which ions can migrate. A wire completes the external circuit through which electron transfer takes place.

If a copper strip is placed in a solution of copper ions, one of the following reactions may

occur:

Cu2+ + 2*e*- → Cu

Cu → Cu2+ + 2*e*-

The electrical potential that would be developed by these reactions prevents their continuation. These reactions are called half-reactions or half-cell reactions. There is no direct way to measure the electrical potential (electromotive force, emf) of a half-cell reaction. Similarly, a zinc strip in a solution of zinc ions has the possible reactions:

Zn2+ + 2*e*- → Zn

Zn → Zn2+ + 2*e*-

But these are also prevented from occurring by the electrical potential that would build up. If the metal electrodes (copper and zinc) in the two solutions are connected by a wire, and if the solutions are electrically connected by perhaps a porous membrane or a bridge that minimizes mixing of the solutions, a flow of electrons will move from one electrode, where the reaction is MI → MIn+ + n*e*-, to the other electrode, where the reaction is M2n+ + n*e*- → 2M.

In this case, the zinc metal goes into solution as zinc ions, and the copper ions plate out.

The overall cell reaction is: Zn + Cu2+ → Zn2+ + Cu

The electromotive force for such a cell, which is written as Zn⎪Zn2+⎪⎪Cu2+⎪Cu, can be measured.

By convention, all half-cell e.m.fs are compared to the e.m.f of the standard hydrogen electrode. The standard hydrogen electrode is defined as a platinum electrode covered with platinum black that is in contact with hydrogen gas at 1 atmosphere pressure and a 1 molar solution of hydronium ions (actually, it is defined for unit activity). The hydrogen electrode half-cell reaction is 2H+ + 2*e*- → H2

The e.m.f of a half-cell, with respect to the standard hydrogen electrode, is called the ***reduction potential.***Standard oxidation potentials, ***E***o, are for 1-molar solutions.

Consequently, the difference between the oxidation potentials of two half-cells is the e.m.f.

They would develop if connected together as a cell. The e.m.f for the Zn-Cu cell described

would be ***E*** = ***E***o red(Zn) – ***E***o red(Cu) = 0.77 - (-0.34) = 1.10 V if the solutions are 1.0 M.

If a cell reaction can be written as *a*A + *b*B → *cC + d*D then the e.m.f of the cell can be expressed in the form of the following equation, developed by Nernst:

***E*** = ***E***o - (RT/*n***F**) ln ([C]*c* [D]*d* / [A]*a* [B]*b*)

If all the concentrations are 1 M, then the natural logarithmic term becomes zero and ***E*** =

***E***o, which is the reason for choosing 1-Molar concentration as the standard condition. If the system is at equilibrium, then

[C]*c*[D]*d*

[A]*a*[B]*b*

and the e.m.f developed by such a cell at equilibrium must be zero. Therefore,

0 = ***E***o *-* (RT*/n***F**) ln **K**c -OR- ln **K**c = *n***F*E***o/RT

In these equations, **F** is Faraday’s Constant (96,485 C/mol e-), *n* is the number of

electrons transferred in the oxidation-reduction step, and R is the gas constant in units of

electrical work (8.314 J/K mol).

To measure the emf of a galvanic cell, a sensitive meter is needed, but it is important that

the meter not draw a significant amount of current. If the current produced by the cell to

be measured is large, the cell will become polarized, and the emf will be decreased.

Many solid state voltmeters have sufficiently high impedance that they can be used to

measure the emf of a cell accurately.

**PROCEDURE**

The Daniell Cell

Place 1.0 M ZnSO4 solution in a 25-ml beaker and 1.0 M CuSO4 solution in another beaker of the same size. The liquid levels should be the same. In the zinc solution, place a clean strip of zinc, and in the copper solution, a clean strip of copper. The zinc strip may be cleaned by dipping it in a beaker of about 2 M HCl. The copper strip can be cleaned by dipping it in a beaker of 2 M HNO3. Rinse the electrodes with deionized water thoroughly before using them.

** Figure One**

Obtain a multimeter along with one red and one black wire. Set up the meter to measure 2V DC Voltage. Attach the red wire to the V port and the black wire to the COM port. Note the sign of the voltage; it must be positive (+) or reverse which electrode the red and black probes are touching. When ***E***o cell is positive, the black electrode is the anode. The cells are connected with a cotton length soaked in 0.5 M potassium chloride (see Figure One above). Electrons will flow from the zinc electrode to the copper electrode because of the reactions occurring in the half-cells:

Zn → Zn2+ + 2*e*-

Cu2+ + 2*e*- → Cu

The overall reaction for the cell is:

Cu2+ + Zn → Cu + Zn2+

Measure the voltage of this cell. Also, measure the voltage of a Daniell cell with

1. 0.10 M ZnSO4 and 1.0 M CuSO4,
2. 1.0 M ZnSO4 and 0.10 M CuSO4.

**RESULTS**

Provide a summary of results pertaining to each of the following. How closely doyour experimental results compare with theoretical calculated results? Brieflycomment.

***E***o for: Zn ⎪ 1.0 M Zn+2 ⎪⎪ 1.0 M Cu+2 ⎪ Cu

Theoretical:\_\_\_\_\_\_\_\_\_\_ V Experimental: \_\_\_\_\_\_\_\_\_ V

***Ecell*** for: Zn ⎪ 0.10 M Zn+2 ⎪⎪ 1.0 M Cu+2 ⎪ Cu

Theoretical:\_\_\_\_\_\_\_\_\_\_ V Experimental: \_\_\_\_\_\_\_\_\_ V

***Ecell*** for: Zn ⎪ 1.0 M Zn+2 ⎪⎪ 0.10 M Cu+2 ⎪ Cu

Theoretical:\_\_\_\_\_\_\_\_\_\_ V Experimental: \_\_\_\_\_\_\_\_\_

**Discussion Questions:**

1. Describe and sketch the reactions taking place at the electrodes as well as any other processes occurring in the Daniell cell (from Part 1) while it is operating. Note that the electrode reactions produce and consume ions at the electrodes.
2. How should the voltage change in the Daniell cell if the zinc solution is made more dilute (and the concentration of the copper solution is kept the same)?

**Pre lab questions**

1. The following data were measured using a nickel electrode as the standard:

Cu2+(aq) + 2*e*- → Cu(s) 0.62 V

Ni2+(aq) + 2*e*- → Ni(s) 0.00 V

Fe2+(aq) + 2*e*- → Fe(s) -0.15 V

Al3+(aq) + 3*e*- → Al(s) -1.38 V

A. Which ion is most easily reduced?

B. Which metal is most easily oxidized?

C. The copper and aluminum electrodes are connected in a battery.

2) Which is the anode? cathode?

3) Which is oxidized? reduced?

4) What will the battery voltage be?

5) Write a balanced net ionic equation for the reaction that takes place.

6) Define Oxidation and Reduction in terms of Electron gain and loss.

**EXPERIMENT EIGHT**

**QUALITATIVE INORGANIC ANALYSIS**

Simple qualitative analysis involves the identification of the constituents of an inorganic substance or a mixture of substances. The inorganic substances are split-up into two types of charged particles one of which is positively charged and the other is negatively charged. The charged particles are called ions or radicals. The positively charged ions are called cation or basic radical. The negatively charged ion is called anion or acid radical.

In the qualitative analysis of an inorganic substance numbers of tests are carried out in order to discover the acidic and basic radical present in it. A test is an experiment along with an observation made to show the presence or absence of a certain substance or class of substances. In the test we note the formation or disappearance of (I) a colour or (ii) a precipitate or (iii) a gas (iv) an odour

The test may be positive or negative. A positive test is one that gives the result indicated in the procedure and shows the presence of the particular radical .A negative test is one which does not give the indicated results and shows the absence of the particular radical. The substances or solutions added to bring about the reactions are called reagents.

**SYSTEMATIC ANALYSIS OFTHE GIVEN INORGANIC SIMPLE SALT**

**PRELIMINARY DRY REACTIONS**

1. **PHYSICAL APPEARANCE**

Examine if the substance is crystalline or amorphous, whether it has a characteristics colour or odour, **but do not taste.** Amorphous substance may be carbonate. A coloured substance indicates the presence of transition element. Cu (ll) salts (hydrated) are blue; CuCl2, Ni and Fe (ll) salt are green; colbalt salts are pink while Fe (lll) and PbO compounds are yellow in colour. If the subatance is colourless or white, transition metal ions are, therefore absent.However if the substance is black a sulphide or an oxide is suspected e.g PbS, NiS, MnO2 and CuO.

1. **FLAME TEST**

The paste of the given salt with Conc. HC l is introduced into the non-luminous part of the flame using a platinum wire cleaned repeatedly with hydrochloric acid to remove traces of previous analytes and the colour is noted. Observe as below

|  |  |
| --- | --- |
| Observation | Inference |
| Golden yellow | Na ion present |
| Brick red | Ca ion present |
| Lilac (violet) | K ion present |
| Bluish green | Cu ion present |
| Pale blue | Pb ion present |
| Pale green | Ba ion present |
| Brilliant white | Mg ion present |
| Gold | Fe ion present |

1. **ACTION OF HEAT**

Add a little of the substance into a clean dry test-tube. Heat gently at first, then strongly. Note the evolution of gas, colour changes and the residue.

1. If the gas is colourless , odourless, neutral to litmus and rekindles glowing splint; it is oxygen from NO3 or MnO4 of alkali metals.
2. If the gas is colourless, odourless fume condenses on the upper and cooler path of the test tube; it is water vapour from hydrated salts.
3. If the gas is colourles and odourless, turns damp blue litmus paper red and turns lime-water milky; it is CO2 from carbonates or hydrogen carbonates.
4. If the gas is colourless with irritating smell, acidic to litmus and decolourizes KMnO4 on a strip of filter paper, it is SO2 from NH4 salt.
5. If a colourless gas with choking smell that turns damp red litmus paper blue or a white sublimate is observed; it is NH3 from NH4 salt.
6. If the substance changes from blue to while after heating, it is CuSO4.5H2O, from blue to brown; it is CuCl2.2H2O and if from yellow to black it is FeCl3.
7. If the residue is yellow when hot but white when cold, the residue is ZnO
8. If the residue is red when hot and yellow when cold, the residue is PbO.

**ACTION OF DILUTE (2M) HYDROCHLORIC ACID SOLUTION**

Put a small quantity of the substance in a test tube and add several drops of bench hydrochloric acid solution. If there is no reaction in the cold, then warm gently and observe evolution of any gas.

1. If there is vigorous effervescence and the gas given off is colourless, odourless, turn damp blue litmus paper red and turns lime water milky, it is CO2 from a CO3 or HCO3
2. If there is effervescence and the gas given off is colourless smells like burning sulphur or irritating, acidic to litmus and decolourizes KMnO4 on a strip of filter paper, it is SO2 from S2O3 or SO3
3. If there is effervescence and the gas evolved is acidic to litmus, smells like a rotten egg and turns Lead (II) ethanoate paper black, it is H2S from S-2
4. If the gas evolved is reddish- brown, with irritating smell, turns starch-iodide paper blue-black and turns damp blue litmus paper red; it is NO2 from NO3-
5. If there is no visible reaction or no gas evolved even on warming; Cl-, Br-, I-, or SO4-2 is suspected

**ACTION OF CONCENTRATED TETRAOXOSULPHATE (VI) ACID**

Put a small quantity of the substance in a test tube; add a few drops of concentrated H2SO4.Observe any reaction, then warm carefully but do not heat strongly. Note that the reaction ofCO3, HCO3, S2O3 with dilute HCl are less vigorous but more vigorous with concentrated H2SO4.In addition, the following observations can be made:

1. If the gas evolved is colourless with irritating smell, acidic to litmus and produces dense fumes with NH3 solution on a strip of filter paper, it is HCl from Cl-
2. If the gas evolved is reddish-brown with irritating smell acidic to litmus and turns CCl4 solution on a strip of filter paper brown. It is Br2 and HBr from Br-
3. If the gas is violet or purple, turns damp blue litmus paper red and forms a blue- black colour with starch paper, it is HI and I2 from I- .

**CONFIRMATORY TESTS FOR CATIONS**

Prepare a solution of the substance for qualitative analysis by using the following solvents in the order given below:

1. Cold water, then warm:
2. Cold dilute HCl, then warm:
3. Cold conc. HCl, then warm:
4. Cold dilute HNO3, then warm and
5. Cold conc. HNO3, then warm.

Always try the cold solvent first, and then warm if necessary. Always remember the solubility of common substances in water.

1. **Action of Dilute Sodium Hydroxide Solution**.

To 1cm3 of the solution of the substance, add sodium hydroxide solution in drops. If a precipitate is formed, add excess of the NaOH solution as follows:

1. If there is a white gelatinous precipitate in drops which is soluble in excess NaOH solution: Zn2+, Pb2+ or Al3+ is present.
2. If there is a dirty white precipitate which is insoluble in excess NaOH solution, Ca2+ is present.
3. If there is a pale blue precipitate, insoluble in excess NaOH solution, Cu2+ is present.
4. If there is a dark green precipitate which is insoluble in excess NaOH solution, and the precipitate turn brown on standing, Fe2+ is present which is oxidized to Fe3+ (brown) on exposure to air.
5. If there is a reddish brown precipitate which is insoluble in excess NaOH solution, Fe3+ is present.
6. If there is a brown or black precipitate which is insoluble in excess NaOH solution, Ag2+ is present.
7. If there is no precipitate or visible reaction, but on warming, a gas with choking smell which turns red litmus paper blue is given off, it is NH3 from an NH4+ salt.
8. **Action of Ammonia Solution**

To 1cm3 of the substance, add ammonia solution in drops. If precipitate is formed, add the ammonia solution in excess and observe as follows:

1. If there is white gelatinous precipitate which is soluble in excess ammonia solution, Zn2+ is present.
2. If there is white gelatinous precipitate which is insoluble in excess ammonia, Pb2+ or Al3+ is present.
3. If there is pale blue precipitate which is soluble in excess NH3 solution to give a deep blue solution, Cu2+ is present.
4. If there is a dirty green precipitate which is insoluble in excess NH3 solution, Fe2+ is present.
5. If there is reddish brown precipitate which is insoluble in excess NH3 solution, Fe3+ is present
6. If there is no visible reaction; Ca2+, Ba2+, NH4+, Na+ or K+ is present.
7. **Additional Confirmatory Tests for Cations**
8. **NH4+**

To small amount of the substance (solid or solution) in a test tube, add a few drops of dilute NaOH solution and warm. A colourless gas with choking and irritating smell which turns damp red litmus paper blue, NH3 is given off.

1. **Ca2+**

TO 1cm3 of the solution, add dilute H2SO4 solution. A milky or white solution which later gives a white precipitate is obtained. The precipitate is CaSO4.

1. **Al3+**

To the solution of the substance, add a few drops of ammonia solution, then add NH4Cl solution. A white precipitate is formed.

1. **Cu2+**

To the solution of the substance, add excess of the NH3 solution. A deep blue solution is obtained.

1. **Fe2+**

To the solution of the substance, add a few drops of concentrated HNO3 and boil for a while. The solution turns brown due to the oxidation of Iron (ii) to Iron (iii).

1. **Fe3+**

To the solution of the substance, add potassium hexacyanoferrate (iii), K4Fe(CN)6 solution. A white solution is obtained.

1. **Zn2+**

To the solution of the substance, add potassium hexacyanoferrate (iii), K4Fe(CN)6, a white solution is obtained.

1. **Pb2+**

To the solution of substance, add a few drops of dilute HCl solution. A white precipitate is formed which is soluble in hot water but reappears on cooling the solution.

1. **Ag2+**

To the solution of the substance, add dilute HCl solution. A white precipitate is formed and i soluble in NH­3 solution.

**(C) Confirmatory test for Anions**

**1. Halides**

Put 1cm3 of the solution into a test tube. Add 1cm3 of dilute HNO3 solution and then add AgNO3­ solution in drops until in excess. Observe as follows, on addition of excess NH3 solution to any precipitate formed:

1. If a heavy white precipitate is formed and is soluble in excess NH3 solution, Cl- is confirmed.
2. If a creamy, white precipitate is obtained and is slightly soluble in excess NH3 solution, Br -is confirmed.
3. If a pale yellow precipitate is obtained and is insoluble in excess NH3 solution, I- is confirmed.

**2. Trioxocarbonates (IV)**

To 1cm3 of the solution of the substance; add either BaCl2 solution or MgSO4 solution. A white precipitate, soluble in dilute HCl confirms CO32-.

**3. Hydrogen Trioxocarbonates (IV)**

To 1cm3 of the solution, add either BaCl2 or MgSO4 solution. If there is no reaction but on boiling the solution, a white precipitate is formed, the presence of HCO3 is confirmed.

**4. Tetraoxosulphates (VI)**

Put 1cm3 of the solution into a test tube, add 1cm3 of dilute HCl and then add BaCl2 solution. A white precipitate which is insoluble in dilute HCl confirms SO42-.

**5. Trioxosulphates (IV)**

Put 1cm3 of the solution into a test tube, add BaCl2 solution. A white precipitate which is soluble in dilute HCl confirms SO32-

**6. Sulphides**

To 1cm3 of the solution in a test tube, add Pb (CH3COO)2 or Pb (NO3)2 solution. A black precipitate confirms S2-.

**7. Trioxonitrates (V)**

To 1cm3 of the solution, add freshly prepared FeSO4 solution. Tilt the test tube to one side and add a few drops of conc. H2SO4 along the side of the test tube. A brown ring is formed at the junction of the acid and the solution confirming the presence of NO3-.

**8. Dioxonitrates (V)**

To 1cm3 of the solution, add freshly prepared FeSO4 solution followed by 2 or 3 drops of CH3COOH solution. A brown solution confirms the presence of NO2-.

**EXPERIMENTAL**

You are provided with two simple salts. Identify the cation and anion present in each of them, following the scheme for qualitative inorganic analysis to the letter.

Carry out all the preliminary tests including action of NaOH band NH3 solutions, it may not be necessary to carry out all the confirmatory tests for anions as well as the additional confirmatory tests for cations, provided you have narrowed down the possible ions from your results of initial tests.

All observations and deductions must be clearly but briefly recorded in your Data Book, do not forget to record the code numbers of your samples.