NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 291

COURSE TITLE: PRACTICAL CHEMISTRY (III) INORGANIC

Course Title : **Practical Chemistry (III)- Inorganic**

Course Code: **CHM 291**

Course Team: **Dr. Uduak Aletan –(Course Writer/Developer) - NOUN**

Dr. Akeem Abayomi- (Course Editor) Dept of Chemistry ,University of Lagos

Dr. Abimbola Ogunsipe-(Programme Leader) – NOUN

Dr . Uduak Aletan (Course Cordinator) – NOUN

Content **PAGE**

CONTENTS **PAGE**

Introduction

Practical Chemistry III- Inorganic is a practical based course compulsory for all Chemistry students in their second year of study. As the name implies, you are required to carry out the experiments in your laboratory. An attempt has been made to guide you through some regulations and operations necessary for your understanding and appreciation of your time in the laboratory.

What You Will Learn in this Course

This course is divided into three modules for your understanding .In the first module you shall be made acquainted to the laboratory regulations, this will help your conduct in the laboratory to avoid unnecessary accidents and injuries. The inclusion of the Units on General Laboratory Procedures will help you to understand most of the equipment you shall come across with in your laboratory. In the second module, you shall carry out experiments on Charcoal analysis, Percentage of water in a hydrate, Gravimetric Analysis of a Soluble Chloride, Complexometric Titration of Zn(II) with EDTA, Determination of hardness of water using complexometric titration. You shall continue in Module 3 with Synthesis of Alum from Aluminum, The Analysis of Alum, Preparation of $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ (Hexaamminecolbalt(III) Chloride and Tris(ethylenediamine), Limiting Reactant , The Empirical Formula of an Oxide , Determination of the Percent Oxygen in Air and Redox Titrations.

The Course Aim

The aim of this course is to acquaint you with the practical aspects of inorganic chemistry which you will need for your second year in chemistry.

Working through this Course

Each unit has specific objectives. Endeavour to achieve these objectives when you go through these units. If after going through any unit, you are not sure you have achieved the set objectives, go through the unit again. Attend the practical classes and make sure you participate fully. Again, go through the objectives after completing the unit to see whether you have understood the concepts treated in the unit.

Read textbooks and other materials which may be provided by the National Open University of Nigeria also go through the sections for further reading to enlighten you better.

The Course Materials

The main components of the course are:

1. The Course Guide
2. Study Units
3. Laboratory Experiments
4. Tutor-Marked Assignments
5. References/Further Reading

Study Units

The followings are the units contained in this course:

MODULE 1

UNIT 1 Laboratory Regulations
UNIT 2 General Laboratory Procedures (1)
UNIT 3 General Laboratory Procedures (2)

MODULE 2

UNIT 1 Charcoal Analysis
UNIT 2 Percentage of Water in a Hydrate
UNIT 3 Gravimetric Analysis of a Soluble Chloride
UNIT 4 Complexometric Titration of Zn(II) with EDTA
UNIT 5 Determination of hardness of water using complexometric titration

MODULE 3

UNIT 1 Synthesis of Alum from Aluminum
UNIT 2 The Analysis of Alum
UNIT 3 Preparation of $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$
UNIT 4 Limiting Reactant

UNIT 5 The Empirical Formula of an Oxide
UNIT 6 Determination of the Percent Oxygen in Air
UNIT 7 Redox Titrations

Presentation Schedule

As you must have read earlier this course is a practical. It is important for that you attend the practical classes that will be organized by your study centers and participate. Submit your report on time. You should guard against falling behind in your work.

Assessment

There are three aspects to the assessment of the course. First is made up of practical assessment, second consists of the Tutor-Marked Assignments and third is the written examination.

The practical work you do will account for 20% of your total course work. Your TMA will account for 30% of your total course work. At the end of the course you will need to sit for a final or end of course examination of two hour duration. This examination will count for 50% of your course mark.

I wish you success in the course and I hope that you will find it both interesting and useful

Sources of Information

- http://www.sciencegeek.net/Chemistry/chempdfs/safetycontract.pdf
- http://www.tezu.ernet.in/academic/Laboratiory_Safety_Rules.pdf
- **http://www-chem.ucsd.edu/_files/lab/study_guide.pdf**
- **http://classes.uleth.ca/200803/chem3830a/Chem%203830%20Lab%20Manual%20-%202008.pdf**
- **http://classes.uleth.ca/200803/chem3830a/Chem%203830%20Lab%20Manual%20-%202008.pdf**
- http://en.wikipedia.org/wiki/Activated_carbon
- http://web.centre.edu/muzyka/organic/lab/24_recrystallization.htm
- http://chemtech.org/cn/cn1105/experiments/water_of_hydration.pdf
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- www.austincc.edu/dsackett/CHEM1411/**lab**/1411exp42.pdf
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- **http://www2.bc.cc.ca.us/kvaughan/chem1a/c1a_gravimetric.pdf**
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- http://en.wikipedia.org/wiki/Complexometric_titration
- .http://vedyadhara.ignou.ac.in/wiki/images/c/cd/UNIT_11_COMPLEXOMETRIC_TITRATIONS.pdf
- **http://standardbase.vapronet.nl/userdata/sbase_beheer/documenten/stappenplannen/Determination_of_hardness_of_water_%28Step-By-Step_Plan%29.pdf**
- **http://www.studymode.com/essays/Complexometric-Determination-Of-Water-Hardness-866293.html**
- **http://www.scribd.com/doc/47084424/Experiment-Complexometric-Titration**
- **http://www.mesacc.edu/~paudy84101/CHM151LL/6B%20Alum.pdf**

- **http://wwwchem.csustan.edu/archive/alum.htm**

- http://www.bc.edu/schools/cas/chemistry/undergrad/gen/fall/Alum.pdf
- http://chemlab.truman.edu/CHEM130Labs/Alum.asp
- http://www.juniata.edu
- http://infohost.nmt.edu/~jaltig/AlumAnalysisAlter.pdf

- http://www.ehow.com/info_8036479_alum-crystals.html

- **http://oliver.chemistry.ucsc.edu/151L/Expt1.pdf**
- www.gonzaga.org/document.doc?id=7496
-
- *2.* www.lahc.edu/classes/chemistry/.../exp%204%20-%20**limiting**%20rf11.p.
-
- 3*www.uccs.edu/Documents/chemistry/nsf/103%20Expt3V-LR.pdf*
- *m.learning.hccs.edu/.../**experiment**-6-**empirical-formula-of-a-compound***

- http://swc2.hccs.edu/pahlavan/intro_labs/Exp_12_Empirical_Formula.pdf
- http://pages.towson.edu/ladon/empiric.html
- *chemistry.about.com › ... ›* Chemistry Test Questions
- *www.bergen.edu/.../CHM%20100%20%20140%20-%20**Empirical**%20a*

- http://www.chemteam.info/**Redox**/WS-**redox-titration**-problems.html

- .http://academic.brooklyn.cuny.edu/chem/maggie/teach/chem41/files/feo.pdf
- http://www.lahc.edu/classes/chemistry/arias/exp%208%20-%20redox.pdf

- http://staff.buffalostate.edu/nazareay/che112/manganate.html
- *chemlabs.uoregon.edu/Classes/Exton/CH228/Percent**Oxygen.pdf***

CHM 291: PRACTICAL CHEMISTRY III– INORGANIC

MODULE 1

UNIT 1 LABORATORY REGULATIONS

1.0 Introduction
2.0 Objective
3.0 Main Content
  3.1 Safety Regulations
  3.2 Laboratory regulations
4.0 Conclusion
5.0 Summary
6.0 Tutor Marked Assignments
7.0 References/Further Reading

1.0 Introduction

While working in the science laboratory, you will have certain important responsibilities that do not apply to other classrooms. You will be working with materials and apparatus which, if handled carelessly or improperly, have the potential to cause injury or discomfort to someone else as well as yourself.

A science laboratory can be a safe place in which to work if you, the student, are foresighted, alert, and cautious.

2.0 Objective

At the end of this unit you should be able :

- To mention some of the safety precautions and laboratory regulations necessary during your experiments in the laboratory.
- Put the safety regulations to use during practical session

3.0 Main Content

3.1 Safety Regulations

The following practices will be followed:

1. Report any accident to the teacher immediately, no matter how minor, including reporting any burn, scratch, cut, or corrosive liquid on skin or clothing.
2. Prepare for each laboratory activity by reading all instructions. Follow all directions implicitly and intelligently. Make note of any modification in procedure given by the instructor.
3. Any science project or individually planned experiment must be approved by the teacher.
4. Use only those materials and equipment authorized by the instructor.
5. Inform the teacher immediately of any equipment not working properly.
6. Clean up any nonhazardous spill on the floor or work space immediately.
7. Wear appropriate eye protection, as directed by the instructor, whenever you are working in the laboratory. Safety goggles must be worn during hazardous activities involving caustic/corrosive chemicals, heating of liquids, and other activities that may injure the eyes.
8. Splashes and fumes from hazardous chemicals present a special danger to wearers of contact lenses. Therefore, students should preferably wear regular glasses inside splash-proof goggles during all lab activities where exposure to chemicals or chemical fumes is possible.
9. Students with open skin wounds on hands must wear gloves or be excused from the laboratory activity.
10. Never carry hot equipment or dangerous chemicals through a group of students.
11. Check labels and equipment instructions carefully. Be sure correct items are used in the proper manner.
12. Never taste anything or touch chemicals with the hands, unless specifically instructed to do so.
13. Test for odor of chemicals only by waving your hand above the container and sniffing cautiously from a distance.
14. Eating or drinking in the laboratory or from laboratory equipment is not permitted.
15. Use a mechanical pipette filler (never the mouth) when measuring or transferring small quantities of liquid with a pipette.
16. When heating material in a test tube, do not look into the tube or point it in the direction of any person during the process.
17. Never pour reagents back into bottles, exchange stoppers of bottles, or lay stoppers on the table.
18. When diluting acids, always pour acids into water, never the reverse. Combine the liquids slowly while stirring to distribute heat buildup throughout the mixture.
19. Keep hands away from face, eyes, and clothes while using solutions, specimens, equipment, or materials in the laboratory. Wash hands as necessary and wash thoroughly at the conclusion of the laboratory period.

20. Report any accident to the teacher immediately, no matter how minor, including reporting any burn, scratch, cut, or corrosive liquid on skin or clothing.
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36. Never pour reagents back into bottles, exchange stoppers of bottles, or lay stoppers on the table.
37. When diluting acids, always pour acids into water, never the reverse. Combine the liquids slowly while stirring to distribute heat buildup throughout the mixture.
38. Keep hands away from face, eyes, and clothes while using solutions, specimens, equipment, or materials in the laboratory. Wash hands as necessary and wash thoroughly at the conclusion of the laboratory period.
39. Dress appropriately as per the requirement of the laboratory. Avoid wearing bulky or loose fitting clothes or dangling jewelry. Wearing laboratory coat in the lab is a must.
40. Never work alone in the lab/ workshop. In case of working alone, make sure that someone knows where you are and what you are doing.
41. Never run or play in the laboratory. No food or drink should be consumed in the laboratory and workshop.
42. Never taste any chemical or solvent and pipette out by mouth. Never smell gases directly.
43. Wear gloves when using any hazardous or toxic material. Wear safety goggles when working with flames, heated liquids or glassware.
43. Do not use any equipment unless you are trained and permitted.

44. When working with electric circuits, be sure that the current is turned off before making adjustments in the circuit. Avoid using of extension cords whenever possible. Never ever use, modify, attach or otherwise change any high voltage equipment without consulting the concerned in charge.
45. Do not leave any ongoing experiment unattended.
46. Know the locations of fire extinguishers, fire blankets in the laboratory.

3.2. Laboratory regulations

You must have a lab Notebook and bring it to the lab every time you have to be in the lab. You should keep a good notebook with all the calculations and the results because your instructor will grade your Lab notebooks at the end of the each experiment. Finally, each member of your group has to write a 5 or 6 page lab report after completing the experiment. This is going to be an individual report therefore, even if your results are the same. The reports you write must be your own work. If your instructor finds out that your report is exactly the same with another member of your group, you will not receive any credit for that report and he/she may consider it as cheating.

Attendance is required and you are expected to attend all scheduled laboratory sessions. **If you miss more than two-lab session without a valid reason you will be automatically dropped from lab**. . Remember this is a group work and if you cannot be there inform other members of your group. Please be also on time since your group members will depend on you to start the experiments.

Format of the Lab Report

You should prepare your lab reports by handwriting. They should include tables and illustrations where necessary. Typically, a lab report should contain the following sections: **title page, introduction, experimental section, results and discussion,** and **references.**

Your title page should be a separate page including the title of the project which might simply be the name of the experiment, your name, name of the course and the date the report

Laboratory Care and Waste Disposal

Remember that the equipment you use in this laboratory will be used by many other students. Please leave the equipment and all workspaces as you wish to find them. After the end of the each lab, clean off your work area. Wash your glassware. When weighing any material on the balances, do not weigh directly onto the balance pan. Weigh your material on a piece of weighing paper. The balances are very sensitive instruments and should be treated with great care.

If you take more reagents than you need, do not put excess back into the bottle. It may be contaminated. Threat it as waste and dispose of it accordingly. It is most likely that, during any experiment you will perform, you will generate some waste chemicals and solutions to dispose of. Never put them down the sink unless specifically told to do so by your instructor. There will be inorganic, organic, and solid waste containers in the lab. Dispose of your waste in appropriate container.

4.0 Conclusion

In this unit you have learnt the safety precautions and laboratory regulations you will need for your work through this course.

5.0 Summary

The chemistry laboratory is not a dangerous place to work as long as all necessary precautions are taken seriously. Everyone who works and performs experiments in a laboratory must follow these safety rules at all times. It is the student's responsibility to read carefully all the safety rules before the first meeting of the laboratory.

6.0 Tutor Marked Assignment

1. What is the reason for prohibiting ALL food, drink, and smoking materials in the labs?

2. What clothing is appropriate for Chemistry lab workers?

3. When you finish working with chemicals, biological specimens, and other lab substances, always A. treat your hands with skin lotion. B. wash your hands thoroughly with soap and water. C. wipe your hands on a towel. D. wipe your hands on your clothes.?

4. If an acid is splashed on your skin, wash at once with
A. soap. B. oil. C. weak base. D. plenty of water.

5. If a piece of equipment is not working properly, stop,turn it off, and tell
A. the custodian. B. your lab partner. C. your best friend in the class.
D. the science instructor.

6. After completing an experiment, all chemical wastes should be
A. left at your lab station for the next class. B. disposed of according to your instructor's directions. C. dumped in the sink. D. taken home.

7.0 References/Further Reading

1. http://www.sciencegeek.net/Chemistry/chempdfs/safetycontract.pdf
2. http://www.flinnsci.com/media/396492/safety_exam_hs.pdf
3. http://www.tezu.ernet.in/academic/Laboratiory_Safety_Rules.pdf
4. **http://www-chem.ucsd.edu/_files/lab/study_guide.pdf**

UNIT 2 General Laboratory Procedures (1)

1.0 Introduction In the previous unit, you were made acquainted to some important rules you need to follow to make your work in the chemistry laboratory a wonderful experience. Nevertheless, it could be a very defeating experience to walk into a laboratory without understanding the use of the equipment for your use. Therefore before you start the practical classes it will be expedient to know the use of some of the equipment you shall meet.

2.0 Objective At the end of this unit, you should be able to explain the use of some simple equipment in your laboratory.

3.0 Main Content

3.1Balances and weighing

Many experiments in chemistry involve weighing at various steps. Much time can be lost during weighing procedures, and one of the principal time wasters is the habit of weighing to a degree of accuracy in excess of the requirements of the experiment. For synthetic work, weighing to 0.1 g or 0.01 g is quite sufficient. Only for analytical work, is greater accuracy required, on the order of 0.001 g or 0.0001 g.

Even if weighing is only effected to the necessary degree of accuracy, time can be wasted in the actual process, and unless some method is used whereby weighing is carried out rapidly, many experiments cannot be done in the time normally available.

At no time are chemicals to be weighed directly onto the pans of the *Analytical Balances.*

3.1.1 Accurate weighing technique: weighing by difference

To weigh an accurate amount of solid (*i.e.* to the nearest 0.001 g or better), place a **weighing bottle** (and cap) on a balance, tare it, remove the bottle from the balance, and place an estimated amount of material into the bottle. If the solid contains large crystals or lumps it should be lightly ground in a mortar before weighing.

The weighing bottle (with contents) is now capped, wiped clean and weighed using the correct procedure on the analytical balance (if the weight is significantly different from desired, remove the bottle from the balance and repeat the above procedure until close. *Immediately* record the weight in your notebook.

Return to the lab, and tip the solid into your flask, vessel or whatever is suitable, no attempt being made to remove the traces of solid which will cling to the weighing bottle. *Return to the balance room* and re-weigh the nearly empty bottle accurately. The loss in weight is the accurate weight of solid taken. This avoids the rather awkward process of washing the entire solid from the bottle and is quicker and more accurate. This method is often used, as it is rarely necessary to weigh out an exact amount. It is bad practice to weigh out, for example, 1.25 g of a solid to make an exact 0.10 M solution. It is better to use the above method, finish up with a weight of 1.32 g and express the solution as:

$$(1.32g/12.6L)M = 0.0105M$$

This avoids the very messy practice of adding and removing odd crystals to try to get an exact weight.

By using the above method it is *never necessary* to have any loose chemicals near a balance, as only a closed bottle is used on the balance.

3.2 Setting up apparatus

When ground-glass joints are used, it is not necessary to lubricate them except when high temperatures or vacuum are involved or an inert atmosphere is vital. If a joint becomes seized, try the following methods of loosening it: (a) rock the cone in the socket, (b) tap the joint gently with a block of wood, (c) warm the joint in a small flame, then tap gently, (d) soak the joint in penetrating oil, then try tapping. A common cause of seizure is a caustic alkali. Try to keep alkalis off the ground-glass, and if they do get on it, wash thoroughly as soon as possible.

Seizures can usually be avoided by disassembling the apparatus immediately after use. Where required, the procedures call for lubricating the joints with silicone grease ("high vacuum grease"). *CAUTION: silicone grease may cause corneal damage. In order to avoid accidental transfer of grease to your eyes, be sure to thoroughly wash with soap and water to remove residual silicone grease from your skin.*

Care should always be taken, when glass apparatus is set up, to avoid **strain**. It is best to start with one piece, and build from there. Take a distillation apparatus as an example:

(a) Lightly clamp the flask at a height convenient for heating,

(b) Attach the still-head, screw-cap adapter and thermometer (no more clamps are needed for these),

(c) Attach the rubber tubing to the condenser, then position a clamp and stand so that the condenser will rest on the lower, fixed, side of the clamp. Attach the condenser to the still-head, and clamp lightly,

(d) Attach and support the receiver adapter and the receiver.

A similar procedure should be followed for the other assemblies.

3.3 Reflux and distillation

Unlike ionic reactions, which are frequently extremely rapid, reactions between covalent substances tend to be slow. Particularly in main-group and organometallic reactions, it may be necessary to keep a reaction mixture hot for a matter of hours. This, coupled with the fact that volatile and inflammable solvents must be employed, makes it necessary for special equipment to be used.

Reflux The use of a reflux condenser is often necessary. It is used whenever a reaction mixture has to be kept boiling for an appreciable time and the solvent is volatile. A water condenser may be used for solvents boiling up to approximately 130 °C, and for higher boiling-point solvents an air condenser is adequate. The flask must never be filled more than half way; the size of flask should therefore be chosen by consideration of the total volume of the reaction mixture. A boiling stone or similar substance should be used to promote even boiling for all reflux procedures which do not employ magnetic stirring.

The purpose of the apparatus is to keep the solution hot without loss of solvent. It is pointless to boil violently; the heating should be controlled so that the solution is merely simmering. The flask may be heated by an **electric heating mantle** controlled by a Variac (**NEVER plug a heating mantle directly into an electrical outlet!)**, or by using an oil bath on an electric hot plate.

Distillation The purpose of distillation is to purify a liquid, or to remove a solvent from a solution. The flask must never be more than half full, a boiling stone or magnetic stirring must always be used, and the choice of condenser is the same as for reflux work. The heating of the flask may be accomplished using any of the usual means. Purification of a liquid by distillation is best performed at a rate not exceeding 2 drops of distillate per second. Alternatively, removing a large quantity of solvent may be done much more rapidly.

Fractional distillation The purpose of fractional distillation is to separate two liquids of different boiling-point. As with other forms of distillation, the flask must never be more than half full, and a boiling stone or magnetic stirring must always be used. In order to get good separation of the liquids, it is essential that the distillation be carried out very slowly. The slower the distillation, the better the separation. A rate of 1 drop of distillate per second should be the aim.

Since the efficiency of the process depends on the fractionating column reaching thermal equilibrium (there should be a gradual increase in temperature from the top to the bottom of the column), best results are obtained if drafts are excluded. In addition, the source of heat should be steady.

3.4 Use of the separatory funnel

The separatory funnel is used for several essential procedures. Except care is taken, its use can be one of the major causes of mechanical loss. The choice of size is particularly important and, as with flasks in distillation, the smallest that will properly do the job, is best.

Separating two immiscible liquids The liquid mixture is poured into the funnel and the funnel is gently agitated to assist in the separation into layers. The funnel should always be stoppered, but if a particularly volatile substance, such as ether, is present, the funnel should be vented occasionally through the stopcock *(hold it slightly inverted while doing this)* to avoid the possible buildup of pressure.

When separation into layers has occurred, the stopper is removed and the lower layer drained into a small flask. Swirling the funnel and once again allowing separation to occur frequently provides a further small sample of the lower layer.

The top layer is poured from the top of the funnel into a second flask. It is a wise precaution to always keep both liquids, even if one of them is to be discarded. It is surprising how often the wrong layer is thrown away!

Washing a crude liquid One of the most common procedures consists of shaking a crude liquid product with an aqueous solution to remove some of the impurities. The reagents should always be used in small quantities, and the process repeated if necessary. Mechanical loss is always greater when large volumes of washing solutions are used.

Gases are often formed in substantial quantities during the cleaning process, thus, it is essential to release the pressure frequently. This is best done by inverting the well-stoppered funnel and “turning on” the tap.

If the required substance is the top layer, then allowing the bottom layer to run off is quite simple. The entire bottom layer of waste should not be run off each time. It is better to leave a small quantity of the aqueous solution, and add further fresh reagent. Careful separation is completed only when running off the last of the various washing solutions. This avoids the risk of inadvertently losing a few drops of the treated product.

When the required substance happens to be the bottom layer, avoiding mechanical loss becomes more difficult. If the product is run off between each wash and then returned to the funnel for the next, the loss can become very great. The best compromise is obtained by using rather large volumes of washing solutions, and decanting the spent solution from the top of the funnel. In this way the product never leaves the funnel until the final wash is over. It is then run out into its receiver, leaving the final washing solution in the funnel.

Liquid extractions The separatory funnel is often used to extract a solute from one solvent by means of a second solvent immiscible with the first. The removal of a solute from water by means of ether is one of the most common examples of this application. The size of the funnel is chosen to accommodate the whole of the aqueous solution. This saves time which would otherwise be spent in repetition. A series of extractions with a small quantity of ether is much more effective than one with a large amount of ether. In practice the volume used is that which gives the smallest manageable top layer, bearing in mind that the ether solution must be decanted from the top of the funnel. If the layer is too small, decantation becomes difficult. The solution is usually extracted about three times with fresh quantities of ether, and all of the ether extracts are decanted into one flask. After the final extraction the aqueous layer is run off and the last ether layer decanted completely

4.0 Conclusion In this unit you have studied some general laboratory procedures you will need for a better appreciation of your laboratory. I hope it will guide your use of the laboratory.

5.0 Summary. In this unit you have not performed any experiment, however you have learnt the following; the use of balances and accurate methods of weighing, techniques involved in setting up apparatus, the use of reflux and distillation sets and finally the use of the separatory funnel.

6.0 Tutor Marked Assignments (TMA)

1 Which of the techniques mentioned in this unit would be appropriate in the separation of a mixture of ethanol and water?

2. In which of the techniques named in this unit is density necessary for the separation of liquid mixtures?

3. Which technique in this unit will be suitable for prolonged heating involving organic solvents?

7.0 References/Further Reading

1. **http://classes.uleth.ca/200803/chem3830a/Chem%203830%20Lab%20Manual%20-%202008.pdf**

UNIT 3 General Laboratory Procedures (2)

5.0 **Introduction** You started with the study of some laboratory procedures in the previous unit. I hope you were able to appreciate the techniques you were introduced to. In this unit, you will get to understand a new set of procedures. This will give you a better chance of understanding the experiments you shall perform in this course.

6.0 **Objective** At the end of this unit you should be able to explain the use of some equipment in your laboratory.

3.0 Main Content

3.1 Filtration methods

There are a variety of techniques used for the separation of a liquid or solution from a solid.

Simple filtration The usage of a filter funnel and a piece of filter paper folded into four is commonly reserved for ionic substances (*e.g.* NaCl) precipitated from aqueous solution. Precipitates obtained in qualitative analysis and inorganic experiments are often rather fine, and cannot be well filtered using a pump. Covalent solids, however, are generally separated from a volatile solvent, and the relative slowness of simple filtration leads to complications caused by evaporation.

It is crucial in simple filtration to ensure that the paper is cautiously folded. The paper must be fixed carefully into the funnel and wetted fully with water, or the suitable solvent, preceding the filtration.

The contents of the filter paper should remain at least 1.5 cm from the top of the paper. These simple precautions can make an intense difference in the time required for a filtration to be completed, and should never be overlooked.

The Büchner funnel and filter pump This method of filtration is the most extensively used when dealing with recrystallized substances. The Büchner funnel may be attached to the flask by means of a cork, but a much more useful device comprises of a flat piece of rubber with a hole in the center able to receive the funnel stem and making a good seal.

The disc of rubber permits, reasonably, any size funnel to be fitted to any size flask. If this method is adopted, then the size of the funnel selected is the least that will contain the solid, and the flask is also selected to be the least that will contain the liquid, if both solid and liquid are necessary. If the solid is to be discarded, then a large funnel can be used to increase the rate of filtration. Conversely, if the liquid is to be discarded, then the flask may be large enough to contain the entire liquid in addition to the washings. The choice of size is very vital, as mechanical loss during filtration can be significant.

The filter-paper disc is placed in the funnel, and wetted with the solvent present in the solution to be filtered. It is crucial that the funnel and flask be perfectly dry. If the solvent involved is ethanol, then the paper may be wetted with water. If available, connect the suction flask to a Woulff bottle (ask the instructor how to use a Woulff bottle). The pump is then turned on and the paper pressed into place. During filtration the pump must never be turned off, as this may cause water from the pump to be drawn back into the filtrate. When all of the material has been filtered, turn on the stopcock of the Woulff bottle to ambient pressure (or disconnect the pump from the flask) while the pump is still running. If some of the solid has not been transferred to the funnel, a portion of filtrate can be retrieved and used for rinsing the residue into the funnel. The solid is washed free of filtrate by pouring a small portion of chilled fresh solvent into the funnel while the pump is disconnected. Lastly, the solid is drained as dry as possible by suction from the pump while applying pressure with a clean glass stopper.

Gravimetric filtration In quantitative work it is important that all of the solid be transferred and retained in the filter funnel. A **filtering crucible** with a porous sintered-glass bottom is the most appropriate apparatus to use. Porosities from 0 (coarse) to 5 (very fine) are available, although for most purposes a porosity of 3 is best; a few fine precipitates will require a porosity of 4.

Prior to usage, the sintered-glass crucible is dried in an oven, cooled, and accurately weighed. To collect the solid the pre-weighed crucible is set in the mouth of the Büchner flask by means of a firm rubber cone. The pump is turned on, and as much supernatant as possible is decanted off through the crucible. The liquid should be directed into the crucible via a glass rod.

The solid is then transferred, using a gentle jet of the appropriate solvent to swill out all particles. If solid clings to the apparatus, it can be collected using a glass rod protected with a **rubber 'policeman'**. The pump suction at this stage should be as gentle as possible; otherwise the porous glass may clog. Finally, the solid and crucible are washed repeatedly to remove all soluble materials, and dried to constant weight.

3.2 Drying methods

The drying of liquids Extreme drying is not usually necessary with organic liquids and drying agents such as *anhydrous calcium chloride* or *anhydrous sodium sulfate* are adequate. Of the two, calcium chloride is the more effective, but also the more messy.

As calcium chloride will remove water and ethanol, it is employed when both need removing. If, however, the drying only needs to remove water; anhydrous sodium sulfate is generally employed. Sodium sulfate will only work at temperatures below 30 °C and should generally be used at room temperature. It is able to remove its own weight of water, but the use of too much drying agent should be not be done too often as this will cause the drying agent to become 'wetted' with the product and a large mechanical loss will be entailed.

In order to dry an organic liquid, whether a product or a solution containing the product, the liquid should be placed in a suitable sized conical flask, fitted with a good stopper or cork, and the drying agent added. The corked flask should be shaken at intervals, and left for at least five minutes, preferably longer.

If sufficient drying agent has been used some should remain unchanged in appearance: i.e. a fine opaque powder of sodium sulfate or firm granules of calcium chloride.

The drying of solids Various methods exist for drying solid materials. When deciding which method to use it is important to know something about the physical properties of the material. For example, if dehydration of a hydrate or melting of an organic solid occurs, recrystallization will have to be repeated resulting in further loss of time and material.

Although the method of air drying takes longer than the others, it is one of the safest for non-deliquescent solids. The damp solid, drained as dry as possible on the filter, is transferred to a watch-glass and spread out evenly. The solid can then be left to dry overnight in a location free of dust and drafts. As an added precaution against dust, a second, larger watch-glass should be placed over the product in such a fashion that free evaporation remains possible. Though the desiccator is ideal for drying many solids, care must be taken when drying hydrates. It is quite possible to lose some water of crystallization if the dehydrating agent is too effective. Thus, samples to be dried should be spread out on a watch-glass and labeled with their name and date.

The desiccator must be regularly recharged with fresh desiccant, and the ground-glass seal kept greased with a minimum quantity of silicone grease, so it appears transparent.

It is important to remember that after opening, a desiccator takes at least two hours to re-establish a dry atmosphere.

A vacuum desiccator is used to speed the drying of a sample. The sample must be covered with a second watch-glass and the desiccator evacuated and filled slowly to avoid blowing the sample about. In order to guard against implosion, a vacuum desiccator must be covered with strong adhesive tape, or be enclosed in a special cage when being evacuated and de-evacuated.

3.3 Recrystallization and purification of solids

Inorganic solids, when first prepared, are rarely pure. The original solid must be recrystallized from an appropriate solvent. If the solvent is a flammable liquid, as it often is, it is better to carry out a recrystallization under reflux, until more experience has been gained. With ethanol, a very common solvent, it is quicker and neater to use a conical flask, but this does entail a risk of fire.

Reflux method The solid is placed in a suitable sized flask, preferably a conical flask as it can be easily put aside to cook, and a condenser attached. A small volume of solvent is poured down the condenser and the mixture is raised to its boiling point. If the entire solid has not dissolved, a bit more solvent should be added after removing the mixture from the hot plate. Repeat this process until the solid just dissolves at the boiling-point. If there are no insoluble solid impurities, the solution will be clear. The mixture should then be removed from the hot plate and slowly allowed to cool to room temperature. Once the solution reaches room temperature, it may be necessary to gently swirl the flask in order to prime crystallization. The solid usually crystallizes upon cooling, but, if crystallization is slow to start, scratching the inside of the flask with a glass rod frequently helps crystals to form. The flask should be cooled to at least room temperature, or preferably lower, by placing it in either iced water or a refrigerator.

The pure product is filtered off at the pump. It is essential for both the filter flask and funnel to be clean and dry, except for the solvent concerned. The mixture to be filtered is poured on to the filter paper and the solid remaining in the flask is washed out with the filtrate. This is important. The filtrate is, of course, a saturated solution of the required solid, and so the filtrate cannot reduce the yield by dissolving some of the crystals. The filtrate should be used for washing out the flask several times, until the entire solid has been transferred to the filter. On no account should fresh solvent be used for transferring the solid to the filter. The recrystallized solid is then dried in a suitable manner, bottled and labeled.

Open flask method This is essentially the same as the previous method, but is carried out directly on the hot plate with an open conical flask. The solvent is only just allowed to come to a boil and then the flask is removed from the heat. At this point, it should be possible to see the vapor condensing inside the flask, and there should not be a risk of fire if care is taken. The obvious advantage of this method is speed. This approach is not suitable for low-boiling solvents such as ether or pentane.

Recrystallization requiring hot filtration If, during a recrystallization, there is an insoluble solid impurity, it becomes necessary to filter the hot solution. Care must be taken that no crystallization occurs during the process as this would block up the filter funnel and cause great difficulty. To avoid this, the following procedure is used:

The crude solid is dissolved in the solvent in the normal way, and when all of the solute has just dissolved at the boiling-point, a further small quantity of solvent is added. This ensures that the solution is not quite saturated. This solution is kept hot while a separate sample of solvent is heated to boiling and then poured through the prepared Büchner funnel. This procedure heats up the funnel and flask. The filter paper, which must be in position, is held in place by a glass rod. The selected funnel should be reasonably large as this will retain the heat better and the filtration will be faster.

The hot solution is rapidly filtered with the pump on full. As soon as all of the solution is through the funnel, the pump is disconnected and the funnel removed. At this stage the solute will almost always have begun to crystallize in the receiving flask. To save mechanical loss, the solution should be kept in the flask and cooled in the normal way. The final filtration to collect the crystals therefore requires another flask.

The use of activated charcoal

Sometimes there are colored impurities present in the crude material to be recrystallized. These are removed from the solution while hot by adsorption onto activated charcoal. The recrystallization is carried out normally until the crude material is dissolved. At this point, a little extra solvent is added, and the mixture cooled slightly. A small amount of activated charcoal is added to the cooled solution. It is important to cool the solution before adding the charcoal, as this material tends to promote boiling. If the solution is not sufficiently cooled prior to the addition of the charcoal, the entire mixture will usually boil over violently.

The mixture with the charcoal is allowed to boil gently for a few minutes, and is then filtered hot. It is important to ensure that the paper is well fitted or charcoal may get around the edges and contaminate the product. As in hot filtration, the funnel should be large so that the filtration is as rapid as possible. The flask should be of a suitable size for the volume of purified solution obtained.

4.0 **Conclusion** This unit like the previous has dealt with some operations needed for your experiments in the laboratory

5.0 **Summary** In this unit, you have studied the following: The various forms of filtration, drying methods, recrystallization and purification of solids

6.0 Tutor Marked Assignments (TMA)

1. What is a drying agent?
2. Mention two uses of activated charcoal.
3. Mention two precautions to be taken during the process of recrystallization

7.0 References/Further Reading

1. **http://classes.uleth.ca/200803/chem3830a/Chem%203830%20Lab%20Manual%20-%202008.pdf**
2. http://web.centre.edu/muzyka/organic/lab/24_recrystallization.htm

MODULE 2

UNIT 1 CHARCOAL ANALYSIS

1.0 Introduction

Fossil fuels represent a large portion of the world's energy supply. They also serve as an economical source of raw materials for the manufacture of products such as plastics, synthetic fabrics, and medicines. A very important property of a fuel is its heat of combustion which is the amount of heat (calories, joules, or **BTU's)** released per amount of fuel (barrels, cubic feet, or tons). The energy rating of a fossil fuel gives us information about its chemical composition. Although charcoal is not a fossil fuel, but amorphous carbon from the incomplete combustion of animal or vegetable matter, its chemical composition can be analyzed in the same fashion as fossil fuels. The average person is more familiar with charcoal as the energy source for cooking on outdoor grills.

2.0 Objectives

At the end of this unit you should be able to perform experiments to determine the ash, fixed carbon, moisture, and volatile combustible matter (VCM) for charcoal.

3.0 Main Content

3.1 Procedure

A. Moisture Content

Support a clean, empty crucible and lid on a clay triangle using a ring stand. Heat the crucible with a hot burner flame for several minutes to burn off any impurities. Handle the crucible and lid with crucible tongs for the remainder of the experiment. Move the crucible and lid to the carrying tray, allow to cool, and weigh to the nearest 0.001 g. Add approximately 1 g of charcoal to the crucible and weigh again. The lid may be weighed separately since its use is not required in the first section of the procedure. Put the crucible in a 100 ml beaker marked for easy identification and place in a drying oven for 1 hour. Allow crucible to cool and reweigh. ***The weight loss represents the moisture content of the charcoal.***

B. Volatile Combustible Matter, VCM

Now support the crucible and dried charcoal in a clay triangle and cover with the lid leaving a slight opening at one side.

Initially, heat the apparatus gently, gradually increasing to a hot flame for several minutes. Use tongs to close the lid completely and allow the sample to cool to room temperature. **Before** weighing the crucible, examine the upper portion of the crucible and the lid for deposits and discolorations. If deposits appear on the lid, heat it directly in the flame. If deposits appear on the crucible, carefully heat the upper portion of the crucible without the lid and avoid heating the charcoal sample. Weigh the crucible, lid and remaining sample, when cool, to the nearest 0.001g. ***The weight loss is the VCM evolved during the heating process.***

C. Ash and Fixed Carbon

Support the crucible in the clay triangle and partially cover it with the lid. Heat the sample intensely and if the sample ignites, use the tongs to cover the crucible until flame is extinguished. Continue intense heating until no black residue remains on the lid or in the crucible. This will require that you periodically use the tongs to rotate the crucible's position in the flame. The residue in the crucible should appear to be a light gray-brown color when the combustion has been completed. Cool the crucible, lid, and contents and weigh. The residue remaining in the crucible is the ash content. The weight loss after the VCM removal is the fixed carbon content. Repeat the entire procedure for a second trial.

3.2 Requirements for Report

Tabulate the data collected in the experiment and calculate the percentages of ash, fixed carbon, moisture and VCM from data. Pay attention to significant digits in the data and reported numbers. Comment on the consistency or inconsistency of values from the two trials.

4.0 Conclusion

Charcoal is a light black residue consisting of carbon, and any remaining ash, obtained by removing water and other volatile constituents from animal and vegetation substances. The moisture, volatile matter, and ash results are typically among the primary parameters used for assessing the quality of a solid fuel material. The moisture result is utilized for calculating the dry basis results of other analytical results. The ash result is utilized in the ultimate analysis calculation of oxygen by difference and for calculating material balance and ash load purposes in industrial boiler systems. The volatile matter result indicates the coke yield on the carbonization process providing additional information on combustion characteristics of the materials, and establishes a basis for purchasing and selling the solid fuel materials. Fixed carbon is a calculated value of the difference between 100 and the sum of the moisture, ash, and volatile matter where all values are on the same moisture reference base.

5.0 Summary

In this unit, you have carried out the analysis of charcoal. You have determined the moisture content, Volatile Combustible Matter, the ash content as well as the fixed carbon

6.0 Tutor Marked Assignments(TMAs)

1. Of the four determinations in the experiment, which is proportional to the heat content or would be equivalent to an energy rating?
2. Identify in each section of the procedure whether a physical or chemical change is being used to analyze the charcoal.

7.0 References/Further reading

1. www.leco.com/index.php/component/edocman/?task=document...
2. www.koriobook.com/read-file/...wils-behgsthom-m-s-**pdf**-394505
3.http://en.wikipedia.org/wiki/Activated_carbon

UNIT 2 Percentage of Water in a Hydrate

1.0 Introduction

Many pure substances combine with water in a fixed mole ratio to yield compounds called hydrates. For example, zinc sulfate combines with water to form crystalline $ZnSO_4.7H_2O$ which is a stable compound at normal atmospheric conditions. All pure samples of this hydrate show the same percentage of water by analysis. Thus, this hydrated compound obeys the law of constant composition. Upon heating a sample of such a hydrate, it may lose all its water of hydration and revert to the anhydrous salt. Substances which have adsorbed water on the surface do not show constant composition and therefore are not hydrates. An example of this would be common table salt, which becomes very sticky on humid when the relative humidity is high. In these cases, the percentage of water is not constant for all samples of a particular compound, and the water is not chemically bonded as part of the crystal structure.

2.0 Objective

By the end of this unit, you shall be able

- to explain the concept of water of hydration
- perform an experiment to determine the percentage of water in an unknown hydrate.
- Define the terms : **efflorescence** , **deliquescence** and **hygroscopy**

3.0 Main Content

3.1Theory Hydrates are crystalline salts that are bonded to water molecules in definite proportions. The weakly bound water is known as either the water of hydration or water of crystallization. The fixed numbers of water molecules that are weakly bonded to the salt are represented as follows:

salt • number of waters
zinc sulfate heptahydrate
($ZnSO_4 \bullet 7\ H_2O$)

The dot represents the weak salt • water bond in the chemical formula. The bond is so weak that simply heating the hydrated salt to liberate the water molecules as vapor can normally break it. If water is added to the now anhydrous salt, the reverse will take place with the waters reattaching themselves to the salt. This is known as a reversible action.

There are three closely related substances that act similar to hydrates but have distinct individual characteristics. These are hydroscopic, deliquescent, and efflorescent substances.

Hydroscopic substances - readily absorb moisture from the air and are used as drying agents (desiccants).

Hygroscopy is the ability of a substance to attract and hold water molecules from the surrounding environment

Deliquescent substances - continue to absorb water from the air until they form a solution.

Deliquescence the process in which a soluble substance picks up water vapor from the air to form a solution.

Efflorescent substances - are hydrates that lose water when simply exposed to the atmosphere.

Efflorescence (which means "to flower out" in French) is the loss of water (or a solvent) of crystallization from a hydrated or solvated salt to the atmosphere on exposure to air.

As previously mentioned, each hydrated salt has water molecules bonded to them in definite proportions. The percent water in the hydrated salt can be calculated, theoretically, using the chemical formula of the hydrate.

$$\%\ H_2O = \frac{(number\ of\ H_2O\ molecules)\ (molecular\ mass\ of\ H_2O)}{molecular\ mass\ of\ hydrate} \times 100$$

3.2 Procedure

Clean and dry a porcelain crucible and cover. Place the empty, covered crucible on a clay triangle supported by a ring on a ring stand. Heat the crucible and cover in the hottest flame of the Bunsen burner for 5 minutes. A dull red glow should be observed on the crucible and cover. This will require that you manipulate the burner to heat uniformly. This will ensured that all volatiles and combustible materials are removed prior to the analysis procedure and that a constant weight for the crucible and cover may be recorded. The crucible and cover must be allowed to cool to laboratory temperature for approximately 15 minutes. Using crucible-tongs transfer the crucible and cover to a carrying tray and weigh them to the nearest 0.001 g. Add 1 to 1.5 g of zinc sulfate heptahydrate to the crucible and weigh the covered crucible to the nearest 0.001g.

Place the covered crucible on the clay triangle with the cover slightly opened. Heat the crucible gently for a few minutes to avoid loss of material from spattering during initial heating.

Remember contents for approximately 15 minutes gradually increasing the temperature of the flame. Allow the crucible to cool on the triangle after removing the flame until it has reached room temperature.

Transfer it to the carrying tray and weigh the covered crucible to the nearest 0.001 g. Reheat the crucible and contents for about 5 minutes and, after cooling, weigh it again. Repeat this heating, cooling and weighing sequence until two consecutive weighings are within 0.005 g. This sequence of heating, cooling and weighing to obtain consistent results is known as heating to a constant weight.

That water boils a t 100°C. Continue to heat the crucible and calculate the actual percentage of water in the zinc sulfate using the gram formula weight of the hydrate and the weight of water indicated in the formula multiplied by 100. Calculate the experimental percentage of water in your hydrate based on water lost as a result of heating divided by the hydrate sample weight multiplied by 100. To evaluate your results and determine how well you did the analysis, you can calculate relative error using the following formula.

$$\frac{\text{Actual Value} - \text{Experimental Value}}{\text{Actual Value}} \times 100 = \text{Percent of Relative Error}$$

An absolute relative error of 3% or less is excellent. If the percent of error is greater than **3%,** think about factors that you observed during the procedure that may have affected your results Modify your actions accordingly for the unknown hydrate sample. Obtain from your instructor an unknown hydrate sample. Repeat the procedure which you used on the known hydrate. Do a minimum of two trials and report the average percentage of water in your unknown hydrate.

DO NOT forget to record your sample number and/or letters.

Requirements for Report

Data tables should be constructed for all hydrate trials so the information is readily found in the report. One sample calculation must be demonstrated for a completed trial. Record all observations and adjustments made to improve your technique.

4.0 Conclusion Water that is chemically combined with other molecules (salt) to form a hydrate mineral that is easily removed through heating.

5.0 Summary

In this unit you have been through the concept of water of hydration and you have also performed an experiment to determine the water of hydration of a salt.

6.0 Tutor Marked Assignments (TMA)

1. Using a suitable reference source, define the following words:
   - Deliquescence
   - Efflorescence
   - Hygroscopy
2. Anhydrous calcium chloride is used inside desiccators to remove moisture. Explain how $CaC1_2$ removes the water vapor.

3. Calcium chloride hexahydrate has the chemical formula $CaCl_2 \cdot 6 H_2O$. What is the theoretical percentage of water?

Solution
The formula weight of CaCl2 • 6 H2O is:
Ca: 1 x 40.1 = 40.1 amu
Cl: 2 x 35.5 = 71.0 amu
H: 12 x 1.0 = 12.0 amu
O: 6 x 16.0 = 96.0 amu
Formula weight of CaCl2 • 6 H2O = 219.1 amu
Formula weight of H2O = 18 amu

$$\% \, H_2O = \frac{(6 \, waters)(18 \, amu)}{219.9 amu} \times 100 \; = 49.3\%$$

7.0 References/Further reading

1. http://chemtech.org/cn/cn1105/experiments/water_of_hydration.pdf

2. www.koriobook.com/read-file/...wils-behgsthom-m-s-**pdf**-394505
3. www.austincc.edu/dsackett/CHEM1411/**lab**/1411exp42.pdf
4. http://en.wikipedia.org/wiki/Efflorescence
5. http://chemistry.about.com/od/chemistryglossary/a/deliquescencedf.htm
6. http://en.wikipedia.org/wiki/Hygroscopy

Unit 3 Gravimetric Analysis of a Soluble Chloride

1.0 Introduction

Gravimetric analysis, which by definition is based upon the measurement of mass, can be generalized into two types; precipitation and volatilization. The quantitative determination of a substance by the precipitation method of gravimetric analysis involves isolation of an ion in solution by a precipitation reaction, filtering, washing the precipitate free of contaminants, conversion of the precipitate to a product of known composition, and finally weighing the precipitate and determining its mass by difference. From the mass and known composition of the precipitate, the amount of the original ion can be determined.

2.0 Objectives

In this unit, you should

(i) explain the theory of gravimetric analysis

(ii) carry out an experiment to demonstrate gravimetric analysis

3.0 Main Content

3.1 Safety and laboratory technique note

During this experiment, avoid getting silver nitrate solution on your hands (or any other part of your body that you splatter it on). If you do, rinse it off immediately. If you don't and then expose your body to light, the skin will turn black and might peel off in a couple of days.
Essentially this is due to the photographic process; the black material coloration due to tiny silver metal particles:

$$AgCl + h\nu \rightarrow Ag + Cl.$$

[When very finely powdered, all metals appear black.]
Don't worry, you won't die or lose the limb. This is rather more evidence of sloppy technique than it is of a health hazard. However, if you are at all concerned, seek medical advice and/or treatment.

3.2 The Unknown

Submit a clean, *dry*, labeled glass weighing bottle to the instructor so that your solid unknown chloride sample can be issued. Your name and matriculation number should be written legibly on this flask with a fine-point permanent marker pen. The bottle must be dry inside and out. ***The bottle must be turned in immediately after you have checked into the laboratory, because you will have to dry the unknown for at least 1 hour in an oven set to a temperature of 110^o C and cool it in your desiccator prior to use.*** Drying overnight or for several days will not harm the unknown. The solid unknown should be a free-flowing powder. If it is not, *very carefully* crush the lumps with a heavy rod or your spatula prior to putting it into the oven. Place the weighing bottle into a clean, dry, labeled 250-mL beaker with its lid tipped sideways. Cover the beaker with a watch glass and place in a drying oven.
Time required for completion: Three to four laboratory periods.

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3.3 Theory

Precipitation is effected by inorganic or organic precipitating agents. Two common inorganic precipitating agents are silver nitrate, which is used to precipitate halide ions such as chloride, and barium chloride, which is used to precipitate sulfate ion. Potassium, ammonium, rubidium, and cesium ions can be precipitated by sodium tetraphenylborate. In all of these precipitation reactions, the products are salts because they are formed by reactions between cations and anions. Thus the bonding is ionic or *electrovalent*.
Organic precipitating reagents contain functional groups that combine with inorganic ions to form insoluble salts. The organic reagent may contain groups such as carboxyl or hydroxyl thationize to form anions that combine with cations to form insoluble salts. In this reaction, the bonding is also electrovalent. Some organic reagents contain nitrogen or oxygen that can combine with metal ions by forming covalent or coordinate bonds. Other organic reagents may contain two or more functional groups that can combine with a single cation to form a ring structure. Such a reagent would be called a *bidentate ligand* if it contained two functional groups, a *tridentate ligand* if it contained three, and so forth. The product formed between a cation and some *multidentate ligand* to form a ring structure is called a *chelate*.
The three major requirements for a good gravimetric analysis are that (a) the reagent will react only with the analyte of interest to form a precipitate, (b) it forms one and only one product with

the analyte and (c) that the analyte precipitates quantitatively from solution, that is, $> 99.99\%$. In aqueous solution silver ion undergoes the following reaction with chloride:

$$Ag + (aq) \ + \ Cl - (aq) \ \leftrightarrow AgCl(s)$$

Silver chloride is a relatively insoluble compound with a solubility product

$$K_{sp} = \left[Ag^{+][}Cl^{-}\right] = 1.8 \ \times 10^{-10}$$

An excess of silver ion is added so that the chloride concentration at equilibrium will be negligible. If enough silver nitrate solution is not used, the precipitation will be incomplete, resulting in a substantial error and a low value for the % Cl in the sample.

3.4 Procedure

Preparation of Filter Crucibles

1. Clean and dry three porcelain filter crucibles (see note below). Make sure crucibles are marked so they can be distinguished from one another. Use a permanent marker, not a paper or tape label.
2. Dry crucibles in the oven at 100-110 °C for one hour or overnight. The crucibles should be put in a labeled beaker and covered with a watch glass when in the oven.
3. Cool the crucibles in a desiccator for 20 minutes and weigh.
4. Repeat Steps 2 and 3, this time oven-drying for only 20 minutes.
5. Repeat this procedure until the mass of each crucible agrees to within 0.3 mg between weighings.

Note: Cleaning Procedure for Porcelain Filter Crucibles

(a) Scrape any large amount of gray or purplish precipitate in the crucible into the waste container for ***Solid AgCl***.

(b) Thoroughly wash the inside and outside of the crucible with a test tube brush and a small amount of soapy water. ***Soak off and remove all paper or tape labels***.

(c) If there is a gray or white residue in the crucible, add about 100 mL of water to a filter flask to dilute the rinse acid or base when it comes through. Mount the filter crucible in the filter flask, add 1-2 mL of concentrated NH_3, let it sit for a few of minutes, then apply a gentle vacuum to pull the resulting solution through the fritted bottom. Follow by rinsing with large amounts of distilled water from a wash bottle. You may need to repeat this procedure 2 or 3 more times. **NOTE:Always break the vacuum first before you turn off the aspirator water.**

(d) If a dark stain remains, empty the contents of the filter flask in the appropriate waste container and add a few mL of conc. HNO_3 to the crucible. Let it sit for a few minutes, apply a gentle vacuum as before, and rinse the crucible thoroughly with distilled water.

(e) If there is a reddish stain in the crucible, empty it and add a few drops of conc.HCl. This should remove it nicely. Proceed as with HNO_3 above. If the crucible does not filter rapidly (1-2 drops per second) after this cleaning, repeat the entire procedure. If it still does not drain rapidly under vacuum, consult with your instructor.

(f) After you are completely done. Rinse the vacuum flask and crucible holder thoroughly with distilled water. Turn on the vacuum and squirt some distilled water down the rubber hose. Place the vacuum flask, crucible holder, and rubber hose back in their proper drawers.

Hazardous Waste Note: The NH_3 waste (basic) container is housed in a separate hood from the HNO_3 and the HCl waste (acidic) containers.

Preparation of the Chloride Unknown Samples

1. Dry the sample in an oven at 110 °C for 1-2 hours or overnight.
2. Weigh out ***accurately***, by difference, three portions of the dried sample of about 0.5 to 0.7 g each to within ± 0.1 mg. **NOTE: *NEVER* transfer chemicals *inside* the balance.**
3. Dissolve each portion in a clean, separate, labeled 400-mL beaker, using 150 mL of distilled water to which about 1 mL of concentrated nitric acid has been added
4. Place a watch glass cover on each beaker.

Precipitation of Chloride with Silver Ion

1. Heat the chloride solutions to gentle simmering on a hotplate and keep each one hot until the AgCl is fully precipitated. **Precipitate the chloride from one unknown solution at a time**.
2. Go to the hood containing the stock silver nitrate solution and carefully **pour about 80 mL of the solution into a 100-mL graduated cylinder**. [Each unknown will require about 50-70 mL to precipitate the Cl^-completely. DO NOT FILL ANY CONTAINER LARGER THAN 100 mL with the stock silver nitrate solution. **Silver nitrate is very expensive please do not waste it.**
3. Stirring constantly **with a glass stirring rod** (do NOT use a magnetic stirrer and stir bar), add the silver nitrate from the graduated cylinder in approximately $5\,mL$ increments to your first unknown solution until the precipitation of the silver chloride is complete. To check for complete precipitation, silver nitrate must be added in small quantities and vigorously stirred. Allow the precipitate to settle a bit and add some more silver nitrate solution (no stirring yet). If the solution becomes cloudy, keep adding. If the solution remains clear, then add a total of about 5% more silver nitrate solution than you have added to that point.
4. Now place the beaker (covered) *in your locker* for at least one hour to "digest" before filtering. This minimizes exposure of the AgCl to light and consequent decomposition.
5. Repeat this precipitation and digestion for your other unknown solutions, one at a time. If you have used a graduated cylinder to monitor the volume of silver nitrate solution used for your first unknown solution, then you can then estimate about how much you need to add to the remaining samples. Simply ratio the volume to be used based on the masses of the two unknown samples that you weighed out.

Filtration and Final Weighing

This procedure should be done separately for each sample in turn.

1. After the solution has digested for a *minimum of 1 hour*, filter the supernatant liquid through a labeled, weighed filter crucible with suction, keeping most of the precipitate in the beaker. *NOTE: Always break the suction on the flask before turning off the water flow on the aspirator.*
2. Test the filtrate in the suction flask for complete precipitation by again adding a few drops of silver nitrate solution. If your filtrate remains clear, dispose of the filtrate in the appropriate waste container.
3. Wash the precipitate with three 25-mL portions of 0.01 M nitric acid (2 drops of concentrated HNO_3 per 100 mL of water) using your washing bottle. [A standard-sized washing bottle will hold about 500 mL.] The washings are poured through the filter crucible and the precipitate is

left in the beaker. If any of the precipitate has dried on the sides of the beaker or the glass stirring rod, scrape them down with a rubber policeman and rinse with small amounts of the wash solution during this process to ensure that 100% of the precipitate will be filtered off into the filter crucible.
4. Stir the bulk of the precipitate up in a small volume of 0.01 M HNO_3 and quantitatively transfer the precipitate to the crucible.
5. After filtering, place the crucibles in a large beaker covered with a watch glass and dry at $120 - 140\ °C$ for 2 hours. You can leave the crucibles overnight, if you return the next day and put them in your desiccator.
6. Cool in a desiccator and weigh.
7. Return them to the oven for 20 minutes. Then cool in the desiccator for 20 minutes and reweigh. Repeat this step until the mass of a crucible with the precipitate agrees to within 0.4 mg.

CALCULATIONS

Calculate the % chloride in the sample. The *gravimetric factor* is given by

m_{Cl}/m_{AgCl}= 35.453 $g\ Cl^{-}mol^{-1}$/143.321 $g\ AgCl\ mol^{-1}$= 0.247368 g Cl^-/g $AgCl$

where *m* = the mass in grams. The mass of chlorine in each sample is therefore

m_{Cl}= m_{AgCl} x gravimetric factor = m_{AgCl} x 0.247368

Finally, the percent Cl^{-}in each sample is:

$\%\ Cl^{-}=\left(m_{Cl}/m_{sample}\right)\ x\ 100\%$

Use the *Q*-test if you suspect that you have an *outlying* or *spurious* value. If so, run at least one more sample through the entire procedure. Retest to see if the spurious value can be rejected. Finally report the average value for your 3 or 4 results and its standard deviation.

Remember, you can always throw out one or more values *for cause* – a specific, known reason that you have documented in your notebook. Example: “There were lots of black specks that looked like dusts belched from the air duct in replicate #2.”

HAZARDOUS WASTE DISPOSAL

Each of the following is to be placed in its proper, labeled Hazardous Waste Container in the hoods. If you are unsure about the container, ASK.
Solid AgCl Precipitate.
NH_3 Washings.
HNO_3 Washings.
Filtrate from Filtration of Precipitated AgCl.

4.0 Conclusion Gravimetric analysis is concerned with the determination of a substance by the process of weighing. The element or radical to be determined is converted into a stable compound of definite composition and the mass of the compound is determined accurately.

5.0 Summary Gravimetric analysis is the quantitative isolation of a substance by precipitation and weighing of the precipitate. An analyte is the substance to be analysed. A precipitating reagent is the reactant used to precipitate the analyte.

6.0 Tutor Marked Assignment (TMAs)

1. **Calculate the amount of Boric acid from Borax**.

   Borax is an alkaline substance, and reacts with conc. HCl to form Boric acid. Boric acid is freely soluble in boiling water and precipitated out in cold water. To get high grade of Boric acid, Borax is treated with conc. HCl as it is volatile in nature and will left any residual traces on crystal surface of Boric acid.

   Weight and dissolve 5 gm of Borax in 15 ml of distilled water. Add 7 ml of conc. HCl, mix thoroughly with glass rod and mark the original volume with glass rod. Evaporate the solution till the volume reduces to half of the original volume. Allow to cool at room temperature. Keep it aside for few min and add ice water. Filter the residue under suction and dry it in air. Weight the compound preparation.

   $Na_2B_4O_7.10H_20 \rightarrow 4H_3BO_3 + 5H_20 + 2NaCl$

   Mol wt of Borax = 381.37gm
   Mol wt of Boric acid = 61.83gm
   Practical yield: X gm

   381.37 gm of Borax = 4 × 61.83 gm of Boric acid
   X gm of Borax = ?
   = X · 4 · 61.83 / 381.37
   = 0.674X gm of Boric acid

2. **Calculate the amount of zinc oxide from zinc sulphate**.

   A solution of zinc sulphate is boiled to convert it into zinc carbonate by adding solution of sodium carbonate. Sodium carbonate is added to precipitate zinc completely as zinc carbonate. Precipitates of zinc carbonate is boiled for few minutes to convert it into zinc oxide and collected in a tarred Gooch crucible. Precipitates are washed with hot water until it gets free from alkali and then dried, ignited and weighed to a constant weight.

   $ZnSO_4 + Na_2CO_3 \rightarrow ZnCO_3 + Na_2SO_4$

   $ZnCO_3 \rightarrow ZnO + CO_2$

   $ZnSO_4 = ZnCO_3 = ZnO$
   $ZnSO_4 = ZnO$

Mol. Weight of $ZnSO_4$ = 168 gm
Mol. Weight of ZnO = 81.38 gm

81.38 gm of ZnO = 168 gm of $ZnSO_4$
1 gm of ZnO =?
= 168 · 1 / 81.38
= 1.984 gm

Ammonium oxalate solution, $(NH_4)_2C_2O_{4(aq)}$, was added to the solution to precipitate the calcium ions as calcium oxalate, $CaC_2O_{4(s)}$.

7.0 References/Further Reading

1. **http://www.chem.tamu.edu/class/majors/tutorialnotefiles/gravimetric.htm**
2. **http://www2.bc.cc.ca.us/kvaughan/chem1a/c1a_gravimetric.pdf**
3. http://www.lahc.edu/classes/chemistry/arias/Lab2GravAnaF11.pdf
4. http://www.chem.uky.edu/courses/che226/labs/020-gravim_cl.pdf
5. **http://www.ausetute.com.au/gravimetric.html**
6. **http://www.web- formulas.com/Formulas_of_Chemistry /Examples_in_Gravimetric_Analysis.aspx**

Unit 4 Complexometric Titration of Zn(II) with EDTA

1.0 Introduction

A complexometric titration is one in which the reaction between the analyte and titrant involves the formation of a complex. In a typical complexometric titration a solution of a complexing agent is added to the analyte solution. This leads to the formation of a stoichiometric complex that is soluble and stays undissociated. Such a quantitative reaction forms the basis of quantitative complexometric determinations. The key steps in designing a typical complexometric determination are

- choosing a suitable complexing agent
- choosing a suitable method of detecting the end point
- choosing the experimental conditions that provides an optimum titration

Complexometric titrations have the advantages of complex formation and at the same time suffer from the limitations of titrimetric methods. For example, although the complex formed is undissociated, it does not suffer from co-precipitation errors as in the case of precipitation titrations. The fact that a complexing agent coordinates with only certain metal ions i.e., it shows selectivity is an added feature of the complex formation. However, on the flip side, the stoichiometry of the complex is not well defined as in a redox, neutralization, or precipitation titration. Further, if the complexing titrant is an organic compound, we need to be careful about the solubility properties of the complex

2.0 Objectives

At the end of this unit you will be able to

(i) explain the concept of complexometric titration
(ii) perform an experiment on complexometric titrations

3.0 Main Content

The Unknown

Submit a clean, labeled 250-mL volumetric flask to the instructor so that your **unknown** zinc solution may be issued. Your name, section number, and your locker number should be written legibly on this flask. The flask does not need to be dry on the inside, but needs to have been rinsed with *deionized water* after it has been washed. Note that *the flask must be turned in at least 1 lab period before you plan to do the experiment* so that the Teaching **Assistants will have time to prepare the unknown.**

***Use only deionized water (not distilled water!)
Throughout the entire experiment***

3.1 Background

This experiment is an example of a classic *titrimetric analysis*. *Classical* methods of analysis such as titrimetric and gravimetric analyses are usually capable of very high precision and accuracy - typically on the order of · · 0.1% or even better if done properly. However, there is always a tradeoff. Usually classical methods are slower and much less sensitive than modern *instrumental* methods of analysis such as atomic absorption spectroscopy, gas and liquid chromatography, and mass spectrometry.

In a titration, an accurately known mass of sample is dissolved in an aqueous solution, often with some sort of chemical treatment such as acid-digestion of solid samples, and diluted with high purity water to an accurately known volume. Then, an accurately known volume of the sample solution, called an *aliquot*, is pipetted into a titration vessel and the analyte of interest is carefully titrated with a standardized solution of an appropriate *titrant* to the *endpoint* or *equivalence point* of the titration. To do this, you need to know when you reach the endpoint. This is often accomplished by means of an *indicator* that undergoes a color change at the endpoint.

From the volume and molarity of the titrant, one can then calculate the number of mols of titrant used. From the known stoichiometry of the reaction between the titrant and the analyte, one can calculate the mols of the analyte and therefore the mass and/or molarity of the analyte. With appropriate calculations, one can then determine the concentration and/or total mass of the analyte in the original sample to complete the analysis.

3.2 Procedure

Preparation of Solutions

EDTA, 0.01 M.

This solution must be prepared at least one day ahead of time, a week is preferable, to ensure that the solute is completely dissolved. EDTA solutions are prepared at an approximate molarity, and then standardized against a solution of a primary standard such as $CaCO_3$.

1. Dissolve about 3.8 g of the dihydrate of the disodium salt ($Na_2H_2Y\ 2H_2O$) and 0.1 g $MgCl_2$ in approximately 1 L of ***deionized*** water in a large beaker or a 1-L plastic bottle using a magnetic stirrer. A small amount of sodium hydroxide can be added if there is any difficulty in dissolving the EDTA. Try not to exceed 3.8 g of the disodium salt because much more than this dissolves only with difficulty.
2. Before use, the EDTA solution should be filtered using a Buchner funnel and suction filtration. See a teaching assistant for the apparatus. [NOTE: Break the suction *before* you turn off the water flow on the vacuum aspirator.]
3. Store the solution in a clean, labeled 1-L plastic bottle that has been rinsed with deionized water. ***Never store reagent solutions in volumetric flasks.***

Ammonia/Ammonium Chloride Buffer Stock Solution, pH 10.

Each titration will require the addition of pH 10 ammonia buffer. The stock buffer solution has been prepared for you, and you should not have to prepare it. The appropriate quantity (7-8 mL) is dispensed directly into your titration flask from the plastic Repipet® repetitive dispenser located in Hood #7. **The buffer should only be added immediately before you titrate an individual sample.** Recipe:

1. Dissolve 64.0 g of ammonium chloride in 600 mL of concentrated ammonia (14.8 M, 28% NH_3).
2. Slowly and carefully add 400 mL deionized water with stirring. This should be sufficient for over 120 titrations.

Calcium Standard Solution.

A $CaCO_3$ solution is prepared as a primary standard for Ca and used to standardize the M EDTA titrant you prepared.

1. Tap out approximately 1 g of predried analytical-reagent-grade $CaCO_3$ in a weighboat. *Accurately* weigh (to within ± 0.1 mg) approximately a 0.25-g sample *by difference* into a 150- or 250-mL beaker. **NOTE: *NEVER* transfer chemicals *inside* an analytical balance.**

2. Add about 25 mL deionized water and then slowly add concentrated HCl **dropwise** with periodic stirring until the sample dissolves completely. Then add 2 drops more. *Keep the beaker covered during the entire dissolution process*. Mild heating will speed the dissolution. **Do *NOT* boil; this will spatter the calcium solution and lead to losses**.

3. Transfer the solution quantitatively into a 250-mL volumetric flask. Rinse the beaker thoroughly with deionized water, and carefully dilute to the mark with an eye dropper or with careful use of your wash bottle. Mix thoroughly.

Because this Ca^{2+} standard solution is used to standardize the EDTA titrant, it must be prepared very carefully so that you know its *exact* molarity. Therefore, an exactly known (to ± 0.1 mg) mass of $CaCO_3$ must be weighed out, dissolved completely, and transferred quantitatively into the 250-mL volumetric flask. ***This is critical***.

Standardization of the EDTA Solution

1. Attach your 50-mL burette to a ringstand, preferably using one with a white ceramic base, and a burette clamp. If the only ringstands available have black bases, cover the base with a completely white sheet of paper before you titrate a sample.

2. Open the burette valve and drain it completely into a "waste" beaker. Squirt down the insides with deionized water a couple of times. ***If any water droplets remain attached to the inside of the burette, you must thoroughly wash the burette with soap and a burette brush to remove them.*** If you leave "reagent spots" in the burette while titrating, the titration volume will be in error. Squirt down the insides of the burette a couple of times with a mL or two of the EDTA solution with a medicine dropper to rinse any remaining deionized water out of the burette.

3. Now close the burette valve and over-fill the burette with your standard EDTA solution. Check to see if any air bubbles are trapped in the tip of the burette. If so, open and close the valve quickly as though you were "squirting" reagent from the burette into the waste beaker until the bubbles have cleared from the tip. Carefully bring the reagent level to somewhere between the 0- and 1-mL marks. **Do not try to bring the level exactly to the 0.00-mL mark**. This is a waste of time. Rinse the burette tip off with a squirt of deionized water, let it drain, and then touch the tip to the side of the waste beaker to remove excess water.

4. Pipet 25.00-mL aliquots of your standard Ca^{2+} solution into each of three or four 250-mL Erlenmeyer flasks. Each aliquot will thus contain one-tenth of the total $CaCO_3$ that was weighed out to prepare the standard solution.

5. *Take each sample to completion* ***before*** *starting the next sample*. Read the initial volume on the burette at least twice. Add 7-8 mL of pH 10 buffer from the Repipet® dispenser, (A repipet is a hand operated pump that dispenses solution. Its volumes are accurate to within about 2%). 15 mL of deionized water, and **3 drops** of Eriochrome Black T indicator, ***immediately prior*** to titrating a sample. The solution should be a pale pink. Do **not** add more indicator to make the solution darker as this can cause problems with the endpoint. Titrate the solution immediately with EDTA against a white background until the LIGHT PINK solution turns a LIGHT SKY BLUE. Read the final volume at least twice.

Titrations must be performed swiftly (but carefully) because the NH_3 will evaporate to some degree and thus the pH of the solution will change. In general, the faster the titrations are performed the better the results will be, as long as the endpoint is not overshot due to excessive haste.

It is advantageous to perform a trial titration to locate the approximate endpoint and to observe the color change. In succeeding titrations, titrate very rapidly to within about 1 or 2 mL of the endpoint, and then titrate very carefully, a drop or half-drop at a time, to the endpoint. Near the endpoint, periodically squirt the sides of the flask and the burette tip and swirl the flask to ensure all the titrant has gotten into the solution in the flask.

The endpoint color change is rather subtle, and sometimes it is slow, so you need to be careful at the end. If you are having trouble with the endpoint color change, see Note 1 at the end of the report for the preparation of "before" and "after" flasks.

Calculate the molarity of the EDTA solution from the volume of EDTA used in the titration of each aliquot. The values (M_{EDTA} and titration volumes) should all agree very closely, to within about ± 0.2% relative standard deviation. If not, titrate additional aliquots until better agreement is reached.

Outlying values can always be rejected *for cause* or **one** outlying value by using the *Q*-test.

Analysis of the Zinc Unknown

1. Carefully dilute your unknown sample in the 250-mL volumetric flask to the mark with deionized water. Mix thoroughly.

2. Pipet 25.00-mL aliquots into each of three or four 250-mL Erlenmeyer flasks. Add 15 mL of deionized water, 9-10 mL of pH 10 buffer, and 3 drops of Eriochrome Black T immediately prior to titrating a sample.

3. Titrate with standardized EDTA until the pink solution turns light blue.

Calculate the milligrams of zinc in the *total* sample. Remember that each aliquot represents one tenth of the total sample volume - a 25-mL aliquot titrated out of 250 mL total volume.

CALCULATIONS

The molarity of the Ca^{2+} standard solution (M_{Ca}) is calculated in normal fashion using the molar mass of calcium carbonate (MM $CaCO_3$) weighed out and the total volume in liters of the standard solution prepared.

$$M_{Ca} = \frac{Moles\ of\ Ca}{L\ solution} = \frac{\left(\frac{mass\ of\ Ca}{MM\ CaCO_3}\right)}{L\ solution}$$

Calculate the molarity of the EDTA from the volume of EDTA used in the titration of each aliquot of the Ca^{2+} standard solution and the known 1:1 stoichiometry between Ca and EDTA in the reaction. If the reaction has 1:1 stoichiometry, then

$$mmol_{EDTA} = mmol_{Ca}$$

The mmol of each constituent is obtained by multiplying the molarity of each of the two solutions times the volume in mL of each solution used to reach the endpoint, ep:

$$M_{EDTA} \times V_{EDTA} = M_{Ca} \times V_{Ca}$$

The volume of the Ca standard solution originally taken was 25.00 mL and the volume of EDTA used is the volume used to reach the endpoint, $V_{ep} = V_{EDTA}$, in mL. Therefore,

$$M_{EDTA} = (M_{Ca} \times V_{Ca})/V_{EDTA} = 25.00 \times M_{Ca}/V_{EDTA}$$

The mmol of zinc determined in an individual titration uses the same 1:1 reaction stoichiometry as for calcium above. Substituting molarity times the volume of EDTA used in each titration of the Zn unknown produces:

$$mmol_{Zn} = mmol_{EDTA} = mmol_{EDTA} \times V_{EDTA} = mmol_{EDTA} \times V_{ep}$$

The mass of Zn obtained in a single titration, in mg, is equal to the number of mmol of Zn times its molar mass (MM):

$$mg_{Zn} = mmol_{Zn} \times MM_{Zn} = mmol_{Zn} \times 65.38\, mg/mmol$$

And the total mass of Zn in the original 250-mL sample is therefore 10 times this amount.

HAZARDOUS WASTE DISPOSAL

Empty all the Ca and Zn solutions that were titrated into the proper Hazardous Waste Bottle for this experiment. If you are unsure of the proper container, ASK.

When you are ***completely*** *done with the experiment, including having received your grade, mix any remaining EDTA titrant, Ca standard stock solution, and Zn unknown solution together in a large beaker. Pour down the drain with copious amounts of cold tap water flowing. The first two solutions are slightly basic and slightly acidic, respectively. When mixed, they will be near neutral. In addition, EDTA, Ca, and Zn are not toxic and in very low concentrations, so disposal directly down the drain is permitted and environmentally safe.*

NOTE

1. Eriochrome Black T Indicator. The color change of Eriochrome black T at the endpoint is rather subtle. It is not an abrupt change from deep red to a dark blue; but rather it is from a light red (or pink) to a pale blue. At least one trial titration is recommended. (You can always discard a "bad" value when you know there is a definite reason for its being bad. Make sure you indicate a possible problem in your notebook at the time you observe it.) If you have trouble distinguishing the endpoint, a "before" and an "after" flask are recommended. Prepare two 250-mL flasks in a similar manner as were the samples – except do not add the 25 mL of Ca solution. Instead, add a total of about 80-90 mL of deionized water to approximate the volume of the sample aliquot (25 mL), the volume of EDTA titrant that would have been titrated into the flask, and the 15 mL of deionized water. Add the indicator and the ammonia buffer. To one flask (the "*before*" the endpoint flask) add a few drops of the Ca solution; to the other flask (the "*after*" flask) add a small amount of EDTA solution to get just past the color change at the endpoint. Stopper the flasks and keep them nearby for comparison of the colors. Titrate against a white background for better discrimination of colors. Sometimes the Eriochrome black T solution goes bad because of air oxidation. If the endpoints seem very indistinct or slow to you, try a fresh bottle of indicator. Alternatively, try adding a small amount of solid Eriochrome black T mixture (1 g indicator ground with 100 g NaCl). A small amount on the end of a spatula is sufficient.

4.0 CONCLUSION Complexometric titration is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous color change is usually used to detect the end-point of the titration.

5.0 SUMMARY In this unit you have being able to learn the concept of complexometric titrations and also carry out an experiment demonstrating complexometric titrations.

6.0 TUTOR MARKED ASSIGNMENT

1. Name two indicators that are suitable for complexometric reactions using EDTA

2. What is the principle of spectrophotometric determination of end point in complexometric titrations?

A***nswer*** *The spectrophotometric method of end point determination in complexometric titrations is based on the change in absorption spectrum on the formation of a complex between the metal ion and the ligand or the conversion of one complex to another***.**

7.0 REFERENCES/FURTHER READING

1. http://ctz116.ust.hk/xyli2/student/courses/CHEM153/labmanual/Chem153_Exp1.pdf
2. http://en.wikipedia.org/wiki/Complexometric_titration
3.http://vedyadhara.ignou.ac.in/wiki/images/c/cd/UNIT_11_COMPLEXOMETRIC_TITRATIONS.pdf

UNIT 5 Determination of hardness of water using complexometric titration

1.0 INTRODUCTION

Hard water is due to metal ions (minerals) that are dissolved in the ground water. These minerals include Ca^{2+}, Mg^{2+}, Fe^{3+}, SO_4^{2-} and HCO^{3-} . When this water evaporates or boils, the difficult to dissolve metal salts remain as a scaly residue. Hard water inhibits the effectiveness of soap and detergents. Calcium ions typically make the most significant contribution to water hardness. This is why hardness is measured in terms of mg $CaCO_3$ /L of solution. Hardness is also reported in units of parts per million (ppm). Water with a hardness value of < 60 ppm is considered "soft" and water with >200 ppm is considered "hard." The disodium salt of EDTA was used to determine the concentration of M^{2+} metal ion impurities in hard water by a complexometric titration. EDTA is a versatile chelating agent. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. Chelating agents are multi-dentate ligands. EDTA acts as a chelating agent because each nitrogen and one oxygen from each of the four carboxylic acid groups has an electron pair to , donate (ligand- a substance that binds with a metal ion to form a complex ion) to a metal ion center, making EDTA a hexadentate ligand which forms an octahedral complex. An indicator, Eriochrome Black T enables the detection of when the EDTA has completely chelated the metal impurities. In the presence of a metal cation, Eriochrome Black T forms a pink complex.

2.0 OBJECTIVE

At the end of this unit you should be able

- Define hardness of water
- Standardize an EDTA solution
- Describe the function of EDTA in the experiment
- to perform an experiment to determine hardness of water using complexometric titration

3.0 MAIN CONTENT

3.1 Principle This is a complexometric titration of calcium and magnesium with an aqueous solution of disodium salt of EDTA at pH value of 10 and Mordant black 11 as an indicator, which forms claret or a violet color in the presence of calcium and magnesium ions.

The sodium salt of EDTA dissociates into ions in aqueous solution
$Na_2Y_2H_2.2H_2O(s) \rightarrow 2Na^+ (aq) + H_2Y^{2-} (aq) + 2H_2O(l)$

During the titration EDTA reacts first with free calcium and magnesium ions in the solution

$Me^{2+} (aq) + H_2Y^{2-} (aq) \leftrightarrow MeY^{2-} (aq) + 2H^+ (aq)$
$Me^{2+} (Ca^{2+}, Mg^{2+})$

and at the end/equivalent point EDTA reacts with the calcium and magnesium ions superseded from their complexes, which were created with the indicator molecules, liberating indicator and causing the color to change from claret or violet to blue.
At the equivalence point the amount is:

$n(Ca^{2+} + Mg^{2+}) = n(EDTA)$

The results are given in amount of substance concentration (molarity).

3.2 Apparatus

Instruments

Calibrated analytical balance   Electric oven for drying

Ordinary laboratory apparatus

Weighing vessel
Burette, 25 mL capacity, graduated in divisions of 0.05 mL, class A or equivalent
2 x Analytical flasks 1000 ml
Polyethylene bottle 1 L
4 x Erlenmeyer flasks 500 mL, 250 mL

Reagents and materials

Ammonia buffer solution
EDTA standard solution

Materials

Ammonium chloride
Ammonia solution w = 25%, ρ (20 0C) = 0.91 g/mL
Disodium magnesium salt of EDTA ($C_{10}H_{12}N_2O_8$ Na_2Mg)
Disodium salt of EDTA dehydrate ($C_{10}H_{14}N_2O_8Na_2.H_2O$)
Mordant black 11 ($C_{20}H_{12}N_3O_7SNa$)
Eriochrome black T
Hydrochloric acid 4 mol/L
Methyl red indicator
Triethanolamine ($(OHCH_2CH_2)_3N$)
Ethanol

Reagent solutions

Ammonia buffer solution

Dissolve 67.5 g of ammonium chloride in 570 mL of ammonia solution. Then add 5.0 g sodium magnesium salt of EDTA and dilute to 1000 mL with distilled water

EDTA Standard volumetric solution c = 10 mmol/L.
Dry a portion of EDTA dihydrate salt for 2 h at 105 0C, dissolve 3.725 g of the dry salt in water and dilute to 1000 mL in the volumetric flask.
Store EDTA solution in a polyethylene bottle and check the concentration at regular intervals.

Standardisation

Standardise the EDTA solution against the calcium reference standard solution by the procedure described in clause below
Use 20.0 mL of the calcium standard reference solution and dilute to 50 mL.
The concentration of the EDTA solution c(EDTA) expressed in millimoles

per litre is given by relationship

$$c(\mathrm{EDTA}) \,.\, V(\mathrm{EDTA}) = c(\mathrm{Ca2+}) \,.\, V(\mathrm{Ca2+})$$

Where

$c(\mathrm{Ca2+})$	is the concentration expressed in milimoles per litre of the standard reference solution
$V(\mathrm{Ca2+})$	is the volume in millilitres of the calcium standard reference solution
$V(\mathrm{EDTA})$	is the volume in millilitres of the EDTA solution used for stadardization

$$c(\mathrm{EDTA}) = \frac{c\,(Ca^{2+}),V(Ca^{2+})}{V(EDTA)}$$

Calcium standard reference solution $c(\mathrm{CaCO_3})$ = 10 mmol/L
Dry a sample of pure calcium carbonate for 2 hours at 150 ^{o}C, and allow cooling to room temperature in a desiccator. Place 1.001 g of it in a 500 mL conical flask and moisten it with distilled water. Add 4 mol/L hydrochloric acid in drops until all carbonate is dissolved. Avoid adding excess acid. Add 200 mL of water and boil for few minutes to strip out carbondioxide. Cool to room temperature and add a few drops of methyl red indicator solution. Add 3 mol/L ammonia solution until the solution turns orange. Transfer the solution quantitatively to a 1000 mL volumetric flask and make up to the mark with distilled water.
1 mL of the solution contains 0.4008 mg (0.01 mmol) of calcium.
Note - Commercially available solution may be used.

Mordant black 11, indicator
Dissolve 0.5 g of mordant black 11, the sodium salt of (1-(1-hydroxi-2naphtylazo-6-nitro-2-naphtol-4-sulfonic acid) in 100 mL triethanolamine. Up to 25 mL ethanol may be added instead of triethanolamine to reduce the viscosity of the solution.
NOTE- To facilitate the detection of the end point, the indicator may be modified by the solution of 0.17 g methanol salt (4-anilido azobenzene sulfonic acid sodium salt.). The color will now change from red to pale grey or green.

3.3 Procedure

Using a pipette transfer 50.0 mL of the test solution to a 250 mL conical flask. Add 4 mL of buffer solution and 3 drops of Mordant black 11 indicator. The color of the solution should now turn to claret or violet and the pH value should be 10.0 ± 0.1.

Titrate immediately. Add the EDTA solution when the color of the solution starts to change from claret or violet to blue. The end point is reached when the last shade has disappeared.

Titrate additional test portion in the following manner.
Transfer 50.0 mL of the test solution in to a flask. Add EDTA solution to the sample amounted 0.5 mL less, than it was consumed for the first sample. Add 4 mL of the buffer solution and 3 drops of mordant black 11 indicator. Add EDTA until the end point is reached.

If the consumption of EDTA is less than 4.5 mL, titrate a smaller sample volume. Add distillated water until reaching a total titrated volume of 50 mL.

If the consumption of EDTA solution exceeds 20 mL, titrate using a small test portion. Add distillated water so that the starting volume is 50 mL.

Expression of the results

The sum of calcium and magnesium contents c (Ca^{2+} + Mg^{2+}) expressed in millimoles per litre is given by the relationships

$$\mathrm{V}(sample).c(Ca^{2+} + Mg^{2+}) = V(EDTA).c(EDTA)$$

$$c(Ca^{2+} + Mg^{2+}) = \frac{V(EDTA).c(EDTA)}{V(sample)}$$

$V(EDTA)$ the volume in millilitres of EDTA used in the titration
$c(EDTA)$ is the concentration expressed in millimoles per litre of the EDTA solution.
$\mathrm{V}(sample)$ is the volume in millilitres of the test solution (normally 50 mL)
For calculation of hardness see the annex.

Precision

The repeatability of the procedure is ± 0.04 mmol/L, corresponding to approximately 2 drops of the EDTA solution

Result

Average $c(Ca^{2+}+Mg^{2+})$ $(mmol/L)$

4.0 CONCLUSION

Hardness of water can be determined using laboratory complexometric titration.

5.0 SUMMARY

In this unit you have learnt the following**:**

- Ground water in particular and fresh water flowing in rivers and canals or waters in ponds and lakes are having different metal salts in different proportions.
- Sometimes these metal ions can be easily removed by boiling or simple precipitation when the quality of water is termed as temporary hardness.
- Some waters have these metal salts in such form that it cannot be removed by simple means.
- This quality of water is known as permanent hardness. It is easy to determine simple metal ions by using simple titration techniques.
- But to establish the exact amounts of various metal ions in a sample of hard water, a complexometric titration is required and these titrations are conducted by using EDTA.
- You have performed an experiment to determine water hardness using complexometric titration

6.0 TUTOR MARKED ASSIGNMENT

1. When determining the total calcium and magnesium ion content in water using EDTA, which of the following is established?

a carbonate hardness $c(\mathrm{Ca^{2+}})$
b magnesium hardness $c(\mathrm{Mg^{2+}})$
c total hardness $c(\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}})$

2. What is the function of EDTA in determination of water hardness ?
3. Mention two indicators used in the complexometric determination of water hardness of water.
4. You are using EDTA with a molarity of .0080 for the titration. You titrate 50.00 mL of water sample using 10.68 mL of EDTA.
   What is the CONCENTRATION of $\mathrm{Ca^{2+}}$ ion?

solution

$$\frac{\text{moles } \mathrm{Ca^{2+}} \text{ion}}{1\ \mathrm{L}} = \frac{(\text{molarity EDTA})\ (\text{mL EDTA added})}{50.00\ \text{mL of water sample titrated}}$$

$$\frac{\text{moles } \mathrm{Ca^{2+}} \text{ion}}{1\ \mathrm{L}} = \frac{(.0080\ \mathrm{M})\ (10.68\ \mathrm{mL})}{50.00\ \text{mL water}} = .0017\ \mathrm{M}$$

What is the hardness?

$$\text{ppm } \mathrm{CaCO_3} = \frac{(\text{mol } \mathrm{Ca^{2+}})\ (1\ \text{mol } \mathrm{CaCO_3})\ (100.1\ \text{g } \mathrm{CaCO_3})\ (10^3\ \text{mg})}{(1\ \mathrm{L})\ \ (1\ \text{mol } \mathrm{Ca^{2+}})\ \ (1\ \text{mol } \mathrm{CaCO_3})\ \ (1\ \mathrm{g})}$$

$$\text{ppm CaCO} = \frac{(.0017\ \text{moles})(1\ \text{mol } \mathrm{CaCO_3})(100.1\ \text{g } \mathrm{CaCO_3})(10^3\ \text{mg})}{(1\ \mathrm{L})\ (1\ \text{mol } \mathrm{Ca^{2+}})(1\ \text{mol } \mathrm{CaCO_3})(1\ \mathrm{g})} = 170\ \text{ppm}$$

5.

7.0 REFERENCES/FURTHER READING

- **http://standardbase.vapronet.nl/userdata/sbase_beheer/documenten/stappenplannen/Determination_of_hardness_of_water_%28Step-By-Step_Plan%29.pdf**
- **http://www.studymode.com/essays/Complexometric-Determination-Of-Water-Hardness-866293.html**
- **http://www.scribd.com/doc/47084424/Experiment-Complexometric-Titration**

MODULE 3

UNIT 1 Synthesis of Alum from Aluminum

5.0 INTRODUCTION

Alums are ionic compounds that crystallize from solutions containing sulfate ion, a trivalent cation such as Al^{3+}, Cr^{3+}, or Fe^{3+} and a monovalent cation such as K^+, Na^+, or NH_4^+. Six of the water molecules bind tightly to the trivalent metal ion; the remaining six molecules bind more loosely to the monovalent cation and the sulfate anion.

In this experiment you will prepare an alum–$KAl(SO_4)_2 \cdot 12H_2O$ [potassium aluminum sulfate dodecahydrate]–from an aluminum beverage can. This compound is widely used in dyeing fabrics, making pickles, making paper and purifying water.

Aluminum is the most abundant metal in the earth's crust (8.3% by weight) and is the third most abundant element after oxygen (45.5%) and silicon (25.7%). Pure aluminum is a silvery-white metal and has many desirable physical and chemical properties: it is light-weight, non-toxic, corrosion-resistant, nonmagnetic, and malleable. Aluminum is commonly combined with other metals such as copper, manganese, silicon, magnesium, and zinc, which produces alloys with high mechanical and tensile strength. You are probably familiar with many uses of aluminum and its alloys.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- Use aluminum from an aluminum can to synthesize a chemical compound, alum, (hydrated potassium aluminum sulfate,$KAl(SO_4)_2.12H_2O$).
- jPerform some stoichiometry calculations, specifically the percent yield of product.

3.0 MAIN CONTENT

3.1 Theory: Aluminum beverage cans generally have a thin coating of plastic on the inside that protects the aluminum from the corrosive action of the chemicals in the beverage. The outside usually has a thin coating of paint. These coatings must be removed before any chemical reactions with the metal can be carried out. The coatings may be effectively scraped off with a metal pan cleaner. A cleaned piece of metal is then dissolved in a potassium hydroxide solution according to the following complete, balanced equation:

The full and net ionic equations are:

$$2Al_{(s)}+2KOH_{aq}+6H_2O_{liq} \rightarrow 2KAl(OH)_{4_{aq}}+3H_{2(g)}$$
$$2Al_{(s)}+2OH_{aq}+6H_2O_{liq} \rightarrow 2Al(OH)^-_{4(aq)}+3H_{2(g)}$$

The $Al(OH)_4^-$ ion is a complex ion called "aluminate." After filtration to remove residual plastic and paint decomposition products, the alkaline solution of $Al(OH)_4^-$ - is **clear** and **colorless**. The H_2 is evolved as a gas and mixes with the atmosphere. The chemical species in solution are potassium ions (K^+) and aluminate ions [$Al(OH)_4^-$] -] ions (plus any unreacted KOH).

Sulfuric acid is now added and two sequential reactions occur. Initially, before the addition of all the acid, insoluble aluminum hydroxide is formed,

$$2KAl(OH)_{4\,(aq)}+H_2SO_{4(aq)} \rightarrow 2Al\,(OH)_{3\,(s)}+2H_2O_{(liq)}+K_2SO_{4(aq)}$$
$$Al(OH)^-_{4(aq)}+H^+_{(aq)} \rightarrow Al(OH)_{3\,(s)}+H_2O_{(liq)}$$

$Al\,(OH)_3$ to give a thick, white, gelatinous precipitate of aluminum hydroxide. As more sulfuric acid is added, the precipitate of $Al\,(OH)_3$ dissolves to form soluble Al^{3+}ions.

The full and net ionic equations are:

$2Al(OH)_{3\,(s)}$ $+3H_2SO_{4\,(aq)} \rightarrow Al_2(SO_4)_{3\,(aq)}$ + $6H_2\,O_{(liq)}$
$Al(OH)_{3\,(s)}$ $+3H^+_{(aq)} \rightarrow Al^{3+}_{(aq)}$+ $3H_2\,O_{(liq)}$

to give aluminum ions, Al^{3+}, in solution. The solution at this point contains Al^{3+}ions, K^+ ions (from potassium hydroxide), and SO_4^{2-}ions (from sulfuric acid). On cooling, crystals of **hydrated** potassium aluminum sulfate, $KAl(SO_4)_2.12H_2O$ (or alum) are very slowly deposited. In the experiment the crystallization process is speeded up by providing a small “seed crystal" of alum for the newly forming crystals to grow on. Cooling is needed because alum crystals are soluble in water at room temperature.

The full and net ionic equations are:

$Al_2(SO_4)_{3\,(aq)}$ $+K_2SO_{4(aq)}$ + $24H_2O_{(liq)} \rightarrow 2\;KAl(SO_4)_2.12H_2O$

$K^+_{(aq)}$ $+Al^{3+}_{(aq)}$ + $22SO^{2-}_{4\,(aq)}$ + $12H_2O_{(liq)} \rightarrow KAl(SO_4)_2.12H_2O_{(s)}$

Finally, the crystals of alum are removed from the solution by vacuum filtration and washed with an alcohol/water mixture. This wash liquid removes any contamination from the crystals but does not dissolve them. It also helps to dry the crystals quickly, because alcohol is more volatile than water.

3.2 Experimental Procedure

CAUTION!! Excess care must be used in handling potassium hydroxide (KOH) and sulfuric acid (H_2SO_4). KOH is corrosive and will dissolve clothing and skin! Sulfuric acid will also burn and dissolve clothing. Wash your hands thoroughly after using either of these solutions!

A piece of scrap aluminum will be provided. Use steel wool to remove as much paint as possible. The inside of the can is protected with a plastic coating and you should remove this also. Weigh the cleaned strip of aluminum to the nearest 0.001 grams.

Cut the Al sample into small squares and place the squares in a clean 100-mL or 150-mL beaker. Perform the following in the hood!! Carefully add 20 mL of 4 M potassium hydroxide, KOH. Bubbles of hydrogen gas should evolve. Place your beaker on a hot plate in the hood to speed up the reaction. When hydrogen bubbles are no longer formed, the reaction is complete. This should take 10-15 minutes. Remove the beaker from the hot plate and allow it to cool at your bench.

The resulting grayish mixture should be filtered to remove unwanted impurities. If the solution is still warm, cool it by placing the beaker in an ice bath. Set up a 250-mL filter flask and Gooch filter crucible or Büchner funnel as demonstrated. Don't forget to clamp the filter flask to some kind of support. Filter the solution slowly. Rinse the beaker two times with small portions (<5 mL) of distilled water, pouring each rinse through the filter. Transfer the clear colorless filtrate to a clean 250-mL beaker.

To the cool solution, slowly and carefully, with stirring, add 15 mL of 6 M sulfuric acid. White lumps of $Al(OH)_3$ should form in the solution . Again working in the hood, heat and stir the mixture to dissolve the white lumps. Excess sulfuric acid may be added dropwise, but no more than 30 mL total, in order to totally dissolve the $Al(OH)_3$, and give a clear solution. Cool the clear solution in an ice bath for at least 20 minutes. Crystals of alum should fall to the bottom of the beaker. If no crystals form, scratch the bottom of the beaker with your stirring rod. If that fails, add a "seed" crystal of alum to facilitate crystallization.

While the solution is cooling, reassemble the filtration apparatus. Be sure to weigh the filter paper at this point. Slowly filter the solution containing the crystals. Rinse the beaker once with 5 mL of cool distilled water and once with 5 mL of isopropyl (rubbing) alcohol, pouring each rinse through the filter. Allow the aspirator to pull air through the crystals until they appear dry, at least 5 minutes. Remove the filter from the flask. More crystals may form in the filtered solution (filtrate). If you have time, filter these crystals as just described, and add these to the first crystal crop.

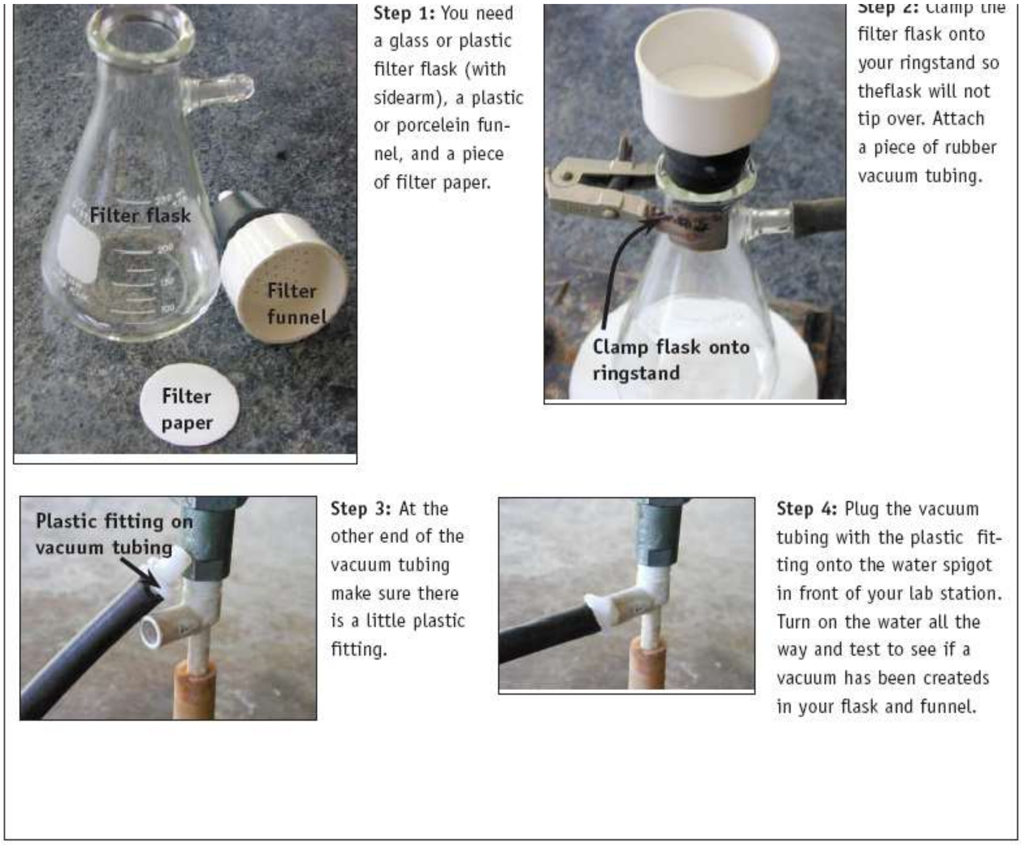
Remove the damp crystals and filter paper from the filter and place them into a weighed beaker. Place the beaker containing your crystals in your locker until next week. After drying, weigh the filter and crystals,and determine the mass of the alum produced.
Calculate the percent yield.

Determine the melting point of the alum crystals using the following procedure. Carefully, push the open end of a capillary tube into your crystals, forcing some of the solid into the tube. Turn the tube over and tap it gently to move the crystals to the sealed end of the tube. Repeat this process until you have about 5 mm of solid in the capillary tube. Carefully, insert the tube into the melting point apparatus. **The apparatus will be HOT if others have been using it!** Note the temperatures at which the alum first appears to melt (*i.e.* when liquid first becomes visible) and at which it is completely melted (all liquid). Discard the capillary tube in the glass bin.

Obtain the literature value for the melting point of alum. Compare your experimental melting point to the literature value. Calculate the percent error.

REPORT

Prepare a brief report describing your observations during the experiment. Report the actual yield, the theoretical yield and the percent yield



Step 1: You need a glass or plastic filter flask (with sidearm), a plastic or porcelein funnel, and a piece of filter paper.

Step 2: Clamp the filter flask onto your ringstand so theflask will not tip over. Attach a piece of rubber vacuum tubing.

Step 3: At the other end of the vacuum tubing make sure there is a little plastic fitting.

Step 4: Plug the vacuum tubing with the plastic fitting onto the water spigot in front of your lab station. Turn on the water all the way and test to see if a vacuum has been createds in your flask and funnel.

4.0 CONCLUSION

Alum is a potassium aluminum sulfate dodecahydrate. It is a white crystal that can be used for water purification, leather tanning, as an astringent, and in baking powder. Alum is made from scrap aluminum metal.

5.0 SUMMARY/CALCULATIONS

CALCULATIONS

The stoichiometry involved in the sequence of reactions leading to the preparation of alum provides the mole relationship between aluminum and alum that is required to calculate the percentage yield.

$$2Al_{(s)} + 2KOH_{aq} + 6H_2O_{liq} \rightarrow 2KAl(OH)_{4_{aq}} + 3H_{2(g)} \qquad (1)$$

$$2KAl(OH)_{4\,(aq)} + H_2SO_{4(aq)} \rightarrow 2Al\,(OH)_{3\,(s)} + 2H_2O_{(liq)} + K_2SO_{4(aq)} \qquad (2)$$

$$2Al(OH)_{3\,(s)} + 3H_2SO_{4\,(aq)} \rightarrow Al_2(SO_4)_{3\,(aq)} + 6H_2\,O_{(liq)} \qquad (3)$$

$Al_2(SO_4)_{3\,(aq)} + K_2SO_{4(aq)} + 24H_2O_{(liq)} \rightarrow 2\ KAl(SO_4)_2.12H_2O$ (4)

$2molAl_{(s)} + 2KOH_{aq} + 4H_2SO_{4(aq)} + 22H_2O_{(liq)} \rightarrow 2\ KAl(SO_4)_2.12H_2O + 3H_{2(g)}$ (5)

MOLAR MASSES
Al, 26.98 g/mol
KAl(SO4)2•12H2O,
474.39 g/mol

The **overall reaction** for the synthesis of alum, equation (5), is obtained by adding reactions (1-4) and canceling like-species. The overall reaction stoichiometry (5) informs us that 2 moles of aluminum will produce 2 moles of alum.

Your *calculations* should proceed as follows:
a) Calculate the number of moles of Al used from the mass of Al used.
b) Knowing that the stoichiometric factor is

Stoichiometric factor $= \frac{2\ mol\ KAl(SO_4)2.12H_2O}{2molAl}$

calculate the quantity of alum), $KAl(SO_4)_2.12H_2O$ in moles, that should be produced theoretically from the quantity (in moles) of aluminum metal used.
Enter this calculation on your report form.
c) Knowing the number of moles of $KAl(SO_4)_2.12H_2O$ expected, calculate
the mass of $KAl(SO_4)_2.12H_2O$ expected (the ***theoretical yield***). Enter this on your report form.
d) Calculate the ***percentage yield*** of alum, if

$$\%\ \text{yield} = \frac{\text{mass of alum obtained (g)}}{\text{mass of alum theoretically obtainable (g)}} \times 100\%$$

Enter the result of your percent yield calculation on your report.

Give the completed report form to your laboratory instructor by the indicated due date. Be sure that your instructor also has the sample of the alum that you prepared.

EXPERIMENTAL DATA
Mass of aluminum used ________________________________
Mass of paper or beaker + $KAl(SO_4)_2.12H_2O$ ______________________
Mass of paper or beaker ______________________
Mass of $KAl(SO_4)_2.12H_2O$ ______________________

6.0 TUTOR MARKED ASSIGNMENT

Show your calculations throughout!

1. How many moles of aluminum metal did you use?

2. Assuming that Al metal is the limiting reagent, what quantity of potassium aluminum sulfate (alum), in moles, is theoretically obtainable?

3. What mass of potassium aluminum sulfate (alum, $KAl(SO_4)_2.12H_2O$), in grams, is theoretically obtainable from your mass of Al? That is, what is the ***theoretical yield*** of alum?

4. What was the ***percentage yield*** of your product, $KAl(SO_4)_2.12H_2O$?

7.0 REFERENCES/FURTHER READING

1. **http://www.mesacc.edu/~paudy84101/CHM151LL/6B%20Alum.pdf**
2. **http://wwwchem.csustan.edu/archive/alum.htm**
3. **http://www.bc.edu/schools/cas/chemistry/undergrad/gen/fall/Alum.pdf**

UNIT 2 The Analysis of Alum

1.0 INTRODUCTION

After a compound has been synthesized, tests should be carried out to verify that the compound formed is indeed the compound desired. There are a number of tests that can be performed to verify that the compound is the one desired. In the previous unit you prepared alum crystals, $KAl(SO_4)_2{\bullet}12H_2O$. In this unit, you will conduct a series of tests to determine if your crystals are really alum.The first test is to find the melting temperature of the compound and compare this value with the accepted (published) value for alum (92.5°C). The second test determines the water of hydration present in the alum crystals. The third test is a chemical test to determine the percent sulfate in your sample of alum.

2.0 OBJECTIVES

At the end of this unit ,you should be able to:

- Determine the melting temperature of a sample of alum.
- Determine the water of hydration of a sample of alum.
- Determine the % sulfate of alum

3.0 MAIN CONTENT

3.1 Materials

Part I : Melting Temperature Test Materials

Melting point apparatus
capillary tubes
alum crystals, $KAl(SO_4)_2{\bullet}12H_2O$
hot plate
Bunsen burner

mortar and pestle

Part II : Water of Hydration Test Materials

crucible with cover	alum crystals, $KAl(SO_4)_2 \bullet 12H_2O$
balance	ring stand, ring, and clay triangle
lab burner	tongs or forceps

3.2 Procedure

Part I Determine the Melting Temperature of Alum

1. Obtain and wear goggles.

2. Use a mortar and pestle to pulverize about 0.5 g of dry alum and place it in a small pile in the mortar. Push the open end of a capillary tube into the pile of the alum powder. Pack alum into the capillary tube to a depth of about 1 cm by tapping the tube lightly on the table top.

3. Insert the capillary tube into the aluminum sample block of the melting point apparatus. Adjust the angle of viewing for maximum comfort.

4. To begin the melt cycle presses '*START'* key. The pump will stop and the unit will heat at maximum rate to the pre-programmed plateau temperature. The screen will show '*HEATING'* along with the current temperature of the block.

5. When melt has occurred press '*STOP'*. The display will change to '*COOLING TO AMBIENT'* and the cooling pump can be heard.

6. Conduct a second test with a new sample of alum in a new capillary tube.

Part II Determine the Water of Hydration of Alum

7. Heat a crucible with cover over a burner flame until it is red hot. Allow the crucible to cool, and then measure the total mass of the crucible and cover. Handle the crucible with tongs or forceps to avoid getting fingerprints on it.

8. Place about 2 g of your alum crystals in the crucible, and then measure the mass of the crucible, cover, and alum. Record this measurement in the data table.

9. Set up a ring, ring stand and triangle over a lab burner. Use tongs or forceps to set the crucible at an angle on the triangle and place the cover loosely on the crucible. Use a lab burner to very gently heat the crucible of alum until you can see no vapor escaping from the crucible. It is important that the vapor does not carry any alum with it. After the vapor is gone, heat the crucible more strongly for five minutes, and then cool the crucible.

10. Measure and record the mass of the crucible, cover, and alum after drying.

11. Reheat the crucible and alum sample for five additional minutes. Cool and measure the mass of the crucible again. If the two masses are the same (or very nearly so), the test is done. If not, repeat the heating and weighing until a constant mass is obtained

Part III Determine the Percent Sulfate of Alum

12. Obtain a clean, dry Gooch crucible and measure its mass. If you are not using a Gooch crucible, then use the finest-grain filter paper available, such as Whatman No. 42, because the very tiny particles of barium sulfate precipitate will pass through most paper filters. Measure and record the mass of the filter paper.

13. To clean a Gooch crucible, assemble the crucible, Walters adapter, and filter flask. Use suction to draw distilled water through the filter pad. Place the crucible in a beaker and dry it in an oven.

14. Measure the mass of about one gram of your alum sample into a 250 mL beaker. Add about 50 mL of distilled water to the beaker of alum and stir the mixture to dissolve the sample.

15. Calculate the volume of 0.20 M $Ba(N0_3)_2$ solution that is needed to completely precipitate the sulfate ions in the beaker of alum solution. Measure out twice the volume that you have calculated, and slowly add it to the beaker of alum solution. Stir the mixture to ensure complete mixing of the reagents. CAUTION: *Handle the barium nitrate solution with care. This solution is toxic.*

16. Select one of the two methods below for preparing the precipitate:

- Set up a ring stand, ring and wire gauze for heating over a lab burner. Place a watch glass over the beaker and heat the beaker of your reaction mixture over a lab burner. Heat the mixture to near boiling for 15 minutes. This step helps collect the particles of precipitate to a larger size and eases the filtering process.
- Use a watch glass to cover the beaker of reaction mixture. Store the beaker in a safe place overnight.

17. Allow the mixture to cool. Filter the beaker of precipitate through the Gooch crucible with suction (or use a filter paper and funnel). Add liquid to the crucible very slowly, because the

DATA TABLE

Part I Melting Temperature Test Results	Trial 1	Trial 2
Melting Temperature (°C)		

Part II Water of Hydration Test Results	Trial 1	Trial 2
Mass of crucible and cover (g)		
Mass of crucible, cover, and alum before heating (g)		
Mass of crucible, cover, and alum after 1st heating (g)		
Mass of crucible, cover, and alum after 2nd heating (g)		
Mass of crucible, cover, and alum after final heating (g)		

Part III Percent Sulfate Test Results	Trial 1	Trial 2
Mass of Gooch filter *or* filter paper (g)		
Mass of alum before reaction (g)		
Mass of Gooch filter *or* filter paper and precipitate (g)		

4.0 CONCLUSION

Alum is a salt compound and contains aluminum, potassium, hydrogen, oxygen and sulfur. A solution of sulfuric acid is used to extract alumina from its ore form, bauxite.

5.0 SUMMARY

In the unit you have been able to carry out an analysis on the alum sample which you synthesized in the previous unit.

6.0 TUTOR MARKED ASSIGNMENTS (TMA)

1. Is your sample alum? Use the results of the three tests to support your answer. Discuss the accuracy of your tests and possible sources of experimental error.

2. Suggest other tests that could be conducted to verify the composition of your alum.

3. If the melting temperature test was the only test that you conducted, how confident would you be in the identification of your sample? Explain.

7.0 REFERENCES/FURTHER READING

1. http://chemlab.truman.edu/CHEM130Labs/Alum.asp
2. http://www.juniata.edu
3. http://infohost.nmt.edu/~jaltig/AlumAnalysisAlter.pdf

4. http://www.ehow.com/info_8036479_alum-crystals.html

UNIT 3 Preparation of $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ (Hexaamminecolbalt(III) Chloride and Tris(ethylenediamine)

1.0 INTRODUCTION

Cobalt has the outer electronic configuration $3d^7 4s^2$ and its highest significant oxidation state is +4. This reflects the trend towards decreased stability of the very high oxidation state on moving across the transition metal series. Cobalt (I) forms some complexes, most with p-bonding ligands. The chemistry of cobalt (I) is better characterized than any other unipositive oxidation state of the first transition series except copper. The two most important oxidation states are cobalt(II) $[Ar]3d^7$ and cobalt(III) $[Ar]3d^6$, and in an aqueous solution containing no complexing agent cobalt(III) is easily reduced to cobalt(II). However, cobalt (III) is more stable in the presence of a complexing agent such as ammonia as shown by the electrode potentials.

$[Co(H_2O)_6]^{3+} + e^- = [Co(H_2O)_6]^{2+}$ $E^o = 1.85V$. $[Co(NH_3)_6]^{3+} + e^- = [Co(NH_3)_6]^{2+}$ $E^o = 0.1V$

Cobalt(II) forms both octahedral and tetrahedral complexes but they are labile and they have a strong tendency to be oxidized by molecular oxygen. The complexes are usually prepared in an inert atmosphere. In aqueous solution the cobalt (II) ion is pale pink because the absorption is weak and occurs in the blue region of the visible. Tetrahedral cobalt (II) complexes are often highly colored owing to their lower order of symmetry relative to the octahedral complexes. The spectrum of $[CoCl_4]^{2-}$ shows a large absorption in the visible part of the spectrum, which accounts for its deep-blue color.

Cobalt (III) salts are difficult to prepare because the ion is a strong oxidizing agent and the chemistry of this oxidation state is largely that of coordination compounds. Cobalt (III) usually forms octahedral complexes and it has a strong affinity for nitrogen donors such as ammonia, amines(e.g. ethylenediamine), nitro groups and nitrogen bonded-SCN groups as well as water molecules and halide ions

2.0 OBJECTIVE

At the end of this unit you be able

- Identify the most important oxidation states
- Describe three methods by which Co(III) salt can be

3.0 MAIN CONTENT

3.1 Preparation of $[Co(NH_3)_6]Cl_3$

Hexaamminecobalt(III) salts may be prepared by any of three methods that depend on oxidation of cobalt(II) ion in ammoniacal solution:

(1) Air oxidation, with formation of the pentamine ion, which is converted to the hexamine by heating with aqueous ammonia under pressure;

(2) Oxidation with an agent such as hydrogen peroxide, iodine, potassium permanganate, lead oxide, or hypochlorite solution;

(3) Oxidation in the presence of a catalyst that allows equilibrium between the pentamine and hexamine ions to be established at room temperature and atmospheric pressure. These compounds may also be prepared indirectly from other hexaminecobalt(III) salts.

In the best of the catalytic methods diamminesilver ion or decolorizing charcoal is used as a catalyst. The method devised by J.Bjerrum in which decolorizing charcoal is catalyst is simple, gives high yields of pure product, and is not time-consuming. A high concentration of ammonium salt is sufficient to stabilize the hexaminecobalt(III) ion, and the carbon serves only to establish the equilibrium. Air is used as oxidant except when the cobalt (II) compound is slightly soluble in the ammoniacal solution, as in the preparation of $[Co(NH_3)_6]Br_3$, for which hydrogen peroxide is preferable.

$4CoCl_2 + 4NH_4Cl + 20NH_3 + O_2 \rightarrow 4[Co(NH_3)_6]Cl_3 + 2H_2O$

3.1.1 Materials required $CoCl_2 \cdot 6H_2O$, NH_4OH, NH_4Cl, HCl, charcoal

3.1.2 Procedure 240g (1mol) of cobalt(II) chloride 6-hydrate and 160g (3mol) of ammonium chloride are added to 200ml of water. The mixture is shaken until almost of the salts are dissolved. Then 4g of activated decolorizing charcoal and 500ml of concentrated ammonia are added. Air is bubbled vigorously through the mixture until the red solution becomes yellowish brown (usually about 4hours). The air inlet tube is of fairly large bore (10mm) to prevent clogging with the precipitated hexamminecobalt(III) salt.

The crystals and carbon are filtered on a Buchner funnel and then added to a solution of 15 to 30ml. of concentrated hydrochloric acid in 1500ml of water; sufficient acid reaction. The mixture is heated on a hot plate to effect complete solution and is filtered hot. The hexamminecobalt(III) chloride is precipitated by adding 400ml of concentrated hydrochloric acid and slowly cooling to $0^{o}C$. The precipitate is filtered, washed first with 60% and then with 95% alcohol, and dried at 80 to $100^{o}C$.

3.2 Preparation of $[Co(en)_3]Cl_3$

Ethylenediamine coordinates with metallic ions through both nitrogen atoms. The five-membered chelate rings that are thus formed are very stable. Many cobalt (III) ammines are converted by aqueous ethylenediamine to ethylenediamine cobalt (III) chloride. Thus, Jorgensen prepared the salt by heating $[Co(NH_3)_5Cl]Cl_2$ with aqueous ethylenediamine. Grossman and Schuck obtained the salt by oxidizing a mixture of cobalt(II) chloride, ethylenediamine, and water. The method described below has been developed from the latter suggestion.

3.2.1 Material required en, HCl, $CoCl_2{\cdot}6H_2O$

3.2.2 Procedure 61g of 30% ethylenediamine is partly neutralized with 17 ml of 6N hydrochloric acid and the resulting mixture poured into a solution of 24 g of $CoCl_2{\cdot}6H_2O$ in 75 ml. of water. The cobalt is oxidized by bubbling a vigorous stream of air through the solution for three hours. The solution allowed to evaporate on a steam bath until a crust begins to form over the surface (the volume will be about 15 to 20 ml.); then 15 ml. of concentrated hydrochloric acid and 30 ml.of ethyl alcohol are added. After cooling, the crystals of $[Co(en)_3]Cl_3$ are filtered and washed with alcohol until the washings are colorless. They are then washed with ether or dried in an oven.

Properties $[Co(en)_3]Cl_3$ crystallizes in orange-yellow needles, which are readily soluble in water but insoluble in the usual organic sovents. Its solubility in 6 N hydrochloric acid is about 3 %. It is stable at temperatures as high as 200^{o} and is decomposed only slowly by hydrogen sulfide and sodium hydroxide.

4.0 CONCLUSION

The preparation of hexammine cobalt(III) salts is prepared from cobalt(II) chloride hexahydrate, $CoCl_2{\cdot}6H_2O$, which is both stable and inexpensive..

Ethylenediamine cobalt (III) chloride is prepared from an aqueous solution of ethylenediamine and virtually any cobalt(II) salt, such as cobalt(II) chloride.

5.0 SUMMARY

In this unit you have been learnt how to perform two experiments to involving the transition element cobalt

6.0 TUTOR MARKED ASSIGNMENTS (TMA)

1. $[CoCl_6]^{3-}$ is orange while $[Co(NH_3)_6]^{3+}$ is yellow. Which of the following

statements is correct?

a) $[CoCl_6]^{3-}$ absorbs orange light.
b) The different colors are due to the different numbers of unpaired electrons on the complexes.
c) The two sets of d orbitals are split further apart in $[Co(NH_3)_6]^{3+}$ than they are in $CoCl_6]^{3-}$
d) The different colors are due to the different charges on the complexes.
2. Consider the complex compound $[Co(NH_3)_6]Cl_3$. What is the oxidation state of cobalt in this compound?

7.0 REFERENCES/FURTHER READING

1. **http://oliver.chemistry.ucsc.edu/151L/Expt1.pdf**

2. http://www.a-levelchemistry.co.uk/aqa%20a2%20chemistry/14.4%20Transition%20Metals/14.4%20Transition%20metals%20home.htm

3.http://courses.chem.psu.edu/Chem112/OldExams/TransMetal%20SampleQuestions.pdf

4 .http://www.sciencegeek.net/Chemistry/chempdfs/safetycontract.pdf

UNIT 4 Limiting Reactant

1.0 Introduction

Most chemical reactions require two or more reactants. Typically, one of the reactants is used up before the other, at which time the reaction stops. The chemical that is used up is called the ***limiting reactant*** while the other reactant is present in ***excess***. If both reactants are present in exactly the right amount to react completely, without either in excess, the amounts of reactants are said to be in a ***stoichiometric* ratio** to each other. The stoichiometric ratio is the mole ratio of the reactants, or reactants to products, as determined by the coefficients in the balanced chemical equation. Since the limiting reactant will determine the amount of product that can be produced during a reaction, it is important to be able to calculate which reactant is the limiting reactant. There are several ways to do this, but each starts with a balanced chemical equation so that the stoichiometry of the reaction is known.

2.0 Objectives

At the end of this unit you will achieve the following:

- Explain limiting reaction
- Explain stoichiometric ratio
- Percent yield
- Perform an experiment to determine limiting reactant using percent yield

3.0 Main Content

3.1 Theory

Many times an analysis will be based on the fact that you have a limiting reactant involved in the chemical reaction. The limiting reactant determines the percent yield of product. Because chemicals react stoichiometrically, only a limited amount of product forms from given amounts of reactants. For example, the analysis of a sample containing soluble sulfate salt such as sodium sulfate can be performed by dissolving the sample in water and adding a solution containing barium chloride to form an insoluble barium sulfate salt and sodium chloride which is soluble.

$$Na_2SO_{4(aq)} + BaCl_{2\,(aq)} \rightarrow BaSO_{4(s)} + 2NaCl_{(aq)}$$

Since all of the salts, except $BaSO_4$, are soluble, the net ionic equation for the chemical reaction is $Ba^{+2}_{(aq)} + SO^{-2}_{4\,(aq)} \rightarrow BaSO_{4(s)}$

.

One mole of barium ion, from $BaCl_2\,.2H_2O$ (244.2g) in solution, reacts with 1 mole of sulfate ion, from 1 mole of Na_2SO_4 (142.lg) in solution, to produce 1 mole of barium sulfate precipitate (233.4g) if the reaction takes place completely. The reaction is referred to as being quantitative since it will allow the determination of the amount of sodium sulfate in the sample. Sodium sulfate is the limiting reactant and to ensure that a total, complete reaction takes place an excess of barium chloride solution is added.

A 1.000 g sample of unknown salt mixture containing sodium sulfate is weighed to the nearest 1mg. The number of moles of sodium sulfate are calculated as if this were a pure sample of the sodium sulfate,

$$1.000\text{g}\ Na_2SO_4 \times \frac{1\,mole\ Na_2SO_4}{142.1g\ Na_2SO_4} \quad = \quad 7.030 \times 10^{-3} moles\ Na_2SO_4$$

thus representing maximum number of moles of sodium sulfate which may be present in the sample. Using the balanced equation:

$1.00\ mole\ SO_4^{-2}\ produces\ 1.00\ mole$ of $BaSO_4$,

Or

$= \quad 7.030 \times 10^{-3} moles\ SO_4^{-2}\ produces \quad 7.030 \times 10^{-3} moles\ \ BaSO_4$

And

$7.030 \times 10^{-3} moles\ \ BaSO_4 \times \frac{233.4g\ \ BaSO_4}{1\ mole\ \ BaSO_4} = 1.641g\ \ BaSO_4$

Thus, 1.641g $BaSO_4$ represents the maximum amount of precipitate that can be formed if the sample is 100% pure. This is referred to as the **theoretical yield** of the product. Since the sample is not pure sodium sulfate, you will obtain less than the theoretical amount which we will call the **experimental value**. The percentage of sodium sulfate in the unknown can be calculated using the **percent yield** formula which is defined as:

$$percent\ yield = \frac{experimental\ yield}{theoretical\ yield} \times 100$$

Many industrial products such as food ingredients, deodorants, mineral waters, and cosmetics would use this procedure for analysis of sulfate ion.

In this experiment an unknown salt mixture containing $Na_2SO_4$is analyzed for the percentage of Na_2SO_4 by adding excess $BaCl_2$ solution to ensure completeness of reaction. The other ingredient in the mixture is a nonreactive, soluble substance which will not interfere with the quantitative reaction. The precipitate, $BaSO_4$, will be vacuum filtered, dried, and weighed to obtain experimental yield of $BaSO_4$. The theoretical yield will be based on 100% activity of the salt mixture sample weighed.

3.2 Procedure

Weigh a clean, empty 400 ml beaker to the nearest 0.001 g. Add about 1.0 g of the unknown salt mixture to the beaker and reweigh the beaker to the nearest 0.001 g.

Calculate the number of moles of sodium sulfate that theoretically are contained in this sample weight. Also calculate the theoretical yield of $BaSO_4$as demonstrated in the theory section of this experiment.

Add 200 ml of distilled water to the beaker and stir with a stirring rod. In the hood, measure 1ml of concentrated HCl in a small graduated cylinder and with the aid of a stirring rod. Add to the solution in the beaker.

CAUTION: If spilled concentrated HC1, hydrochloric acid, is a severe skin irritant-flush affected area with large amounts of water.

In graduated cylinder, measure 50 ml of $BaCl_2$ 0.5 M and add to the solution in the beaker and stir for several minutes with a stirring rod. Allow the precipitate to settle. Verify that the amount of barium chloride added to the solution does, in fact, represent an excess of the reactant.
With the stirring rod in the beaker, cover the beaker with a watch glass and place the entire apparatus on a hot plate. Heat at low setting to maintain solution temperature between $80\text{-}90^0C$ for 1 hour. Check the temperature of the solution with your thermometer occasionally.
Avoid boiling the solution. Heat approximately 100ml of distilled water in a beaker to be used as the washing solvent.
While the solution is heating, assemble the vacuum filtration apparatus. Two types of filters will be used: a Buchner funnel with a paper filter and a fritted glass filtering crucible.
The advantage of vacuum filtration is the speed of isolation for a solid product from solution. One trial will be done recovering the precipitate on the paper and a second trial will recover the solid in the filtering crucible. It will require the recorded weight of both, paper and crucible. The order in which these two isolation methods are done is not a significant factor.
Before the filtration process is started, tip the beaker and allow the precipitate to settle under the lip of the beaker. While the solution is still hot, using beaker tongs, decant the supernatant liquid trying to minimize solid transfer to the filter. Wash the precipitate several times with warm distilled water, using a rubber policeman to remove any solid adhering to the sides of the beaker.
Using the wash bottle, transfer the precipitate to the filtering medium and rinse several times with the warm distilled water. Allow air. to be drawn through the filtering medium for several minutes after the last rinse. Break the vacuum seal at the filtering flask and remove the filtering medium to a clean, dry, preweighed, marked watch glass. Place the watch glass and filtering medium in drying oven for several hours or overnight. When the precipitate is dry, allow it to cool and weigh watch glass and filtering medium.
Calculate the weight of $BaSO_4$ isolated. Calculate the percent yield of the reaction. Report the average percentage yield on two trials.

4.0 **Conclusion** A limiting reactant is the reagent that is completely consumed during a chemical reaction. Once this reagent is consumed the reaction stops. An excess reagent is the reactant that is left over once the limiting reagent is consumed. The maximum theoretical yield of a chemical reaction is dependent upon the limiting reagent thus the one that produces the least amount of product is the limiting reagent.

5.0 **Summary** In this unit, you have studied about limiting reactant, excess reactant(reagent) stoichiometric ratio and percent yield .You have also performed an experiment to determine limiting reactant using percent yield.

6.0 Tutor Marked Experiment

1. Using a suitable reference source, define the following words:
a. Limiting reactant
b. Excess reactant
c. stoichiometric ratio
2 Take the reaction: $NH_3 + O_2 \rightarrow NO + H_2O$. In an experiment, 3.25 g of NH_3 are allowed to react with 3.50 g of O_2. a. Which reactant is the limiting reagent? **O_2**
b. How many grams of NO are formed? **2.63 g NO**
c. How much of the excess reactant remains after the reaction? **1.76 g NH_3 left**
3.Consider the reaction of $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$

a. What is the theoretical yield of C_6H_5Br if 42.1 g of C_6H_6 react with 73.0 g of Br_2? **71.8 g C_6H_5Br**

b. If the actual yield of C_6H_5Br is 63.6 g, what is the percent yield? **88.6%**

4. Use the following reaction: $C_4H_9OH + NaBr + H_2SO_4 \rightarrow C_4H_9Br + NaHSO_4 + H_2O$ If 15.0 g of C_4H_9OH react with 22.4 g of NaBr and 32.7 g of H_2SO_4 to yield 17.1 g of C_4H_9Br, what is the percent yield of this reaction?

61.8%

7.0 References/Further reading

1. www.gonzaga.org/document.doc?id=7496

2. www.lahc.edu/classes/chemistry/.../exp%204%20-%20**limiting**%20rf11.p.

3*www.uccs.edu/Documents/chemistry/nsf/103%20Expt3V-LR.pdf*

UNIT 5 The Empirical Formula of an Oxide

1.0 Introduction

Chemical formulas indicate the composition of compounds. A formula that gives only the simplest ratio of the relative number of atoms in a compound is the empirical formula or simplest formula. The ratio usually consists of small whole numbers. A formula that gives the actual numbers of each type of atom in a compound is called the molecular formula. The numbers in a molecular formula will be whole number multiples of the numbers in an empirical formula. To determine the molecular formula of a compound, we need to know both the empirical formula and the **molar mass** of the compound.

2.0 Objectives

At the end of this unit, you will be able to:

- Describe the concept of empirical formula.
- Determine the empirical formula of a metal oxide.
- Determine the mass and mole ratios of elements.
- Perform basic a laboratory measurements of mass and volume using appropriate glassware and equipment.

3.0 Main Content

3.1 Theory

A **chemical formula** is the simplest way to express information about the atoms that constitute any given chemical compound. A chemical compound is composed of atoms of two or more elements chemically combined in definite proportions. For example, H_2O and CO are compounds whereas H_2 is a diatomic element.

The atoms in a compound are held together by chemical bonds. The chemical formula helps identify each constituent element by its chemical symbol and indicates the number of atoms of each element in the compound. If a molecule contains more than one atom of a particular element, this number is indicated using a subscript after the chemical symbol. For example Copper (I) sulfide has a chemical formula of Cu_2S. In this compound there are two atoms of copper and one atom of sulfur. Copper and sulfur are combined in a ratio of 2:1. This formula also means that there are 2 moles of copper for every mole of sulfur.

The total mass of each element in a compound depends on the number of its atoms. For example, in compounds, CO and CO_2, the number of oxygen atoms are respectively, one and two. In other words, the mass of oxygen in CO_2 is twice as much as in CO. Yet another way to describe this is that one mole of carbon combines with one mole of oxygen in CO (mole ratio: 1:1) and one mole of carbon combines with two moles of oxygen in CO_2 (mole ratio: 1:2). This suggests that elements always combine in definite proportions by mass or moles. Accordingly, ratio of moles of the constituent elements in a compound is nearly always a ratio of small, whole numbers.

The formula containing the lowest possible whole number ratio is known as the empirical formula. The empirical formula does not necessarily indicate the exact number of atoms in a single molecule. This information is given by the molecular formula, which is always a simple multiple (**n**) of the empirical formula, i.e., Molecular formula (**MF**) = Empirical formula (**EF**) x **n**. The value of "**n**" can be derived by dividing the actual molar mass of the compound and empirical formula mass. Molar masses of the compounds are obtained from various experimental procedures including mass spectrometry technique.

To understand the behavior of a chemical compound one must first know its chemical formula. The process of the discovery of chemical formula of a compound begins with the determination of the ratio of the individual elements in a known mass of the compound (determination of empirical formula).

For most ionic compounds, empirical formula is the same as the compound's molecular formula. However, for covalent compounds the empirical formula is not necessarily the same as the molecular formula of the compound. For example, the empirical formula of water, H_2O, is the same as its molecular formula. The empirical formula of hydrogen peroxide is HO, but its molecular formula is H_2O_2. To determine whether or not a covalent compound's empirical and molecular formulas are the same, we need to know the molar mass of the compound.

To find the empirical formula we must combine the elements to form the compound under conditions that allow us to determine the **mass** of each element. From these data, the **moles** of each element may be determined. By dividing the moles obtained for each element by the smallest number of moles, we obtain quotients that are in a simple ratio of integers or they are easily changed to a simple ratio by multiplication process.

Sample calculations: Determination of an empirical formula of a compound based on experimental data Type equation here.is shown below.

Example: A strip of aluminum weighing 0.690 g is ignited yielding an oxide that weighs 1.300 g. Calculate the empirical formula of the compound formed.

We will follow the following strategy:

a. Determine the mass of each element.

b. Convert masses of elements to their respective moles.

c. Divide each of the moles by the smallest mole number.

d. Multiply the mole ratios with whole number integers until a whole number is obtained for each element.

a. We must first determine the mass of aluminum and oxygen in the oxide formed. Given we started with 0.690 g of aluminum, it yielded 1.300 g of an oxide.

$$\text{Mass of oxygen} = \text{Mass of product (aluminum oxide)} - \text{mass of aluminum}$$

i.e. $$Mass\ of\ oxygen = 1.300\ g - 0.690\ g$$
$$= 0.610\ g\ of\ oxygen$$

b. Now that we know the mass of aluminum and oxygen, we can calculate moles of each element.

$$Moles\ of\ Al = Mass\ of\ Al \times \frac{1\ mol\ Al}{Gram\ atomic\ mass\ of\ Al}$$

$$= 0.690g\ Al\ \frac{1\ mol\ Al}{26.982g\ Al}$$

$$= 0.0256\ mol\ Al$$

$$Moles\ of\ O = Mass\ of\ O\ \times \frac{1\ mol\ O}{Gram\ atomic\ mass\ of\ O}$$

$$= 0.610g\ O\ \frac{1\ mol\ O}{15.999g\ O}$$

$$= 0.0381\ mol\ O$$

c. Since we now know the moles of each element, ratio of atoms may be determined by dividing the moles of each element by the smallest number of moles.

$Aluminum\ = \frac{0.0256\ mol}{0.0256\ mol} = 1.00$ $Oxygen\ = \frac{0.0381\ mol}{0.0256\ mol} = 1.49$

The ratio is 1.00 atom Al: 1.49 atoms O
This ratio can be changed to a whole number ratio by multiplying by a factor of 2.
i.e. (1.00 atom : 1.49 atoms O) x 2
2 atom : 2.98 atoms O;
Simple rounding gives 2 atom Al : 3 atoms O
Therefore the empirical formula of Aluminum oxide formed = $\boldsymbol{Al_2O_3}$.

3.2 Concept of the experiment

In this experiment, after a known mass of magnesium is burned, the product will consist of magnesium oxide together with a small amount of magnesium nitride (Mg_3N_2). Next, we add water to convert this small amount of nitride to magnesium hydroxide, $Mg(OH)_2$ with the liberation of ammonia, NH_3 (the water will not react with the magnesium oxide). Further heating will cause conversion of the hydroxide to the oxide with the loss of gaseous water. In summary, the following reactions take place:

Reaction of magnesium with molecular oxygen:

$$Mg\ (s)\ +\ O_2\,(g)\ \rightarrow\ 2\ MgO\ (s)$$

Reaction of magnesium with molecular nitrogen

$$3\ Mg\ (s)\ +\ N_2\,(g)\ \rightarrow\ Mg_3N_2\,(s)$$

Reaction of magnesium nitride with water

$$Mg_3N_2\,(s)\ +\ H_2O\ (l)\ \rightarrow\ Mg(OH)_2\,(s)\ +\ NH_3\,(g)$$

Reaction upon heating magnesium hydroxide:

$$Mg(OH)_2\,(s)\ +\ \Delta\ \rightarrow\ MgO\ (s)\ +\ H_2O\ (l)$$

In the end, all magnesium will have been converted to magnesium oxide. You can then calculate the mass of oxygen that is present in the oxide from its mass and the original mass of the magnesium. The laws of conservation of mass, as well as the concept of a mole, will lead you to the method by which you can determine the empirical formula of this oxide.

Materials and Equipment

Balance, furnace, crucible, crucible tongs, wire gauze, magnesium ribbon, sandpaper, medicine dropper, tweezers

3.3 Procedure

1. Obtain a crucible, wash, rinse, and dry it.

2. Heat the crucible for about 5 min in a furnace at 200°C. Remove the crucible from the furnace and allow the crucible to cool (5-10 min).

CAUTION: Avoid burning your fingers. Do not touch the crucible at any time during this experiment.
3. While waiting, weigh approximately 0.2 g of magnesium ribbon (if it is not bright, clean the surface with sandpaper). Record the mass.
4. When the crucible is cool, transfer it to the pan of a balance using crucible tongs while holding a wire gauze under the crucible, but do not put the wire gauze on the pan. If you must wait to use the balance, do not place the crucible directly on the bench.

5. Measure and record the mass of the crucible.

6. Repeat steps 2, 4 and 5 until two consecutive masses differ by no more than +0.01 g or any other precision that is stipulated by your laboratory instructor. Record the mean or average value of these two masses. You will use this result in subsequent calculations.

7. Fold the magnesium ribbon into a loose ball that will fit completely inside the crucible.

8. Weigh and record the mass of the crucible with the magnesium.

9. Return the crucible to the furnace, using crucible tong.

10. Heat the crucible with its contents in the furnace at 800 °C for 45 min.

During this waiting period, you will write the first written exam!
11. Take out crucible and put it on a wire gauze and let it cool to room temperature. The contents should be white or slightly gray.

12. Add a few drops of distilled water from a medicine dropper directly on the contents. The smell of ammonia may be evident at this point.

13. Heat the crucible until the contents are dry. Next heat the crucible strongly for 8-10 min in a furnace to convert the hydroxide to the oxide.

14. Allow the covered crucible and its contents to cool.

15. Weigh and record the new mass of the crucible with MgO.

16. Calculate the empirical formula from your recorded masses.

17. Clean the crucible and all other items used.

Laboratory Data Sheet
Results

Make sure you report your answer using the correct number of significant figures for each mass!

a. $Mass\ of\ empty\ crucible\ (g)\ (2\ weighings)$ 1.________
2.________

b. Average mass of empty crucible (g) ___________

c. Mass of crucible with Mg before heating (g) ___________

d. Mass of Mg (g) (c – b) ___________

e. Mass of crucible and oxide after heating(g) ___________

f. Mass of magnesium oxide (g) (e – b) ___________

g. Mass of oxygen (O) = mass magnesium oxide – mass Mg (f – d) ___________

$Moles\ Mg\ =\ mass\ Mg\ /\ Molar\ Mass\ Mg$ ________ $moles\ Mg$

$Moles\ O\ =\ mass\ O\ /\ Molar\ Mass\ O$ ________ $moles\ O$

$Mol\ ratio\ Mg\ :\ O\ (moles\ Mg/moles\ O)$ _____ : _____

$Empirical\ formula\ of\ magnesium\ oxide$: ____________

$Actual\ formula\ of\ magnesium\ oxide\ based\ upon\ their\ charges$: ___________

$Is\ your\ formula\ same\ as\ actual\ formula?$ _____________

$If\ no, then\ explain\ why\ you\ did\ not\ get\ the\ same\ formula$:

Write balanced chemical equations along with their physical states for the following reactions:

a. Magnesium with molecular oxygen: ____

b. Magnesium with molecular nitrogen: ____

c. Magnesium nitride with water: ______________________________________

d. Heating magnesium hydroxide: ______________________________________

4.0 Conclusion

The empirical formula is the simplest formula for a compound. A molecular formula is the same as or a multiple of the empirical formula, and is based on the actual number of atoms of each type in the compound.

5.0 Summary

In this you have been able to Describe the concept of empirical formula, determine the empirical formula of a metal oxide, determine the mass and mole ratios of elements and finally perform a basic laboratory measurements of mass and volume using appropriate glassware and equipment.

6.0 Tutor Marked Assignment (TMA)

1. The empirical formula of a compound was determined to be "**CH**" and its molar mass was found to be 78.12 amu, what is the value of the simplest multiplier (**n**) of empirical formula to be used to determine its molecular formula?

Hint $Empirical\ formula\ mass\ =\ (atomic\ mass\ of\ C\ +\ atomic\ mass\ of\ H)\ =\ (12.01\ +\ 1.01)\ amu\ =\ 13.02\ amu.$

$$Simplest\ multiplier\ \text{“}n\text{”}\ = \frac{Molar\ mass}{Empirical\ formula\ mass}$$

2. What is the empirical formula of a compound containing 47.37% carbon, 10.59% hydrogen and 42.04% oxygen?

3. What is the empirical formula for a compound containing 26.57% potassium, 35.36% chromium, and 38.07% oxygen?
4. A sample of an oxide of nitrogen is found to contain 30.4% nitrogen. What is its empirical formula?

7.0 References/Further Reading

1.m.learning.hccs.edu/.../**experiment**-6-**empirical-formula-of-a-compound**
2. http://swc2.hccs.edu/pahlavan/intro_labs/Exp_12_Empirical_Formula.pdf
3. http://pages.towson.edu/ladon/empiric.html
4. chemistry.about.com › ... › Chemistry Test Questions
5. www.bergen.edu/.../CHM%20100%20%20140%20-%20**Empirical**%20a

UNIT 6 Determination of the Percent Oxygen in Air

1.0 Introduction

Air is a homogeneous mixture of gases such as nitrogen, oxygen, argon, and trace amounts of other elemental gases and carbon dioxide. The amounts of each gas can be measured both by weight and volume to determine the percent composition. In this experiment, the students will measure gas volumes using gas measuring burets. Since gases are very sensitive to changes in temperature and pressure, the students should carefully note atmospheric pressure, laboratory and water temperatures.

2.0 Objectives

At the end of this unit , should be able to perform an experiment is to determine the percentage by volume of oxygen in air.

3.0 Main Content

3.1 Theory

Consider for a moment the air that you breathe. Since the time of the ancient Greek philosophers, people have realized that air is critical to life, though with little understanding of why.

We now know that the most common gases in air are nitrogen (78%), oxygen (about 21%), and argon (almost 1%). Other molecules are present in the atmosphere as well, but in very small quantities.

In this laboratory experiment, you will perform a procedure to verify the oxygen content of

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Anyone who has witnessed rust on a car, bicycle or barbed wire fence knows that this reaction occurs spontaneously, though the rate can be very slow. To hasten the process and complete the data collection in one laboratory period, we will first “activate” the iron by washing it with acetic acid. It is believed that a small amount of acid catalyzes the reaction, though the mechanism is not well understood. On the other hand, an excess of acid could interfere with the results by reacting with the iron itself, to form hydrogen gas.

The experimental set-up is shown in the figure As the oxygen in air reacts with iron to form solid iron(III) oxide, the volume of the trapped air should decrease and water will enter the test tube. This change in volume is equal to the volume of oxygen consumed in the reaction.

Assuming that the length of the test tube is proportional to its volume and that the change in the length of the column of air in the test tube is due only to the removal of oxygen, the percentage of oxygen can be determined by calculating the change in the volume of air in the test tube.

$$\%\, O_2 = \frac{constant\ water\ level\ reading\ (mm)}{tube\ lenght (mm)}$$

To ensure that all oxygen is completely reacted, iron will be present in excess. A second question that you will attempt to answer in this experiment is what is the optimal quantity of iron to be used? To find the answer to this question, it will be necessary to perform a series of experiments. Rather than doing these all yourself, you will pool data with others in the class.

3.2 Procedure

1. Fill a 15-cm test tube completely with water. Pour the water into a 100-mL beaker and weigh. Record the temperature of the water.
2. Measure the length in millimeters of the test tube. Measure to the point halfway between the end and beginning of the rounded end. Attach a plastic metric ruler with two rubber bands so that the metric length begins at the lip of the tube. The rubber bands should be placed around the bottom half of the test tube, leaving your view of the top half unobstructed.
3. Fill a 400-mL beaker about ¾ full with water.
4. Obtain a small piece of steel wool from the front bench. Measure and record the mass.

Steps 5 – 7 should be done quickly while working in a fume hood. You will need the weighed piece of steel wool, forceps, and the test tube used in step 1.

5. Holding the steel wool with forceps, rinse thoroughly with acetone. (This will remove any oils from the surface of the steel wool.) Shake off excess acetone in the acetone waste bucket.
6. Soak the steel wool in a 50:50 vinegar/water mixture for 1 minute, making sure that all of the steel wool is under the surface of the solution. Remove the steel wool and shake off excess solution in the acetic acid waste bucket.
7. Pull apart the steel wool to increase the surface area and insert it into the bottom of the test tube. Push the steel wool loosely into the test tube with a glass stirring rod.
8. Working back at your station, cover the end of the test tube with your finger and quickly invert the test tube assembly into the beaker of water, as shown in figure 1, removing your finger once the opening of the test tube is under water. *If necessary, adjust the 0.0 mm ruler mark to the water level inside the tube.* **Record the time.**

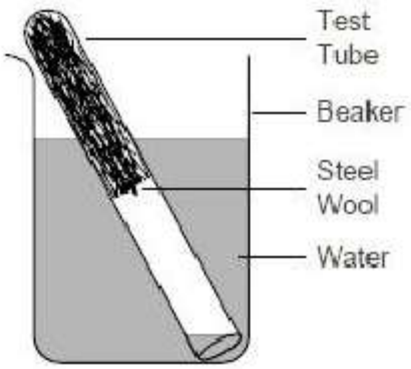


Figure 1. Experimental set-up

9. After 5 minutes, move the test tube so that the water level inside the test tube is equal to the water level inside the beaker. You will find this easiest to accomplish by holding the ruler against the side of the beaker. Measure and record the height of the water in the test tube and then rest it on the bottom again.
10. Measure and record the height of the water in the test tube every five minutes using the procedure in step 9 until the water level stops changing. Take two or three readings at the final constant level.
11. Remove the wire from the test tube, record its color, discard it and clean the test tube.
12. Repeat steps 3 - 11 with a fresh piece of steel wool.

3.3 Calculations

Steps 1 – 3 may be done while collecting data (above) and must be completed before leaving lab.

1. For each trial, prepare an Excel table and record the water level (mm), time (minutes) and percent change in the water level reading.
2. Graph the percent change in the water level reading versus time. (Curves from both trials may be recorded on the same graph.
3. Record your value for the mass of iron used, the percent volume of oxygen in air and the time it took to reach constant volume on the class summary table in lab. Before leaving, copy the class information into your lab notebook.
4. Calculate the class average and standard deviation for the percent volume of oxygen.
5. Calculate the total volume of the test tube, based upon the mass of water measured in step 1 and the density. The density of steel is 7.9 g/mL at 20°C. . What percentage of the tube volume was occupied by the steel wool for
a) the lightest piece of steel wool?
b) 1.0 g of steel wool?
c) the heaviest piece of steel wool?

4.0 Conclusion

Report your values for the percent oxygen in air, as well as the class mean and standard deviation. Comment on the reproducibility of the results. How does your value compare to the class value and the accepted value (20.833%)? Explain the comparison by reference to errors in your procedure and any assumptions that were made. (When thinking about assumptions, recall what you know about the behaviors of gases, including solubility, partial pressures and the temperature-volume relationship.)

For this experiment, we also want to determine the optimal amount of steel wool that should be used. Is there a minimum value, below which the time frame becomes too long? Is there a maximum value beyond which there is no time advantage noticed? What about the volume occupied by the steel wool itself? What percentage of the total volume does it occupy and at what point does it become significant? Consider both of these factors when trying to determine an optimal mass of iron to use for this procedure.

Discuss these results in terms of collision theory. Why did rates change as the mass of iron was increased? How would they have been impacted if the steel wool was in a tight wad, rather than spread out? What was the role of the acetic acid and how does a catalyst function?

5.0 Summary

In this unit you have been able to perform an experiment to determine the percentage by volume of oxygen in air.

6.0 Tutor Marked Assignments (TMA)

1. In step 9 you equalized the water levels inside the test tube and beaker. What was the purpose of this step?
2. If you had done this experiment at the top of Mt. Everest, would the results be the same? Explain your answer.

7.0 References

1. *chemlabs.uoregon.edu/Classes/Exton/CH228/Percent**Oxygen**.pdf*

UNIT 7 Redox Titrations

1.0 Introduction

Reactions in which substances undergo changes in oxidation number are referred to as oxidation-reduction reactions or redox reactions. Oxidation is defined as an algebraic increase in oxidation number, or a process in which electrons are lost. Reduction is defined as an algebraic decrease in oxidation number or a process in which electrons are gained. Oxidation-reduction processes must occur simultaneously. The species that gains electrons is called the oxidizing agent, therefore it is reduced. The species that loses electrons is called the reducing agent, therefore, it is oxidized.

2.0 Objective

At the end of this unit should be able to perform an experiment in two parts

- To standardize a potassium permanganate solution will be against a sample of potassium oxalate.
- To use the standard permanganate solution to find the concentration of iron (II) in a ferrous solution (g/L).

3.0 Main Content

3.1 Theory

Potassium permanganate,$KMnO_4$, is a strong *oxidizing agent*. Permanganate,MnO_4^-, is an intense dark purple color. Reduction of purple permanganate ion to the colorless Mn^{2+} ion, the solution will turn from dark purple to a faint pink color at the equivalence point. No additional indicator is needed for this titration. The reduction of permanganate requires strong acidic conditions.
In this experiment, permanganate will be reduced by oxalate, $C_2O_4^{2-}$in acidic conditions. Oxalate reacts very slowly at room temperature so the solutions are titrated hot to make the procedure practical. The unbalance redox reaction is shown below.

$$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2 \ (acidic\ solution)$$

In part I of this experiment, a potassium permanganate solution will be standardized against a sample of potassium oxalate. Once the exact normality (eq/L) of the permanganate solution is determined, it can be used as a standard oxidizing solution. In part II of this experiment, the standard permanganate solution will be used to find the concentration of iron (II) in a ferrous solution (g/L).
The unbalanced redox reaction is shown below.

$$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+} \textit{(acidic solution)}$$

Phosphoric acid will be used to ensure that the ferric product, Fe^{3+}remains in its colorless form.

3.2 Experiment

Equipment and Reagents (Day 1)

- $KMnO_4$ solid
- weighing paper
- burette
- 500 mL Florence Flask
- $K_2C_2O_4\ H_2O$
- Ring Stand
- Rubber Stopper
- Analytical Balance
- Burette Clamp
- Hot plate or Bunsen burner
- 250 mL Erlenmeyer flask
- 6 NH_2SO_4

Procedure (Day 1)

***Part (I) - Preparation of a 0.1 N $KMnO_4$ Solution*.**

1. On a centigram balance, weigh about 1.0 g $KMnO_4$ crystals on a piece of weighing paper. Add the crystals to a $500\ mL$ Florence Flask.
2. Add about $350\ mL$ of distilled water to the flask.
3. Heat the solution with occasional swirling to dissolve the $KMnO_4$ crystals. Do not boil the solution. This may take about 30 minutes.
4. Allow the solution to cool and stopper. You will need this solution for both day 1 and day 2.

Part (II) - Standardization of a $KMnO_4$ solution.

1. On weighing paper, weigh about $0.2 - 0.3\ g$ of $K_2C_2O_4\ H_2O$ on the analytical balance. Record the exact mass. Transfer the sample to a $250\ mL$ Erlenmeyer flask.
2. Rinse and fill the burette with the $KMnO_4$solution.
3. Add $50\ mL$ of distilled water and $20\ mL$ of 6 N H_2SO_4 to the oxalate sample in the Erlenmeyer flask. Swirl to dissolve the solids.
4. Heat the acidified oxalate solution to about $85\ °C$. Do not boil the solution.
5. Record the initial burette reading. Because the $KMnO_4$solution is strongly colored, the top of the meniscus may be read instead of the bottom.
6. Titrate the hot oxalate solution with the $KMnO_4$solution until the appearance of a faint pink color.
7. Record the final burette reading and calculate the volume of $KMnO_4$used in the titration.
8. Discard the titration mixture down the drain and repeat the titration with a new sample of oxalate for a total of 2 trials.

9. An oxalic acid solution may be used to wash the burette and the titration flask if a brown stain remains in the glassware.

Calculations

1. Using the half-reaction method, write a balanced redox equation for the reaction of permanganate with oxalate in an acidic solution.

2. Calculate the equivalent weight of the oxalate reducing agent from the molar mass of the oxalate sample and the equivalence of electrons lost by the reducing agent in the oxidation half-reaction.

$$equivalent\ weight = \frac{184\ g/mol}{\#\ of\ electrons\ eq/mol}$$

3. Use the sample mass and the equivalent weight to calculate the number of equivalents of oxalate in each sample.

$$equivalence\ of\ reducing\ agent = \ sample\ mass\ g \times \ \frac{eq}{\_\ g}$$

At the equivalence point, the equivalence of the reducing agent is equal to the equivalence of the oxidizing agent.

$$eq_{red} \ = \ eq_{ox}$$

4. Calculate the normality of the $KMnO_4$ solution from the equivalence of the oxidizing agent and the volume used in the titration.

5. Calculate the average normality of the permanganate solution.

Equipment and Reagents (Day 2)

- Unknown Fe^{2+}solution
- $KMnO_4$ solution
- Burette Clamp
- 250 mL Erlenmeyer Flask
- 25 mL pipet
- Ring Stand
- 6 NH_3PO_4
- Pipet bulb

Procedure (Day 2)

Part (III) – Determination of the Mass of Iron in a Ferrous Solution.

1. Pipet a $25\ mL$ sample of the unknown Fe^{2+} solution into a $250\ mL$ Erlenmeyer flask.

2. Add 50 mL of distilled water and 12 mL of 6 NH_3PO_4 into the flask.

3. Fill a burette with the standard $KMnO_4$solution and record the initial burette reading.

4. Titrate the sample with the standard $KMnO_4$ to a faint pink end-point and record the final burette reading. Calculate the volume of $KMnO_4$ used.

5. Discard the ferric solution down the drain and repeat the titration with a new sample of the ferric solution for a total of 2 trials.

6. After all trials, discard the purple permanganate solution in the appropriate waste container in the fume hood.

7. Oxalic acid may be used to remove any brown stains left on the glassware.

4.0 Conclusion/Calculations

1. Using the half-reaction method, balance the redox reaction of permanganate with iron (II) in acidic media.
2. Calculate the equivalence of $KMnO_4$titrated.

$Equivalence\ of\ oxidizing\ agent$= $\mathrm{N_{ox}} \times V_{ox}$ =($\frac{\mathrm{eq}}{\mathrm{L}}$)×$L$
mass concentrations for the ferrous unknown solution.

At the equivalence point, the equivalence of the oxidizing agent is equal to the equivalence of the reducing agent.

$$eq_{ox} = eq_{red}$$

Determine the normality of the ferric reducing agent.

$$N_{red} = \frac{eq_{red}}{0.025L}$$

3. Calculate the molarity (mol/L) of the ferrous solution.

$$M_{Fe} = \frac{N_{Fe}}{n}$$

(n = moles of electrons lost in the oxidation half-reaction.)

4. Calculate the mass concentration (g/L) of iron in the unknown solution by multiplying the molar mass of iron by the molarity of the ferrous solution.

$$mass\ concentration = \frac{mol}{L} \times \frac{56g}{mol} = \frac{g}{L}$$

5. Calculate the average mass concentrations for the ferrous unknown solution.

5.0 Summary

In this unit, you have been able to perform an experiment with two parts. In the first part, you standardized a potassium permanganate solution against a sample of potassium oxalate to determine the exact normality (eq/L) of the permanganate solution .In the second part of the experiment, you used the standard permanganate solution to find the concentration of iron (II) in a ferrous solution (g/L).

6.0 Tutor Marked Assignments (TMAs)

1. Explain the following terms
   a. oxidizing agent
   b. reducing agent

2. A solution contains both iron (II) and iron(III) ions. A 50.0 mL sample of the solution is titrated with 35.0 mL of $0.00280\ M\ KMnO_4$, which oxidizes Fe^{2+} to Fe^{3+}. The permanganate ion is reduced to manganese (II) ion. Another $50.0\ mL$ sample of solution is treated with zinc metal, which reduces all the $Fe^{3+}$to Fe^{2+} . The resulting solution is again titrated with of $0.00280\ M\ KMnO_4$, this time $48.0\ mL$ is required. What are the concentrations of Fe^{2+} to Fe^{3+} in the solution?

Solution: 1) **The stoichiometric relationship of permanganate to Fe(II):**

$$5Fe^{2+} + 8H^+ MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

is five to one.

2) Calculate moles of Fe(II) reacted:

(0.00280 mol / L) (0.0350 L) = 0.000098 $mol\ of\ MnO_4^-$,

(0.0000980 $mol\ Mn$) (5 $mol\ Fe$ / 1 $mol\ Mn$) = 0.000490 $mol\ Fe(II)$

3) **Determine the TOTAL iron content:**

$(0.00280\, mol\ /\ L)\ (0.0480\, L)\ =\ 0.0001344\, mol\ of\ MnO_4^-,$

$(0.0000980\, mol\ Mn)\ (5\, mol\ Fe\ /\ 1\, mol\ Mn)\ =\ 0.000672\, mol\ of\ total\ Fe$

4) **Determine Fe(III) in solution and its molarity:**

$$0.000672\, mol\ -\ 0.000490\, mol\ =\ 0.000182\, mol$$

$$0.000182\, mol\ /\ 0.050\, L\ =\ 0.00364\, M$$

5) Determine molarity of Fe(II):

$$0.000490\, mol\ /\ 0.050\, L\ =\ 0.0098\, M$$

7.0 References/Further Reading

1. http://www.chemteam.info/**Redox**/WS-**redox-titration**-problems.html
2.http://academic.brooklyn.cuny.edu/chem/maggie/teach/chem41/files/feo.pdf
3. http://www.lahc.edu/classes/chemistry/arias/exp%208%20-%20redox.pdf
4. http://staff.buffalostate.edu/nazareay/che112/manganate.html