COURSE
GUIDE

CHM 291
PRACTICAL INORGANIC CHEMISTRY (III)

Course Team   Dr. Uduak Aletan (Course Writer/Developer) -
NOUN
Dr. Akeem Abayomi (Course Editor) - Department
of Chemistry
University of Lagos
Professor Ayi Anyama Ayi- (Course Reviewer)
Department of Pure and Applied Chemistry,
University of Calabar, Calabar, Nigeria.
Dr. Emeka C. Ogoko (Head of Department)
Department of Pure and Applied Science - NOUN

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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 FOUR 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 the chemistry of first row transition elements. The purpose of this experiment is to examine some of the solution chemistry of the transition elements along with chemical change involving ionic precipitation reactions. In particular, you will be looking for evidence of complex formation and change in oxidation state –two important general characteristics of transition elements. You will investigate the action of reducing agents on the higher oxidation states, the action of the metals on common acids. Analysis of suspected double salts will be carried out as well as a quantitative analysis for iron (II) and copper (II) ions in order to establish their molar ratio. In unit 4, zinc is used to reduce a yellow solution of ammonium vanadate (V) to a mauve solution containing vanadium (II) ions. The redox chemistry of vanadium is further demonstrated to illustrate the presence of several different oxidation states to show how it is possible to change from one oxidation state to another.

Module 3 gives the redox titration for determination of iron (II) by manganite (VII) acidic solution. This is followed bya kinetic study of the reaction between manganite (VII) ions and ethanedioic acid. The preparation and analyses of coordination compounds along with colours associated with ligand changes in some coordination compounds of copper are illustrated in module 4

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
Unit 3   General laboratory procedures

Module 2

Unit 1   Precipitation reactions
Unit 2   Investigation of transitional properties of d-block elements
Unit 3   Chemistry of vanadium
Unit 4   Chemistry of chromium

Module 3

Unit 1   Chemistry of manganese
Unit 2   Redox reactions of iron

Module 4

Unit 1   Preparation of a Coordination Compound
Unit 2   Colours associated with ligand changes in some co-ordination compounds of copper(II)
Unit 3   Preparation and analysis of chloropentaamine cobalt (III) chloride, $[Co(NH3)5Cl]Cl_2$

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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

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MODULE 1

Unit 1   Laboratory regulations
Unit 2   General laboratory procedures
Unit 3   General laboratory procedures

UNIT 1   LABORATORY REGULATIONS

CONTENTS

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 to work if students can observe the health and safety rules.

2.0   OBJECTIVES

By 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.

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 theeach experiment. Finally, each member of
your group has to write a 5 or 6page 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.

3.3   Format of the Lab Report

Your lab reports should be handwritten and should include tables and
illustrations where necessary. A typical, 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 of
the report

3.4   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. At the end of each lab work, clean off your work
area, and 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. Treat 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.

3.5   Risk Assessments

Risk Assessments are most conveniently made on a standard form; an example is shown overleaf. The procedure is straightforward - always bear in mind that the intention is to protect you from any risks. The steps in making an assessment are:

1.   Write down the procedures you will be using (chemicals used or made, quantities, concentrations, techniques and any non-chemical hazards).
2.   Use reference sources to identify any hazardous chemicals you are planning to use or make. The appropriate warning symbol should be on reagent bottles and in suppliers' catalogues.
3.   Record the nature of the hazards involved and the way you might be exposed to the hazard.
4.   Decide what protective or control measures to take so that you can carry out your practical work healthily and in safety.
5.   Find out how to dispose of any hazardous residues from your practical work.

The protective measures you need to take will depend on your laboratory as well as your experiment. The experiments in this course have been assessed for use in a well-lit, well-ventilated and uncrowded laboratory. Where conditions are different, additional protective measures may be necessary. The most common mishaps in the laboratory involve splashes from liquids (especially in the eye) and burns from hot apparatus.

3.6   Good laboratory practice

As well as the specific protective measures to be taken when hazardous chemicals are being used, there are also general procedures to be observed in all laboratories at all times.

i. Long hair should be tied back and you should not wear 'wet look' hair preparations, which can make hair unusually flammable. Do not let ties, scarves or cardigans hang freely, where they could be a fire hazard. We strongly recommend the wearing of laboratory coats to avoid damage to clothing.

ii. Eating, drinking and chewing are not permitted in laboratories. It is, in fact illegal to permit eating, drinking or indeed smoking or the application of cosmetics in any area which could be contaminated with hazardous chemicals.

iii. Eye protection should be worn whenever a Risk Assessment requires it, or whenever there is any risk to your eyes. This includes, for example, washing up at the end of the lesson and even when you have finished practical work, as long as other students are still working.

iv. You should find that the chemicals that you are going to use are in clearly labelled stock bottles, with the name of the chemical, any hazards, and the date of acquisition or preparation. When taking liquids from a bottle, remove the stopper with one hand and keep the stopper in your hand whilst pouring from the bottle. This way, the stopper is likely to be replaced at once and to remain uncontaminated. Pour liquids from the opposite side to the label, so that it does not become damaged by corrosive chemicals.

v. Study carefully the best techniques for safely heating chemicals. Small quantities of solid can be heated in test tubes; liquids present greater problems, because of the risk of 'bumping' and 'spitting'. Boiling tubes are safer than test tubes (because of their greater volume), but should be less than one-fifth full. You are likely to point test tubes away from your own face, but do remember the need to do the same for your neighbours. Use a water bath to heat flammable liquids; NEVER use a naked flame.

vi. When testing for the odour of gases, the gas should be contained in a test tube (not a larger vessel) and the test tube held about 10-15 cm from your face, pointing away. Fill your lungs with air by breathing in and then cautiously sniff the contents of the test tube, by using a hand to waft the vapours to your nose. Slowly bring the test tube nearer, if necessary. If you are asthmatic you should not smell gases without a report from other students because gases such as chlorine are harmful.

vii. You must always clear up chemical spillages straight away. Whilst a few spills may need chemical neutralisation or similar treatment, most minor spills can be wiped up using a damp cloth. (Don't forget to rinse it afterwards.)

viii. In the event of getting a chemical in your eye, or on your skin, flood the area with large quantities of water at once. Keep the water running for at least 10 minutes (20 minutes for alkalis in the eye). Rubber tubing on a tapis the most convenient way of doing this.

Even if the chemical reacts exothermically with water, provided a large quantity of water is used, the heating effect will be negligible.

ix.   A heat burn from apparatus, scalding liquids or steam is treated by immersing the area in cool water for at least 10 minutes. Preferably use running water from rubber tubing, fixed to a tap.

x.   Report all accidents at once.

SELF ASSESSMENT EXERCISE

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

ii.   What clothing is appropriate for Chemistry lab workers?

iii.   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.?

iv.   If an acid is splashed on your skin, wash at once with
       a.   soap.
       b.   oil.
       c.   weak base.
       d.   plenty of water.

v.   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.

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.   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

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2. http://www.flinnsci.com/media/396492/safety_exam_hs.pdf
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4**. http://www-chem.ucsd.edu/_files/lab/study_guide.pdf**

UNIT 2   GENERAL LABORATORY PROCEDURES (1)

CONTENTS

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   OBJECTIVES

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

*   explain the use of some simple equipment in your laboratory.

3.0   MAIN CONTENT

3.1   Balances 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. A typical analytical balance is shown in Figure1. 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) **(Fig.2)** 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.

Fig. 2 Weighing bottles

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:

$$\left(\frac{1.32}{12.6}\right) M = 0.105\ M$$

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

3.2. 1Reflux
The use of a reflux condenser is often necessary (Fig.3). 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
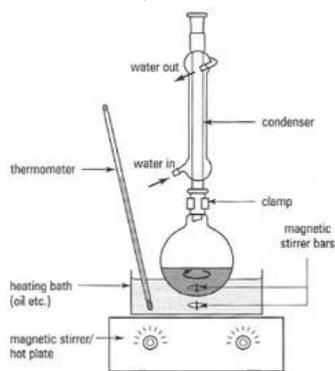
Fig. 3 Simple reflux set-up

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. In the reflux process, the reactants are dissolved or suspended in a suitable solvent, the solvent is boiled and then condensed so that it returns to the reaction flask. Once set up, a reaction carried out under reflux can be run for minutes, hours or even days to promote the required reaction. The basic components for a reflux apparatus shown in figure 3 are: a reaction flask; a reflux condenser; a heat source; a coolant source, usually water, for the condenser.

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.

3.2.2 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.

3.2.3 Fractional distillation

The purpose of fractional distillation is to separate two liquids of different boiling-point. Figure 4 gives the experimental set for fractional distillation apparatus. 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.
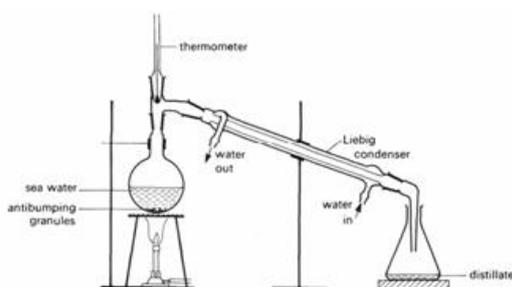
Fig. 4 Fractional distillation set-up

3.3   Use of the separating 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.

3.3.1 Separating two immiscible liquids

The liquid mixture is poured into the funnel (Fig. 5) 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.
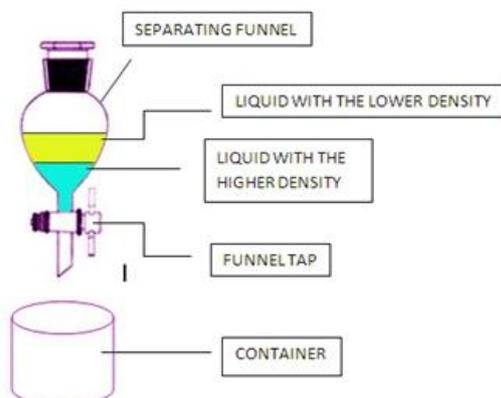
Fig. 5 Separating funnel

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.

3.3.2 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.

3.3.3 Liquid extractions

The separating funnel (Fig. 5) 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

SELF-ASSESSMENT EXERCISE

i.   Which of the techniques mentioned in this unit would be appropriate in the separation of a
ii.   mixture of ethanol and water?
iii.   In which of the techniques named in this unit is density necessary for the separation of liquid mixtures?
iv.   Which technique in this unit will be suitable for prolonged heating involving organic solvents?

4.0   CONCLUSION

In this unit you have studied some general laboratory procedures you will need for a better appreciation of your laboratory. 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   TUTOT-MARKED ASSIGNMENT

1.   Which of the techniques mentioned in this unit would be appropriate in the separation of a
2.   mixture of ethanol and water?
3.   In which of the techniques named in this unit is density necessary for the separation of liquid mixtures?
4.   Which technique in this unit will be suitable for prolonged heating involving organic solvents?

7.0   REFERENCES/FURTHER READING

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UNIT 3   GENERAL LABORATORY PROCEDURES (2)

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1.0   Introduction
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1.0   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.

2.0   OBJECTIVES

By 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.

3.1.1 Simple filtration

The usage of a filter funnel and a piece of filter paper folded into four (Fig.6a) 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 (Fig. 6b) 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.
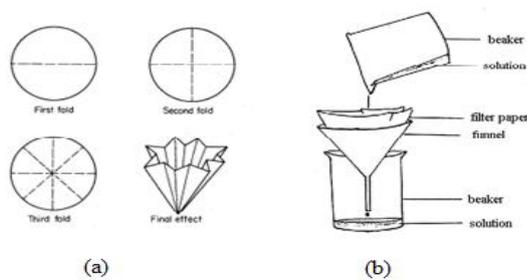
Fig. 6 Filtration apparatus (a) filter paper and its folding (b) filtration process

3.1.2 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 as shown in figure 7.

Figure 7 Vacuum filtration

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.

3.1.3 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

3.2.1 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 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.

3.2.2 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.

3.3.1 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.

3.3.2 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.

3.3.3 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.

3.3.4 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.

3.4   In text questions and answers

ITQ. 1. Rock salt is impure salt mined from the ground. With the help of diagram, explain simple experimental processes to obtain pure salt from the rock salt.

ITA. 1   Step 1. Crush about 5g of rock salt and add to 50cm3 of water in a 100cm3 beaker.   Heat and stir.
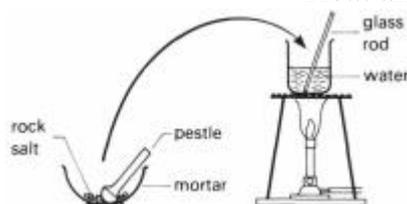
Step 2: Pour the mixture into a funnel containing a folded filter paper. Collect the filtrate in a dish
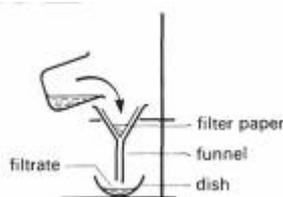
 Step 3: Heat the salt solution gently until it starts to 'spit'.

Step 4: Continue heating the solution over a beaker of boiling water until dry salt remains in the dish
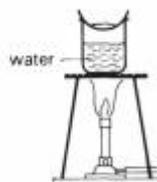
ITQ 2. At which stages do the following processes occur: dissolving, filtration, evaporation?

ITA 2. Dissolving occurs in step 1, filtration in step 2 and evaporation in step 4

SELF-ASSESSMENT EXERCISE

i.   What is a drying agent?
ii.   Mention two uses of activated charcoal.
iii.   Mention two precautions to be taken during the process of recrystallization
iv.   Distillation is a process of purifying liquids. Draw a diagram and outline two   experiments you could do to show that sea water is not pure water.
v.   Fractional distillation is used to separate mixtures of liquids that have different boiling points into parts or fractions. With suitable diagram, demonstrate this principle using a mixture of water and ethanol

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-MARED ASSIGNMENT

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

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MODULE 2

UNIT 1   PRECIPITATION REACTIONS

CONTENTS

1.0   Introduction
2.0   Objectives
3.0   Main content
         3.1   Procedure
         3.2   Discussion
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4.0   Conclusion
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6.0   Tutor-Marked Assignment
7.0   References/Further Reading

1.0   INTRODUCTION

It is important for us to understand exactly what is going on when a precipitate is formed. In all the experiments which you are about to carry out, the chemicals are ionic and in solution the ions are totally mobile and independent of each other. Consider for example an aqueous copper (II) chloride and aqueous sodium hydroxide shown inside a test tube.

The solution of copper(II) chloride contains $Cu^{2+}_{(aq)}$ and $Cl^-_{(aq)}$ ions – Solution A

Solution A: Cu²⁺ und Cl- ions
moving about randomly in
aqueous solution

The solution of sodium hydroxide contains $Na^+_{Iaq)}$ and $OH^-_{(aq)}$ ions – Solution B

You will notice formation of a blue precipitate on reacting solutions A and B together. In this reaction, two of the oppositely charged ions get attracted to each other in very large numbers and created a three-dimensional ionic lattice. Thus the precipitate that formed is between the $Cu^{2+}_{(aq)}$ and $OH^-_{(aq)}$ ions. This reaction cannot have been between the $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ ions, because sodium chloride is a soluble substance according to the 'solubility rules'. However, copper(ll) hydroxide is insoluble, as are most hydroxides, so this must be the identity of the blue precipitate. Its formula is $Cu(OH)_2$ and it was created when the copper(II) ions in the copper(II) chloride solution combined with the hydroxide ions in the sodium hydroxide solution in a 1: 2 ratios, i.e.

Solution 3: Na⁺ and OH⁻ ions moving randomly in aqueous solution

$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} = Cu(OH)_2(s)$ Eq. 1
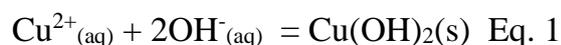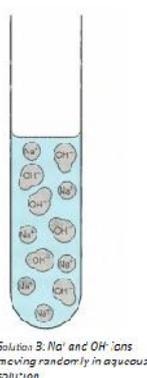
Notice that the sodium ions, $Na^+_{(aq)}$, and the chloride ions, $Cl^-_{(aq)}$, do not feature in the reaction at all. They are present in the mixture, of course, but they do not interact in any way, and at the end of the reaction they are still present and as   mobile as they ever were. For this reason, they are often known as 'spectator ions'. If you had filter the mixture, they would have pass through the filter paper and formed the filtrate as a solution of sodium chloride, whereas the solid blue copper (II) hydroxide would have be the residue on the filter paper.

The equation 1 above is known as an 'ionic equation' because it involves the interaction of ions. Spectator ions are always omitted in ionic equations, because the intention is to illustrate precisely what is happening in the solution, ignoring any ions which do not change. The 'full' equation for the reaction is in fact:

The Cu2+ and OH- ions
come together to form a
precipitate of Cu(OH)₂

$CuCl_{2(aq)} + 2NaOH_{(aq)} = Cu(OH)_2(s) + 2NaCl_{(aq)}$ Eq.2

But the ionic equation given in Eq. 1 is more useful because it represents the chemical change occurring. The type of chemical change to be studied in this module is ionic precipitation. In order to do this, you will need to know the basic 'solubility rules' for inorganic compounds.

SOLUBILITY RULES'

1.   Sodium, potassium and ammonium compounds are always soluble in water
2.   All nitrates are soluble in water
3.   Most chlorides are soluble in water; lead chloride and silver chloride are common exceptions to this rule
4.   Most sulphates are soluble in water; lead sulphate and barium sulphate are common exceptions to this rule
5.   Most oxides, hydroxides and carbonates are insoluble in water; those of sodium and potassium are soluble. Calcium hydroxide is slightly soluble in water

2.0   OBJECTIVES

The main objective of this experiment is to study the type of chemical change called ionic precipitation

3.0   MAIN CONTENT

3.1   Procedure

Use a spatula to transfer a tiny quantity of each of the compound provided in Table 3.1 to a test tube, enough to cover just the end of the spatula. Add about 5 cm ' of de-ionised (or distilled) water and shake the tube, and stir using a glass rod if necessary, to see whether the solid is capable of dissolving in water. If you use too much solid, it may be hard to tell whether any has dissolved. Note the colour of any solution formed. You may need to hold a test tube of water alongside for comparison, because

some of the solutions may be very pale in colour. If the solid does not dissolve record this fact in your table. Keep any solutions formed for the next experiment, otherwise dispose of your mixture down the sink.

3.2   Discussion

Four of the experiments carried out above should have produced solutions: the ones with copper(II) chloride, iron(II) sulphate, iron(III) nitrate and potassium carbonate. To each of these four solutions now add a few drops of dilute (0.4 M) sodium hydroxide solution. Use a glass rod to stir the mixtures obtained and record your observation as shown in Table 3.1

Table 3.1

Name of compound	Formula	Appearance	Solubility in water	Colour of solution
Copper(II) chloride				
Iron(II) sulphate				
Iron(III) nitrate				
Iron(III) oxide				
Magnesium carbonate				
Potassium carbonate				

If you study your table you will observe that coloured precipitates were formed with Cu^{2+}(aq), Fe^{2+}(aq) and Fe^{3+}(aq) ions:

• Cu^{2+} (aq) ions form a blue precipitate with aqueous sodium hydroxide
• Fe^{2+} (aq) ions form a 'dirty' green precipitate with aqueous sodium hydroxide
• Fe^{3+}(aq) ions form a 'rusty' brown precipitate with aqueous sodium hydroxide.

The different colour of precipitate formed by Fe2+(aq) and Fe3+(aq) ions when added to aqueous sodium hydroxide is a very useful means of distinguishing between them.

3.3   In-text questions and answers

ITQ 1. When a solution of sodium chloride is added to a solution of copper(II) nitrate, no precipitate is observed. However, there is a precipitate formed when copper (II)chloride   solution is added to a

solution of sodium hydroxide. Explain with the help of chemical equations. Write the complete molecular equation and the net ionic equation for the precipitation reaction.

ITA 1. Sodium chloride consists of Na+ and Cl- ions in solution, copper nitrate consist of Cu^{2+} and NO_3^- ions. When the two solutions are mixed together:

NaCl: Na^+ + Cl^-

$Cu(NO_3)_2$: Cu^{2+} + NO_3^-
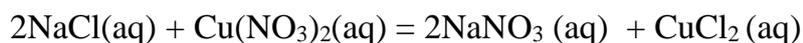
$2NaCl(aq) + Cu(NO_3)_2(aq) = 2NaNO_3 (aq) + CuCl_2 (aq)$
Both $NaNO_3$ and $CuCl_2$ are soluble in aqueous solutions and no precipitate is formed

The formula of sodium hydroxide is NaOH, while that of copper (II) chloride is $CuCl_2$. Both of these salts are soluble in water, but will form a solid precipitate immediately if these two solutions meet. This is because copper (II) hydroxide $[Cu(OH)_2]$ is insoluble in water.

$CuCl_{2(aq)} + 2NaOH_{(aq)} = Cu(OH)_2(s) + 2NaCl_{(aq}$
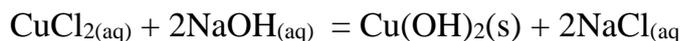
SELF-ASSESSMENT EXERCISE

You will be provided with the compounds listed in the Table below. Observe the compounds and check their solubility in water, the colour of aqueous solution and what happens on addition of dilute NaOH solution

Name of compound	Formula	Appearance	Solubility in water	Colour of solution	Addition of NaOH(aq)
Copper(II) chloride					
Iron(II) sulphate					
Iron(III) nitrate					
Potassium carbonate					

1.   Were any of the metal compounds you used coloured? If so identify their positions in the periodic table
2.   Did the formula for any of the compounds include the formula for water? If so, what does this tell you about the solid?
3.   Did the compounds obey the solubility rules?
4.   Construct ionic equation for each of the reactions with sodium hydroxide

4.0   CONCLUSION

- In conclusion, precipitation reaction takes place in aqueous solutions or medium in an ionic state.
- The reaction takes place between ions present in the aqueous solutions, forming the product
- The products formed at the end of precipitation reaction are the precipitates which are insoluble in aqueous solutions.
- Precipitation reactions are known as ionic reactions since the ions actively take part in the reaction and form the product.
- These reactions depend on the temperature, concentration of the solution, buffer solution, etc.

5.0   SUMMARY

A Chemical reaction occurring in aqueous solutions where two ionic components (cationic and anionic) combine to form insoluble salts is known as precipitation reaction. The salts formed are precipitates and are the products of precipitation reaction. Thus by definition, precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution.

The precipitation reaction is the double displacement reactions involving the production of a solid form residue called the precipitate. The reaction also occurs when two or more solutions with different salts are combined, resulting in the formation of insoluble salts that precipitates out of the solution.

Whether or not such a reaction occurs can be determined by using the solubility rules for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the solubility rules before determining the state of the products and writing a net ionic equation. The ability to predict these reactions allows scientists to determine which ions are present in a solution, and allows industries to form chemicals by extracting components from these reactions.

6.0   TUTOR-MARKED ASSIGNMENT

1. Were any of the metal compounds you used coloured? If so identify their positions in the periodic table
2. Did the formula for any of the compounds include the formula for water? If so, what does this tell you about the solid?
3. Did the compounds obey the solubility rules?
4. Construct ionic equation for each of the reactions with sodium hydroxide

7.0   REFERENCES/FUTHER READING

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UNIT 2   INVESTIGATION OF TRANSITIONAL PROPERTIES OF D-BLOCK ELEMENTS

CONTENTS

1.0   INTRODUCTION

The d- and f-block elements are generally referred to as the transition elements. They are located between the s and p-block elements and their properties reflect transition from electropositive nature of the s-block to electronegative nature of the p-block elements. The d-block elements are characterized by the gradual filling of the penultimate (n-1) d orbitals of the main shell of atom. The valence shell configuration of the d-block elements can be represented by $(n-1)\ d^{1-10}ns^{1-2}np^o$. One or two electrons are found in ns-state, while the other valence electrons are in (n-1) d state. In the f-block elements, the ante penultimate orbitals of the main shell of the atoms are being filled up with electrons. The atoms of these elements have their electronic configuration as $(n-2)\ f^{1-14}(n-1)\ d,^{0-2}ns^2$. Transition elements can therefore be defined as those elements, which in their elementary state or in any of their commonly occurring oxidation states have partly filled d- or f-orbitals. With this definition, Cu, Ag and Au (the coinage metals) are considered transition elements because in their commonly occurring oxidation states $Cu^{2+}(3d^9)$, $Ag^{2+}\ (4d^9$, $Au^{3+}\ (5d^8)$, their d-orbitals are partly filled. From chemical point of view, it is appropriate to consider Zn, Cd and Hg as transition metals. Although these elements both in their elementary state $[(n-1)\ d^{10}\ ns^2]$ and in their +2 oxidation state $[(n-1)d^{10}]$, do not possess partly filled (n-1)d orbitals,

their chemical behaviour is, on the whole similar to that of the other transition elements (Ayi, 2019) .

2.0   OBJECTIVES

The objective of this experiment is to examine some of the solution chemistry of the transition elements. In particular, you will be looking for evidence of complex formation and change in oxidation state –two important transitional characteristics of d-block elements.

By the end of this unit you should be able to

* identify the d-block elements in the periodic table
* write the electronic configurations for the atoms of the first transition series Sc-Zn
* explain the reason transition element exhibit variable oxidation states

3.0   MAIN CONTENT

3.1   Experiment 1: Investigation of transition metals in their lowest oxidation states

For this set of tests use 0.1 M solutions of salts of the metals in their lower oxidation states (titanium(III)sulphate,. vanadium(III)alum, chromium(III)chloride, manganese(II) chloride, iron(II) sulphate, iron(III) chloride, cobalt and nickel chlorides, copper (II) sulphate, silver nitrate, zinc and cadmium chlorides, mercurous nitrate and mercury (II) chloride).

(a)   Add 2.0 M sodium hydroxide dropwise until an excess is present.
(b)   Add 2.0 M ammonia dropwise until an excess is present.
(c)   Add 1.5 M sodium carbonate.
(d)   Add 0.1M ammonium thiocyanate until an excess is present.
(e)   Acidify with 2M hydrochloric acid and pass hydrogen sulphide.
(f)   If there is no reaction in (e), add 2.0 M ammonia until alkaline.
(g)   Add 2.0 M sodium hypochlorite solution and warm gently.

Look for the precipitation of insoluble compounds and for colour changes. Try to work out what has happened; for example, if a precipitate dissolves in an excess of a reagent it is likely that a complex has been formed. Tabulate your results as shown below

Table 2 Transitional properties of d-block elements

	Ti(III) solution	V(III) solution	Cr(III) solution	Mn(III) solution	Fe(II) solution	Fe(III) solution	Co(II) solution	Ni(II) solution	Cu(II) solution	Zn(II) solution
NaOH										
NH₃										
Na₂CO₃										
NH₄SCN										
HCl + H₂S										
NaOCl + heat										

3.2   Experiment 2: Solution chemistry of transition elements

The solution of the following metal salts should be prepared in the concentration specified below:

a)   Potassium chromate, 0.2 mol dm^{-3} K$_2$CrO$_4$ (is a carcinogen, mutagen and skin   sensitiser. It is also toxic to aquatic life. Wear splash-proof eye-protection if   transferring   large   amounts. Avoid skin contact).

b)   Potassium manganate(VII) 0.2 mol dm^{-3} (is hazardous to the aquatic environment Avoid direct contact and store in the dark, stains glass, plastic, clothing and skin).

c)   Ammonium vanadate(V), 0.2 mol dm^{-3} NH$_4$VO$_3$ (acidified with sulphuric acid) (is a mutagen and very toxic if inhaled (but not by other routes).

d)   Cobalt nitrate 0.5 mol dm^{-3} (is a carcinogen, mutagen, reproductive toxin, skin and respiratory sensitiser and hazardous to the aquatic environment).

e)   Copper(II) sulphate solution, 0.2 mol dm^{-3}, CuSO$_4$ (aq) (causes eye damage and is   hazardous to the aquatic environment).

f)   Iron(III) nitrate 0.2 mol dm^{-3},   Fe(NO$_3$)$_3$.9H$_2$O (aq) and

g)   Iron(II)sulphate 0.2 mol dm^{-3}, FeSO$_4$.7H$_2$O (aq) are of low hazard

h)   Silver nitrate, 0.1 mol dm^{-3}, AgNO(aq) is a skin/eye irritant. Keep separate from organic waste containers.

i)   Zinc powder, Zn (s) (is FLAMMABLE and hazardous to the aquatic environment).

The chemical reagents required for this experiment are:

j)   Ammonia solution, 3 mol.dm^{-3} NH$_3$ (aq) (is CORROSIVE and a respiratory irritant).

k)   Sodium hydroxide solution, 1 mol dm^{-3} NaOH (aq), (is CORROSIVE).

l)   Hydrochloric acid 1 mol dm^{-3} HCl (aq),

m)   Potassium thiocyanate 0.1 mol dm^{-3}, KSCN (aq),

n)   Potassium iodide 0.2 mol dm^{-3}, starch solution, Put two separate drops of the solutions of each of the elements from vanadium to zinc in the appropriate test tubes. Observe carefully and try to give explanations for your observations

Table 3: Solution Chemistry of transition elements

Vanadium (V)	add one drop of dilute hydrochloric acid and a small piece of zinc.
Chromium (Cr)	add one drop of silver nitrate solution.
Manganese (Mn)	add one drop of iron(II) solution.
Iron (Fe)	add one drop of potassium iodide solution. After one minute add one drop of starch test solution.
Cobalt (Co)	add one drop of ammonia solution.
Copper (Cu)	add one drop of ammonia solution.
Zinc (Zn)	add two drops of sodium hydroxide solution.

3.3   Discussion

3.3.1 Vanadium

Bubbles (of hydrogen) are seen. The yellow colour of the ammonium vanadate (vanadium(V) ions) gradually changes (as the vanadium is reduced) to blue due to the formation of the vanadium(IV) ions (VO2+). The colour changes to green due to vanadium(III) ions (V3+) and possibly to lilac due to vanadium(II) ions (V^{2+}) (although this species is a strong reducing agent and is very air-sensitive).

3.3.2 Chromium

A red precipitate of silver chromate(VI) is seen. This is an interesting example of the modification of the colour of a coloured anion (yellow chromate(VI) by a colourless cation (silver(I)).

3.3.3 Manganese

The deep purple colour of the potassium manganate(VII) gradually fades, first to the brown manganese(IV) oxide then to the very pale pink

manganese(II) ions. (Manganese(II) compounds in solution usually appear virtually colourless. However, a bottle of a solid manganese(II) salt – *e.g* the sulphate – is pink.)

3.3.4 Iron

A yellowish colour (due to iodine) starts to form as the iron(II) oxidises the iodide. Addition of starch produces the characteristic intense blue-black colour of the starch– iodine complex.

3.3.5 Cobalt

The addition of one drop of ammonia gives a deep green precipitate. Addition of further ammonia gives a green or brown solution.

3.3.6 Copper

The addition of ammonia gives a light blue precipitate of copper(II) hydroxide together with the deep blue tetra-amminocopper(II) ion.

3.3.7 Zinc

A white precipitate of zinc hydroxide is observed. (Zinc is not a transition metal because it only has one oxidation state in its compounds and the Zn^{2+} ion has a full d-sub-shell.) In-text questions

3.5   In text questions (ITQ) and answers (ITA)

ITQ 1. Consider the loss of electrons one at a time from typical transition elements. What resulting   electron configurations do you think might be reasonably stable**?**
ITA 1**.** Stable electron arrangements might be expected from loss of
(a)   all 3d and 4s electrons giving a noble gas configuration
b)   the 4s electrons only, leaving the 3d untouched
c)   the 4s and some 3d electrons leaving the 3d sub-shell half-filed.

ITQ 2. Work out the oxidation states of the transition elements in the following ions and compounds:

(a) MnO_4^-
(b) MnO_2
(c) K_2MnO_4
(d) $Cr_2O_7^{2-}$
(e) K_2CrO_4
(f) Cr_2O_3
(g) $KCrO_3Cl$

(h) VO_2^+
(i) $VOCl_4$
(j) V_2O_5
(k) NH_4VO_3

ITA 2. (a) +7 (b)+4, (c) +6, (d) +6, (e) +6, (f) +3 (g) +6   (h) +5 (i) +4 j)
+5 (k) +5

SELF-ASSESSMENT EXERCISE

Carry out the following test on each metal salt solution, record your
observation and comment on your observation.

Solutions of metal ions	Test	Observation	Explanation
V	add one drop of dilute hydrochloric acid and a small piece of zinc.		
Cr	add one drop of silver nitrate solution.		
Mn	add one drop of iron(II) solution.		
Fe	add one drop of potassium iodide solution. After one minute add one drop of starch test solution.		
Co	add one drop of ammonia solution.		
Cu	add one drop of ammonia solution.		
Zn	add two drops of sodium hydroxide solution.		

2.Which element among the ones that you have tested does not behave as
a transition element? Give concise reason for your answer.

4.0   CONCLUSION

We have been able to look a metals which are able to exhibit variable
oxidation states, which is key to much of their characteristic chemistry.

5.0   SUMMARY

A closer look at the electronic configurations of the first row transition elements, it will be noted that atoms of chromium and copper have only one 4s electron, whereas all the others have two. When transition elements form ions it is always the s-electron which is lost first, leaving the atom with an excess positive charge. This excess charge has the effect of pulling all the electrons a little closer and in the process, the 3d orbitals occupy a lower energy level than the 4s. This explains why the 3d and 4s orbitals are close together for the transition elements.

6.0   TUTOR-MARKED ASSIGNMENT

1.   Carry out the following test on each metal salt solution, record your observation and comment on your observation.
2.   Which element among the ones that you have tested does not behave as a transition element? Give concise reason for your answer.

7.0   REFERENCES/ FURTHER READING

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UNIT 3   CHEMISTRY OF VANADIUM:

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1.0   INTRODUCTION

Vanadium as a transition element exhibits variable oxidation state of +5, +4, +3, +2, +1, 0 and (-1). On heating, vanadium combines directly with non-metals to form their corresponding compounds. Vanadium in +5 oxidation state is oxidizing and stable compounds are formed with strongly electronegative elements like oxygen and fluorine. Thus the chemistry of V^{5+} is dominated by the formation of pentafluoride, oxohalides and penta-oxide: VF_5, VOF_3, V_2O_5. Zinc is used to reduce a yellow solution of ammonium vanadate(V) to a mauve solution containing vanadium(II) ions. The intermediate oxidation states of vanadium(IV) (blue) and vanadium(III) (green) are also seen. This is to demonstrate that different oxidation states of transition metal ions often have different colours and that electrode potentials can be used to help predict the course of redox reactions (via the 'anticlockwise rule' or otherwise).

The relevant half reactions and redox potentials are as follows:
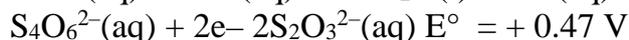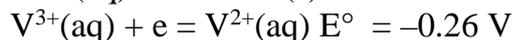
$Zn^{2+}(aq) + 2e = Zn(s)$ E° $= -0.76$ V
$V^{3+}(aq) + e = V^{2+}(aq)$ E° $= -0.26$ V
$Sn^{2+}(aq) + 2e = Sn(s)$ E° $= -0.14$ V
$VO^{2+}(aq) + 2H+(aq) + e- H_2O(l) + V^{3+}(aq)$ E° $= +0.34$ V
$S_4O_6^{2-}(aq) + 2e- 2S_2O_3^{2-}(aq)$ E° $= + 0.47$ V
$VO^{2+}(aq) + 2H^+(aq) + e = H_2O(l) + VO^{2+}(aq)$ E° $= +1.00$ V
So zinc will reduce $VO^{2+}(aq)$ to $V^{2+}(aq)$, tin will reduce $VO^{2+}(aq)$ to $V^{3+}(aq)$ and no further and thiosulphate ions will reduce $VO^{2+}(aq)$ to $VO^{2+}(aq)$ and no further.

2.0   OBJECTIVES

This is to demonstrate that different oxidation states of transition metal ions often have different colours and that electrode potentials can be used to help predict the course of redox reactions

3.0   MAIN CONTENT

The purpose of this experiment is to illustrate the presence of several different oxidation states for vanadium, and to show how it is possible to change from oneoxidation state to another. The object of the experiment is to start with a solution containing vanadium with oxidation number + 5, and to selected reducing agents which will reduce it to each of the other oxidation numbers. The most convenient starting material is solid ammonium vanadate (V), NH_4VO_3. When ammonium vanadate is acidified the vanadium becomes part of a positive ion, VO; (aq), in which the vanadium still has an oxidation number of + 5. You are provided with this solution. The other oxidation numbers of vanadium are included with this one in the table below.

Table 4 Different species of vanadium ions in solution

Ion	Oxidation state	Colour of solution
VO_2^+ : Dioxovanadium(V)	+5	Yellow
VO^{2+} : Oxovanadium(IV)	+4	Blue
V^{3+} : Vanadium(III)	+3	Green
V^{2+} : Vanadium(II)	+2	Mauve

3.1   Experiment 1: Illustrating the oxidation states of vanadium

3.1.1 Materials

One 1 dm^3 conical flask, Filter funnel, boiling tube, Dropping pipette, Four petri dishes (optional), Access to an overhead projector (optional), Test-tubes and rack (optional).

The quantities given for the chemical reagents are for one demonstration. Ammonium vanadate(V), NH_4VO_3) (11.7 g), zinc powder (15 g), 100 cm^3 of approximately 0.25 mol dm^{-3} potassium permanganate (potassium manganate(VII), $KMnO_4$) in 1 mol dm^{-3} sulphuric acid. Dissolve 4 g of potassium permanganate in 100 cm^3 of 1 mol dm^{-3} sulphuric acid). About 1 g of powdered tin (optional), about 10 cm^3 of approximately 1 mol dm^{-3} sodium thiosulphate solution (optional). Dissolve about 25 g of sodium thiosulphate-5-water in 100 cm^3 of water, 1 dm^3 of 1 mol dm^{-3} sulphuric acid.

3.1.2 Method

Before the demonstration Make up a 0.1 mol dm^{-3} solution of ammonium metavanadate by dissolving 11.7 g of solid in 900 cm^3 of 1 mol dm^{-3} sulphuric acid and making up to 1 dm^3 with deionised water. This yellow solution is usually represented as containing VO_2^+(aq) ions (dioxovanadium(V) ions) in which vanadium has an oxidation number of +5.

- Place 500 cm^3 of the ammonium metavanadate solution in a 1 dm^3 conical flask and add about 15 g of powdered zinc.
- This will effervesce and give off hydrogen on reaction with the acid. The solution will immediately start to go green and within a few seconds will turn pale blue, the colour of the VO^{2+}(aq) ion in which the vanadium has an oxidation number of +4. The short-lived green colour is a mixture of the yellow of V^{5+} and the blue of V^{4+}.
- The blue colour of VO^{2+} is similar to that of the Cu^{2+}(aq) ion. Over a further fifteen minutes or so, the colour of the solution changes first to the green of V^{3+}(aq) ions and eventually to the mauve of V^{2+}(aq) ions.
- The green of V^{3+}(aq) is the most difficult to distinguish. If desired, decant off a little of the solution at each colour stage, filter it to remove zinc and stop the reaction and place in a petri dish on the overhead projector to show the colour more clearly. When the reaction has reached the mauve stage, filter off a little of the solution into a boiling tube and add acidified potassium permanganate solution dropwise.
- This will re-oxidise the vanadium through the +3 and +4 oxidation states back to V^{5+}. Take care with the final few drops to avoid masking the yellow colour of vanadium(V) with the purple of permanganate ions.

3.2   Discussion

A white background is vital if the colour changes are to be clearly seen. If desired, prepare solutions containing V^{4+} and V^{3+} beforehand for comparison. This is recommended for teachers who are not familiar with these colours. This can be done as follows.

V^{5+}:
Take a little of the original ammonium metavanadate solution in a test-tube and add approximately 1 mol dm^{-3} sodium thiosulphate solution dropwise until no further colour change occurs and a light blue solution is obtained. If too much thiosulphate is added, the solution will gradually go cloudy due to the formation of colloidal sulphur by reaction of the

excess thiosulphate with acid but this will not affect the blue colour of V^{4+}.

V^{3+}:
Take a little of the original ammonium metavanadate solution in a test-tube and add a spatula-full of powdered tin. Leave this for about five minutes and then filter off the tin to leave a green solution containing $V^{3+}(aq)$ ions.

3.3   In-text questions and answers

ITQ. Carry out the following test on ammonium trioxovanadate (V) sample and present your results in a tabular form with a summary of the reactions taking place in each test procedure.

1.   Place about 0.25 g (one spatula measure) of ammonium trioxovanadate(V) in a conical flask and add about 25 cm^3 of dilute sulphuric acid. Carefully add about 5 cm^3 of concentrated sulphuric acid and swirl the flask until you obtain a clear yellow solution.

2.   Pour about 2 cm^3 of this vanadium[V) solution into each of two test tubes ready for later tests.

3.   To the conical flask add 1 - 2 g (one spatula measure) of zinc dust, a little at a time. Swirl the flask at intervals and record any observed colour changes.

4.   When the solution has become violet (you may need to heat the flask for this final change), filter about 2 cm^3 into each of three test-tubes.

5.   To one of the three tubes add, a little at a time, an excess of acidified potassium manganite(VII) solution, shaking after each addition, until no further change is observed.

ITA 1

Test	Observations	Typical reactions taking place
NH_4VO_3 + Dil H_2SO_4	The white solid turned red and dissolved to a yellow solution	VO_3^- VO_2^+
Vanadium(V) + Zinc dust	Effervescence occurred and the yellow solution turned green, blue,	VO_2^+ VO^{2+} V^{3+} V^{2+}

	green again and finally pink	
Vanadium(II) + KMnO$_4$	The violet solution became green, blue, green, yellow and finally pink	V^{2+} V^{3+} VO^{2+} VO$_2^+$

ITQ 2.
How do you explain the first appearance of a green colour in the solution? What are the subsequent changes in colour and why do these changes occur?

ITA 2.
The first appearance of a green colour is due to a mixture of yellow vanadium(V) and blue vanadium(IV). The subsequent changes are due to continuing reactions:

Blue   green: V(IV)   V(III)
Green   Violet: V(III)   V(II)
These changes are reversed on adding manganate(VII) except that when oxidation is complete, the solution is pink.

SELF-ASSESSMENT EXERCISE

Carry out the following experiments with the ammonium metavanadate salt, **E**, and record your results and observations. Give what explanations you can.

(a) Heat it.
(b) Heat it with a little sodium hydroxide solution.
(c) Treat it with a little concentrated hydrochloric acid.
(d) Add to its solution in water a little concentrated hydrochloric acid and a piece of granulated zinc, or some zinc powder.
(e) To its solution in water add a little potassium iodide solution and a little dilute hydrochloric acid. Boil gently for a time.
(f) Add to its solution in water a little hydrogen peroxide and acidify with dilute sulphuric acid.

4.0   CONCLUSION

The experiment in this unit has illustrated the presence of several different oxidation states for vanadium, and how it is possible to change from one oxidation state to another. Zinc has been used as a reducing agent, while KMnO$_4$ act as oxidizing agent.

5.0   SUMMARY

Vanadium pentoxide V_2O_5 can be thermal decomposition of ammonium vanadate:

$2NH_4VO_3 \qquad V_2O_5 + 2NH_3 + H_2O$

V_2O_5 is an orange solid that melts at 650 °C. It is amphoteric in nature dissolving both in acidic and basic solution. In acid it dissolves to form hydrated pervanadyl ion VO_2^+ (aq), while in alkali it forms vanadates the actual specie present in solution depends on the pH and the total concentration of vanadium. On dissolving V_2O_5 in strong aqueous NaOH, a colourless solution containing a tetrahedral VO_4^{3-} ion, is obtained. When this solution is progressively acidified, polymerization of the oxy ions occurs giving dimers, trimers, petamers etc. In acidic medium (pH = 2), a brown precipitate of V_2O_5 separates and redissolves at still lower pH (pH 1) to give a pale-yellow solution of dioxovanadium VO_2^+ ion.

6.0   TUTOR-MARKED ASSIGNMENT

1 (a)   Write down the electronic configuration (s p d electrons) of
    (i)   an atom of chrornium,
    (ii)   a chromium ion
 (b)   State the oxidation state (number) of chromium in
    (i) $Cr_2O_7^{2-}$
    ii) CrO_4^{2-}

7.0   REFERENCES/FURTHER READING

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UNIT 4   THE CHEMISTRY OF CHROMIUM

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       3.2   Change of oxidation states of from +6 to +3 to +2: $CrSO_4$
       3.3   Reduction of dichromate(VI) ions to chromate(III) ions by H_2O_2
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1.0   INTRODUCTION

Chromium as a transition metal exhibits variable oxidation state of +2, +3 and +6. It dissolves in non-oxidizing mineral acids like HCl and H_2SO_4 with evolution of hydrogen and formation of chromous compounds.

$$Cr + 2HCl = CrCl_2 + H_2$$
$$Cr + H_2 SO_4 = CrSO_4 + H_2$$
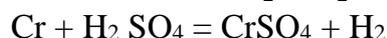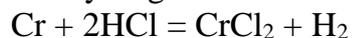
HNO_3 whether dilute or concentrated and aqua regia renders the metal passive. At elevated temperature, chromium reacts with non-metals like sulphur, halogens, carbon, nitrogen and oxygen to form their corresponding compounds.

Chromium in +6 oxidation state has a d^o configuration and it is oxidizing in acid solution. Compounds are therefore formed with electronegative ligands like Oxygen, fluorine and chlorine. Examples are CrO_3, CrO_4^{2-}, $Cr_2O_7^{2-}$, CrO_2F_2, CrO_2Cl_2.

2.0   OBJECTIVES

The main objective of this experiment is to illustrate an interesting redox chemistry of chromium.

3.0   MAIN CONTENT

3.1   Change of oxidation state from +3 to +6: Potassium dichromate, $K_2Cr_2O_7$

In this preparation, chromium (III) is oxidized to chromium (VI) in alkaline solution, using hydrogen peroxide as the oxidizing agent. The chromate is converted to dichromate by acidification after the removal of any excess of hydrogen peroxide.

$$2CrCl_3 + 10KOH + 3H_2O_2 = 2K_2CrO_4 + 6KCI + 8H_2O$$
$$2K_2CrO_4 + 2CH_3CO_2H = K_2Cr_2O_7 + 2CH_3CO_2K + H_2O$$
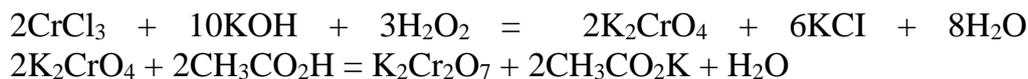
Dissolve 14 g (0. 05 mole) of chromium(III) chloride hexahydrate in 40 ml of water in a 250 ml beaker. Add slowly, with stirring, a solution of 17 g (0'25 mole) of potassium hydroxide in 40 ml of water. The green precipitate of chromium (III) hydroxide formed partially redissolves. Now warm the mixture gently, do not boil, and add slowly with stirring, 60 cm^3 of '20 volume' (2M) hydrogen peroxide. When it has all been added, bring the solution to the boil for a few minutes to destroy any excess of oxidizing agent, then filter hot through a large (7 crn) Buchner funnel. Transfer the solution of potassium chromate to an evaporating basin and boil away half the liquid. Add to the hot solution 5 ml (0.09 mole) of glacial acetic acid, and cool the solution in a refrigerator or ice-bath. Filter off the orange crystals formed, wash with a small volume of iced water and dry in a desicator containing sodium hydroxide

3.2   Change of oxidation state from +6 to +3 to + 2: Chromium(II) sulphate solution, $CrSO_4$

When a chromate is acidified it forms a dichromate (see above) and this solution is readily reduced in acid solution to the +3 state. Further reduction to chromium (II) can only be accomplished if air is rigorously excluded from the system. Hence all solutions should be boiled to remove dissolved air, and an inert or reducing atmosphere is required in the reaction vessel. This can be achieved by fitting the flask with an efficient Bunsen valve.

Dissolve 3g (0'01 mole) of potassium dichromate in 10 ml of water, add 10 ml of 2M sulphuric acid and 3 g (an excess) of zinc and fit the conical flask with a stopper carrying a Bunsen valve. The solution will change first to green, then eventually to a clear blue. When exposed to the air, the blue chromium (II) ions are rapidly oxidized to green chromium (III).

3.3   Reduction of dichromate(VI) ions to chromate(III) ions by hydrogen peroxide

On adding the hydrogen peroxide solution (5 %), to aqueous solution of potassium dichromate (0.2 moldm^{-3}), the reaction mixture immediately turns a deep blue colour. After a while bubbles are seen and the colour gradually fades to a pale blue-green due to hexa-aquachromium(III) ions. The reaction is:

$$Cr_2O_7^{2-}{}_{(aq)} + H_2O_{2(aq)} + 8H^+{}_{(aq)} \quad 2Cr^{3+}{}_{(aq)} + 5H_2O_{(l)} + 2O_{2(g)}$$
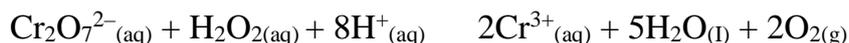
3.4   In-text questions and answers

ITQ 1.
A standard solution of potassium dichromate was prepared by accurate weighing 5.88g of $K_2Cr_2O_7$ and dissolving in 1 L of distilled water. From the weight taken, calculate the exact molarity of your solution.

ITA 1.

$$\frac{Mass}{Molar\ masss} = \frac{C \times V}{1000}$$

$$\frac{5.88}{294.185} = \frac{C \times 1000}{1000} = 0.019987\ M$$

SELF-ASSESSMENT EXERCISE

1   Carry out the following experiments with substance Z: $KCr(SO_4)_2$
   (a)   Dissolve a little in cold water.
   (b)   Warm the solution from (a).
   (c)   Add sodium hydroxide solution drop by drop to the solution from (b) until there is an excess   of alkali.
   (d)   Add a little hydrogen peroxide to the solution from (c), and warm.
   (e)   Acidify the solution from (d) with dilute sulphuric acid. Add a layer of ether, and another   drop   of   hydrogen peroxide.
   (f)   To its solution in water add barium chloride solution and dilute hydrochloric acid.
   (g)   Carry out a flame test on Z.
          Record your results in a tabular form stating your observation and explain the reactions as   far as you can.
2 (a)   Write down the electronic configuration (s p d electrons) of
   (iii)   an atom of chrornium,
   (iv)   a chromium ion
 (b)   State the oxidation state (number) of chromium in
   (i) $Cr_2O_7^{2-}$
   ii) CrO_4^{2-}

(c)   Classify the following changes as oxidation reduction and/or acid-base giving a reason in each case.
   i) $Cr_2O_7^{2-}$ CrO_4^{2-}
   ii) $Cr_2O_7^{2-}$ Cr^{3+}

(d)   By reference to standard electrode potentials suggest three reagents which would affect the change in (c)(ii).

4.0   CONCLUSION

The interesting redox chemistry of chromium has been demonstrated. Chromium in +6 oxidation state with d^0 electronic configuration has been converted to + 3 (d^3) and +2 (d^4).

5.0   SUMMARY

Starting with Cr(III), it is possible to get to Cr(VI) in potassium dichromate, $K_2Cr_2O_7$ by using oxidizing
agent such as hydrogen peroxide. Reduction to lower oxidation state can be achieved by using reducing
agents such as zinc dust.

6.0   TUTOR-MARKED ASSIGNMENT

1 (a)   Write down the electronic configuration (s p d electrons) of
      (i)   an atom of chrornium,
      (ii)   a chromium ion
 (b)   State the oxidation state (number) of chromium in
      (i) $Cr_2O_7^{2-}$
      ii) CrO_4^{2}

7.0   REFERENCES/ FURTHER READING

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MODULE 3

Unit 1   Chemistry of manganese
Unit 2   Chemistry of iron

UNIT 1   CHEMISTRY OF MANGANESE

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1.0   INTRODUCTION

Manganese is more electropositive than its neighbours in the transition series. It is outstandingly reactive. It liberates hydrogen from water and dissolves readily in dilute mineral acids to form Mn(II) salts. In +2 oxidation state, manganese has a d^5 configuration. This symmetrical d^5 configuration confers extra stability on Mn^{2+} compounds, consequently Mn(II) ions shows high resistance to oxidation and reduction. Manganese (II) forms series of salts with all common anions, most of which are soluble in water. For example manganese(II)sulphate $MnSO_4.7H_2O$ contains the aqua complex ion $[Mn(H_2O)_6]^{2+}$.

Mn(III) has a d^4 configuration and is strongly oxidizing in aqueous solution. There is a high tendency for Mn(III) compounds in solution to disproportionate into Mn^{4+} as in MnO_2 and $Mn^{2+}_{(aq)}$. Stable compounds are formed mainly by O-donor ($C_2O_4^{2-}$, SO_4^{2-}) and strong field ligands like CN^-. Mn(III) compounds are obtained either by oxidation of Mn(II) salts or by reduction of $KMnO_4$.

Mn(IV) has a symmetrical d^3 configuration and few complexes of the type $K_2[MnX_6]$ (X=F, $ClCO_3$, CN) are known. The most important compound of manganese in +4 state is the manganese dioxide MnO_2 which is an

oxygen deficient solid The chemistries of Mn(V) and Mn(VI) are dominated by oxo compounds and are stable in alkaline solution as the blue permanganite ion $MnO_2{}^{3-}$ and the dark green manganate ion $MnO_4{}^{2-}$ respectively (Ayi, 2019).

2.0   OBJECTIVES

The purpose of this experiment is to make samples of some of the less common oxidation states of manganese.

3.0   MAIN CONTENT

The less common oxidation states of manganese can easily be predicted from the readily available Mn(VII), Mn(IV) and Mn(II). The predictions can equally be tested in Experiment s. For instance, it has been proposed that Mn(VI) compounds might be formed by reaction between Mn(VII) and Mn(IV). The feasibility of such reactions in aqueous solution of varying pH can be predicted if the electrode potentials for appropriate half-cells are known. For standard' acid conditions, such as $[H^+(aq)] = 1$ mol dm^{-3} or pH = 0:
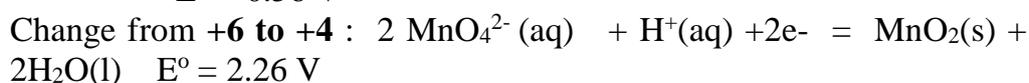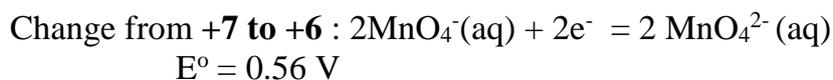
Change from **+7 to +6** : $2MnO_4{}^-(aq) + 2e^- = 2\ MnO_4{}^{2-}(aq)$
             $E^o = 0.56\ V$
Change from **+6 to +4** : $2\ MnO_4{}^{2-}(aq) + H^+(aq) + 2e- = MnO_2(s) + 2H_2O(l)$ $E^o = 2.26\ V$
 A cell reaction converting Mn(VII) and Mn(IV) to Mn(VI) is obtained by reversing the second half-equation and adding to the first:

$2MnO_4{}^-(aq) + MnO_2(s) + 2H_2O(I) = 3MnO_4{}^{2-}(aq) + 4H^+(aq)$ $E^o = -2.26\ V + 0.56\ V = -1.70\ V$
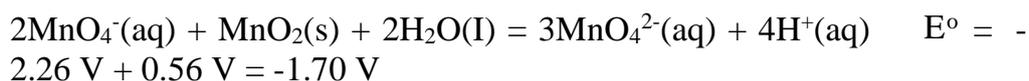
Since E^o is large and negative, the reaction will not proceed from left to right to any measurable extent. Indeed, any Mn(VI) obtained by other means would be expected to disproportionate completely in acid conditions. (The same conclusion may be reached by applying the 'anticlockwise rule' to the two half-equations.)

We also see that reducing $[H^+(aq)]$ would shift equilibrium to the right and make the desired reaction more likely. We should therefore consider alkaline conditions.

Electrode potentials for 'standard' alkaline conditions, namely $[OH^-(aq)] = 1$ mol dm^{-3} or pH = 14, are as follows:
Change from +7 to +6: $2MnO_4{}^-(aq) + 2e^- = 2MnO_4{}^{2-}(aq)$: $E^o = 0.56\ V$
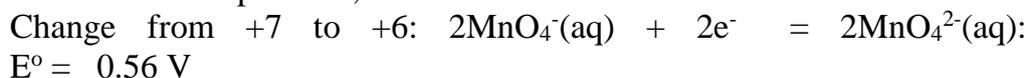
Change from +6 to + 4: $MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- = MnO_2(s) + 4OH^-$ (aq): $E^o = 0.60$ V
A cell reaction converting Mn(VII) and Mn(IV) to Mn(VI) is obtaied by reversing the second half-equation and adding to the first:

$2MnO_4^-(aq) + MnO_2(s) + 2OH^-(aq) = 3MnO_4^{2-}(aq) + 2H_2O(l)$: $E^o = -0.04$ V

Here we see that E^o is negative again, but this time very small, so that we might expect the reaction to produce an equilibrium mixture containing significant proportions of both reactants and products. Furthermore, we should be able to shift the equilibrium to the right by increasing $[OH^-(aq)]$, thus producing more Mn(VI) in the equilibrium mixture.

3.1   In-text questions and answers

ITQ 1.
 Predict the feasibility of making Mn(III) from Mn(II) and Mn(IV) under conditions of varying pH. Use these electrode potentials:
$MnO_2(s) + 4H^+(aq) + e = Mn^{3+}(aq) + 2H_2O(1)$: $E^o = 0.95$ V
          Eq.1
$Mn^{3+}(aq) + e = Mn^{2+}(aq)$: $E^o = 1.51$ V
          Eq.2
$Mn(OH)_3(s) + e^- = Mn(OH)_2(s) + OH^-(aq)$: $E^o = -0.10$ V   Eq.3
$MnO_2(s) + 2H_2O(1) + e = Mn(OH)_3 + OH^-(aq)$: $E^o = 0.20$ V
          Eq.4
    ITA 1. For acid conditions, combining equations 1 and 2 gives:
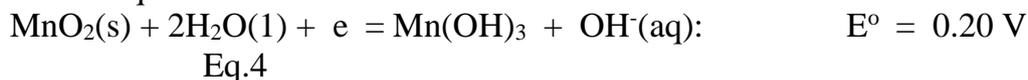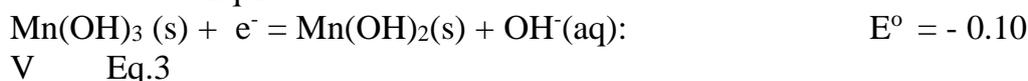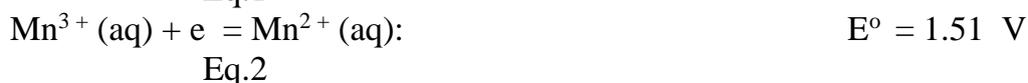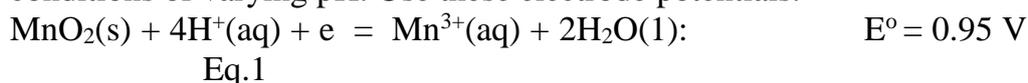
$MnO_2(s) + 4H^+(aq) + Mn^{2+} = Mn^{3+}(aq) + 2H_2O(1$: $E^o = -0.56$ V
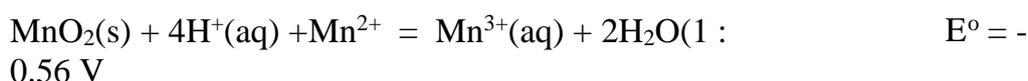
Since E^o is negative and fairly large, the reaction will not proceed from left to right to any measurable extent under standard conditions. Increasing $[H^+(aq)]$ would shift equilibrium to the right, but not sufficiently to give an appreciable amount of Mn3+ because E^o is outside the range of reversibility (i.e. -0.4 V to + 0.4 V).

For alkaline conditions, combining equations 3 and 4:
$MnO_2(s) + 2H_2O(1) + Mn(OH)_2(s) + OH^-(aq) = Mn(OH)_3 + OH^-(aq)$:
 $E^o = + 0.33$ V
Since E^o is positive, but less than 0.40 V, we should expect this reaction to proceed from left to right to an equilibrium mixture containing significant amounts of both reactants and products. However, since two of the reactant are solids, we might expect the reaction to be slow. Since
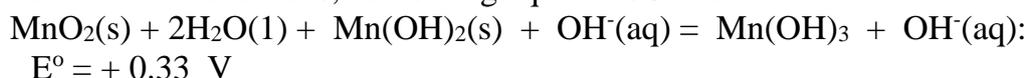
[OH⁻(aq)] does not appear in the final equation, changing its concentration will not change E^o.

3.2 Experiment 1: Investigation of uncommon oxidation states of manganese

3.2.1 Requirements

Safety spectacles and protective gloves, 6 test-tubes and rack, potassium manganate(VII) (permanganate) solution, 0.01 M $KMnO_4$, sulphuric acid, dilute, 1 M H_2SO_4, sodium hydroxide solution, 2 M NaOH, manganese(IV) oxide (manganese dioxide), MnO_2 spatula stirring rod filter funnel and 3papers manganese(II) sulphate-4-water, $MnSO_4 \cdot 4H_2O$ sulphuric acid, concentrated. H_2SO_4.

3.2.2 Method A

1. Put about 5 cm³ of potassium manganate(VII) solution in each of three test-tubes.
2. To one of the three tubes add about 3 cm³ dilute sulphuric acid and to another add about
3. cm³ sodium hydroxide solution.
4. To each of the three tubes add a little solid manganese(IV) oxide and stir for about a minute.
5. Filter enough of each mixture into a clean tube to see the colour of the filtrate clearly. Use a fresh filter paper for each mixture.
6. One of the tubes should now have in it a clear green solution of Mn[VI). Add to this a little dilute sulphuric acid.

3.2.3 Method B

a. Dissolve about 0.5 g manganese(II) sulphate in about 2 cm³ of dilute sulphuric acid in a test-tube.
b. Carefully add about 10 drops concentrated sulphuric acid and cool the tube under a running tap.
c. Add a few drops of potassium manganate[VII] solution to obtain a deep red solution of Mn(III).
d. Dilute the red solution with about five times its volume of water, wait a few moments, and note any colour change.

3.2.4 Method C

i. In each of two test-tubes dissolve a little manganese(II) sulphate in water and add an equal volume of sodium hydroxide solution to obtain a precipitate of manganese(II) hydroxide.

ii.   To one of the two tubesJ add a little manganese(IV) oxide and stir.
iii.   Let both tubes stand for a few minutes and note any changes.

Method A

1.   Explain why only one of the three mixtures reacted to give green Mn(VI).
2.   What happened when acid was added to Mn[VI)? Explain.

Method B

1   Explain what happened when the Mn(III) solution was diluted
2   Can you see any sign of Mn(III) in the tubes?
3.   What is different about the conditions of this experiment (Method C) compared with the one in method B,which makes its success less likely? What happens in the test-tube which had no manganese(IV) added? Suggest an explanation.

Method C

1   Can you see any sign of Mn(III) in the tubes?
2.   What is different about the conditions of this experiment (Method C) compared with the one in Method B which makes its success less likely?
3.   What happens in the test-tube which had no manganese(IV) added? Suggest an explanation.
4. $KMnO_4$ is widely used in the laboratory as strong oxidants. The MnO_4^- can be reduced at different pH to Mn(II), Mn(IV) or Mn(VI). With chemical equations only, show the different stages of reduction specifying the pH medium and the electrode potentials.

4.0   CONCLUSION

In this unit we have been able to demonstrate that interconversions from one oxidation state to another are possible.

5.0   SUMMARY

Variable oxidation state is just one of the characteristics of transition elements. But all of them are related in some way to electron configuration and oxidation state.

6.0 TUTOR-MARKED ASSIGNMENT

1. Also carry out, and interpret, qualitative tests on the solution of the suspected double salt using:
    (a) 2M ammonia, (b) 2M sodium hydroxide, (c) ammonium thiocyanate solution.
2. Potassium manganate(VII) in acid solution may be used to determine the concentration of iron(II) ions by titration.

7.0 REFERENCES/ FURTHER READING

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UNIT 2   REDOX REACTIONS OF IRON

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1.0   INTRODUCTION

Potassium manganate(VII) is a well-known oxidising agent, usually used in solutions acidified with a plentiful supply of dilute sulphuric acid. The following electrode potentials show that manganate(VII) ions should oxidise iron(II) ions:

$Fe^{3+}(aq) + e^- = Fe^{2+}(aq)$: $E^o = +0.77V$ Eq. 1
$MnO_4^-(aq) + 8H^+(aq) + 5e^- = Mn^{2+}(aq) + 4H_2O(l)$ $E^o = +1.51$ V Eq. 2
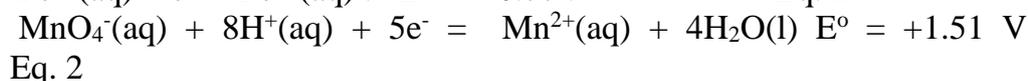
Combining these two half-equations gives the overall equation for the reaction:
$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) = 7 Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$ Eq.3
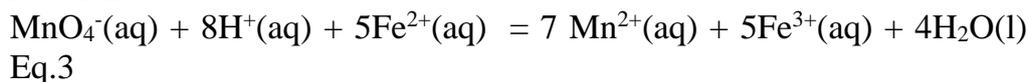
Thus in acid solution 1mole of MnO_4^- (aq) reacts with 5 moles of Fe^{2+}(aq). Solutions containing MnO_4^-(aq) ions have an intense purple colour, whereas those containing Mn^{2+}(aq) ions are almost colourless. Solutions containing Fe^{2+}(aq) ions can be titrated against potassium manganate(VII) solution. The colour of the manganate(VII) is discharged, the end-point of the titration being the point at which the addition of one more drop of potassium manganate(VII) gives a permanent purple colour. This titration forms the basis of an analytical technique for the estimation of iron which can be used to analyse a popular 'iron tonic'.

A mixture of two salts such as iron(II) sulphate and copper(II) sulphate in solution in non-equimolar proportions could be allowed to crystallize out together. The crystals obtained have a distinctive shape, and if the

product is a true double salt the cations should be present in a whole-number ratio.

2.0   OBJECTIVES

The main objective of this quantitative analysis for iron(II) and copper(II) ions is to establish their molar ratio

3.0   MAIN CONTENT

Redox titrations depend on the transfer of electrons between the two reacting species in solution. They may or may not be self-indicating. Examples include:

a.   Determination of copper(II) by displacement of iodine followed by titration with sodium thiosulfate.
b.   Reaction of ethandioate ions with potassium manganate(VII).
c.   Determination of iron(II) by reaction with potassium manganate(VII).

Potassium manganate(VII), $KMnO$, is a self-indicating reagent, which turns from the deep purple manganate(VII) ions to the nearly colourless manganese(II) ions.

$$MnO_4^- \;\;{}_{(aq)} \;+\; 8H^+ \;\;{}_{(aq)} \;+\; 5e \;\;=\;\; Mn^{2+} \;\;{}_{(aq)} \;+\; 4H_2O_{(l)}$$

It is a good oxidising agent in acidic solution.
Iron(II) ions are pale green in solution. They are oxidised by manganate(VII) ions in acidic solution to iron(III), which are pale yellow in solution.

$$MnO_4^- \;(aq) + 8H^+ \;(aq) + 5Fe^{2+} \;(aq) = Mn^{2+} \;(aq) + 4H_2O(l) + 5Fe^{3+} \;(aq)$$
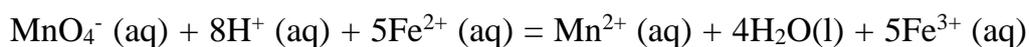
The stoichiometric ratio of reaction is given by the coefficients of the balanced equation above. If 25 cm^3 of a known concentration of potassium manganate(VII) solution is placed in a conical flask and an unknown iron(II) solution run into the flask from a burette, the end point of the titration is given by the disappearance of the purple manganate(VII) ion colour. This reaction scheme may be used to determine several things. For example:

1.   The concentration of an unknown iron(II) solution
2.   The number of moles of water of crystallisation in an iron(II) salt.
3.   The percentage iron in an alloy
4.   The mass of iron in an iron tablet
5.   The mass of iron in an iron tablet

Iron supplements contain soluble iron(II) salts to replenish them in the human body in case of deficiency. Iron is an essential mineral used in many functions, specifically in the transport of oxygen. Iron deficiency can occur through poor diet, or as a consequence of blood loss through menstruation or injury. Iron supplements usually contain about 50mg per tablet of iron(II). Potassium manganate(VII), Mr = 158.034, is a good primary standard, being available to a high degree of purity, having a large relative mass and being stable in the environment.

3.1   Experiment 1: Analysis of iron tablets

Iron(II) sulphate solution contains Fe^{2+}(aq) ions. These ions have a tendency to react with water which eventually makes the solution go brown and become cloudy. This has been minimized by adding some sulphuric acid. Weigh accurately two 'ferrous sulphate' tablets. Grind up the tablets with a little I M sulphuric acid, using a pestle and mortar. Through a funnel, transfer the resulting paste into a 100 cm^3 volumetric flask. Use further small volumes of 1M sulphuric acid to rinse the ground-up tablets into the flask. During this process, you must take great care to ensure that all the particles of tablet get into the flask. When this has been done, add sufficient 1M sulphuric acid to make up the solution to exactly 100 cm'. Stopper the flask and shake it to make sure that all the contents are thoroughly mixed. They will not all be in solution although the Fe^{2+} ions which were present in the tablets will be dissolved. Titrate 10.0 cm^3 portions of the solution with 0.0050 M potassium manganate(VII). The end-point is marked by the first permanent purple colour. Brown or red colours should not be allowed to develop; the remedy is to add more 1M sulphuric acid.

3.2   In-text questions and answers

ITQ 1. What are the reasons for using excess 1.0 M sulphuric acid during the experiment?

ITA.1 There are two reasons, the first has to do with the behaviour of solutions containing Fe^{2+} ions. These ions have a tendency to react with water which eventually makes the solution go brown and become cloudy. This has been minimized by adding some sulphuric acid. The second reason has to do with the equation for oxidations involving potassium manganate(VII).

ITQ 2.
Results from a typical experiment are shown below:
Mass of potassium manganate(VII) used: 1.58 g
Volume of potassium manganate(VII) used for the titration = 10 cm^3.
   Titration results:

Titre	1	2	3
Final burette reading (cm^3)	28.20	27.95	27.90
Initial burette reading (cm^3)	0.00	0.05	0.00
Volume (cm^3)	28.20	27.90	27.90

Using the above data,
i)   Calculate the concentration of potassium manganite(VII)
ii)   The mass of iron in 250 cm3 of solution
iii)   The mass of iron per tablet

ITA 2.
To calculate the concentration of KMnO$_4$: Concentration of standard potassium manganite

(VII) solution : $=$ 1.58/158.034 $=$ 0.01 mol dm^{-3}

$$No. of\ moles\ of\ MnO_4^- = \frac{C\ x\ V}{1000} = \frac{0.01\ x10}{1000} = 0.0001\ mols$$

i.   MnO$_4^-$ (aq) + 8H$^+$ (aq) + 5Fe^{2+} (aq) = Mn^{2+} (aq) + 4H$_2$O(l) + 5Fe^{3+} (aq)
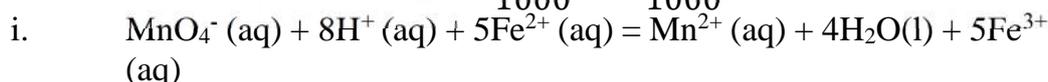
Therefore, from the reaction stoichiometry, 1 mole of MnO$_4^-$ requires 5 mols of Fe^{2+}. Therefore, moles of iron(II) = 5 x 0.0001 =   5.00   x   10^{-4} mol
This is in 27.90 cm^3, therefore in 250 cm^3 there is
(250/27.9) x 5.00 x 10^{-4} = 8.96 x 5 x 10^{-4} moles of iron = 4.48 x 10^{-3} mol.

ii.   Therefore mass of iron in 250 cm^3 = 56 x 4.48 x 10^{-3} g = 0.25 g
Hence, mass of iron per tablet = 250 mg

3.3   Experiment 2: Analysis of double salts
.
3.3.1 Requirements for this experiment

Titration apparatus and a standard flask. Standardized 0.02 M permanganate. Standardized 0.I M sodium thiosulphate, 0.5 M potassium iodide, Starch indicator.

3.3.2 Method

The suspected double salt is prepared as follows: add 50 g of hydrated copper (II) sulphate to 100 cm^3 of 2M sulphuric acid and heat to 75 ºC. Then add 45 g of hydrated iron (II) sulphate and, when dissolved, decant from any residue and chill the solution to 0°. Collect the crystals at the pump, and dry at room temperature. Prepare a standard solution of the salt

(roughly 40 g/L) by accurate weighing. Determine the iron (II) by titrating aliquots after acidification with 2M sulphuric acid, with the 0.02 M potassium permanganate. Determine the copper (II) by titrating aliquots after treatment with excess 0.2 M potassiumiodide, with the 0.1 M sodium thiosulphate.

Use the equations of the reactions to calculate the molar ratio of iron (II) ion to copper (II) ion:
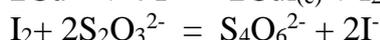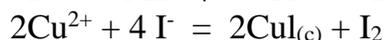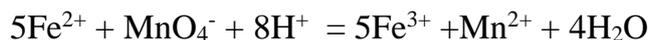
$$5Fe^{2+} + MnO_4^- + 8H^+ = 5Fe^{3+} + Mn^{2+} + 4H_2O$$
$$2Cu^{2+} + 4 I^- = 2CuI_{(c)} + I_2$$
$$I_2 + 2S_2O_3^{2-} = S_4O_6^{2-} + 2I^-$$

SELF-ASSESSMENT EXERCISE

1.   Also carry out, and interpret, qualitative tests on the solution of the suspected double salt using:
     (a) 2M ammonia, (b) 2M sodium hydroxide, (c) ammonium thiocyanate solution.

2.   Potassium manganate(VII) in acid solution may be used to determine the concentration of iron(II) ions by titration.

     a.   Copy, complete and balance the equation:
          $MnO_4^-(aq) + $ -------(aq) $ + 5Fe^{2+}(aq)= $ ------(aq) $ + $ ------(aq) $ + $ ------(1)

     b.   0.350 g of a sample of impure iron wire was reacted with excess sulphuric acid to convert the iron into a solution of iron (II) ions. The impurities may be assumed   to be inert. The solution was made up to exactly 100 cm^3 in a volumetric flask. 10.0 cm^3 portions of this diluted solution required 11.8 cm^3 of 0.0100 M potassium manganate(VII) for complete reaction.
          i.   Explain why this titration is said to be self-indicating.
          ii.   Calculate the number of moles of $KMnO_4$ used in the titration; the number of moles of Fe^{2+} (aq) used in the titration; the mass of iron in the sample of iron wire and the percentage purity of the iron wire.

3.   A salt containing iron (III) ions (2.41 g) was dissolved in dilute sulphuric acid and zinc was added to reduce the $Fe^{3+}(aq)$ to Fe^{2+} (aq). The resulting solution was made up to 100 cm^3 with dilute sulphuric acid and 10.0 cm^3 portions were titrated with 0.0200 M

potassium manganate(VlI) solution. Exactly 10.0 cm^3 of the 0.0200 M KMnO$_4$ was required.

a   Show by using electrode potentials that zinc should reduce Fe^{3+}(aq) to Fe^{2+} (aq).

b   Why was the solution made up to 100 cm^3 ' by using dilute sulphuric acid rather than water?

c   Calculate the percentage of iron, by mass, in the original salt.

4.0   CONCLUSION

The iron (II) ions present in a solution could be determined by titrating aliquots after acidification with 2M sulphuric acid, with the 0.02 M potassium permanganate. Also the copper (II) ions could be determined by titrating aliquots after treatment with excess 0.2 M potassium iodide, with the 0.1 M sodium thiosulphate.

5.0   SUMMARY

When   potassium iodide solution is used as a reducing agent, the iodide will be oxidised to elemental iodine. This will give a colour to the solution which will mask the colour of the metalion. The iodine can be reduced back to colourless iodide by reaction with sodium thiosulphate solution.

$$S_2O_6^-(aq) + 2e- = 2S_2O_3^{2-} \qquad Eo = + 0.09 \text{ V}$$

In order to know if iron has change its oxidation state, a suitable test is to add sodium
 hydroxide solution. Iron(II) ions give a green precipitate when sodium hydroxide solution
is added, whereas iron(III) ions give a red-brown precipitate.

6.0   TUTOR-MARKED ASSIGNMENT

1.   Also carry out, and interpret, qualitative tests on the solution of the suspected double salt using:
      (a) 2M ammonia, (b) 2M sodium hydroxide, (c) ammonium thiocyanate solution.
2.   Potassium manganate(VII) in acid solution may be used to determine the concentration of iron(II) ions by titration.

7.0   REFERENCES/FURTHER READING

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MODULE 4

UNIT 1   PREPARATION OF A COORDINATION COMPOUND

CONTENTS

1.0   Introduction
2.0   Objectives
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                3.1.1   Materials
                3.1.2   Method
        3.2   In-text questions and answers
4.0   Conclusion
5.0   Summary
6.0   Tutor-Marked Assignment
7.0   References/Further Reading

1.0   INTRODUCTION

One of the characteristic properties of transition elements is their ability to form complex compounds. This ability is attributed to the presence of vacant (n-1)d orbitals and existence of variable oxidation states. The formation of complex compounds is through a donor-acceptor interaction involving a central metal atom/ion with vacant orbitals and a molecule or ion possessing a lone-pair of electrons. The metal atom/ion with vacant orbitals acts as the acceptor atom, while the molecule or ion with lone-pair(s) of electrons serves as the donor. The bond resulting from this type of interaction is called coordinate covalent bond and the compound formed is known as coordination (or complex) compound (Ayi, 2019). A complex or coordination compound therefore consists of a central metal atom surrounded by a set of electron pair donors called ligands. According to N. V. Sidgwick (1927), the central metal ion/atom in complexes, tend to surround it self with sufficient ligands to attain an electron count equal to that of the noble gas of the same period. For example in the complex $[Co(NH_3)_6]Cl_3$, the central atom, cobalt is in +3 oxidation state with 24 electrons; to attain the Krypton configuration of 36 electrons, Co^{3+} ions accepts six electron pairs from the ammine ligands.

Sidgwick called this number of electrons the effective atomic number (EAN). The effective atomic number (EAN) is the total number of orbital electrons shared or unshared, possessed by an atom in a specified complex compound. The concept of EAN rule is of great importance as it can be used in rationalizing the coordination numbers and structures of complex compound.

Coordination compounds result when a Lewis acid and a Lewis base react together to form a Lewis acid-base adduct (or coordination complex). A classic example of this is the reaction of the electron deficient molecule, BF_3 (Lewis acid), with NH_3 (Lewis base) to form BF_3- NH_3 (Figure 1), which contains a coordinate covalent bond between the boron and nitrogen atoms, and in which the boron has an octet of electrons. The NH_3 molecule is called a ligand because of the fact that it has a lone pair of electrons which it can donate to the electron deficient BF_3.
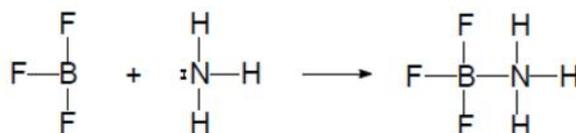
Scheme 1

Transition metal salts found on the laboratory shelf are good examples of coordination complexes. For example, a bottle labelled $NiCl_2 \cdot 6H_2O$ should really be labelled as $[Ni(H_2O)_6]Cl_2$,, because the six water molecules are actually ligands which coordinate to the nickel centre to form an octahedral complex ion (Scheme 2). Note that the **water molecules are all equivalent** and are positioned at the apices of an octahedron, with angles of 90° between adjacent Ni-OH$_2$ bonds. Water is called a monodentate ligand (one donor centre), but if more than one donor site is joined by some chemical linkage then polydentate ligands with several points of attachment result.
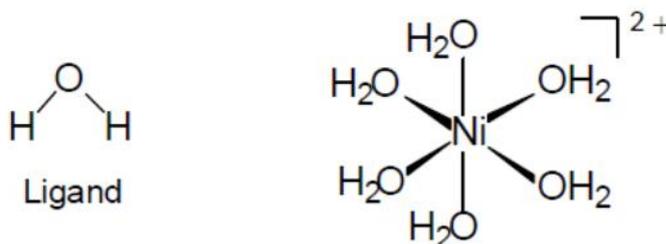
Scheme 2

Polydentate ligands with six (i.e hexadentate) or even more donor centres are known. The binding of polydentate ligands to a metal ion results in *chelation*, with the formation of stable *chelate* rings. The oxalate anion is a good *chelating* ligand, with two oxygen donor centres, and a double negative charge. These two factors impart high stability to the coordination complexes formed by oxalate.

The tris-oxalatocobaltate(III) ion is shown in Scheme 3. This ion has the same octahedral geometry and oxidation number as the tris-oxalatoferrate(III) ion which you will be preparing in this experiment.

oxalate ion   tris-oxalotocobaltate (III) ion
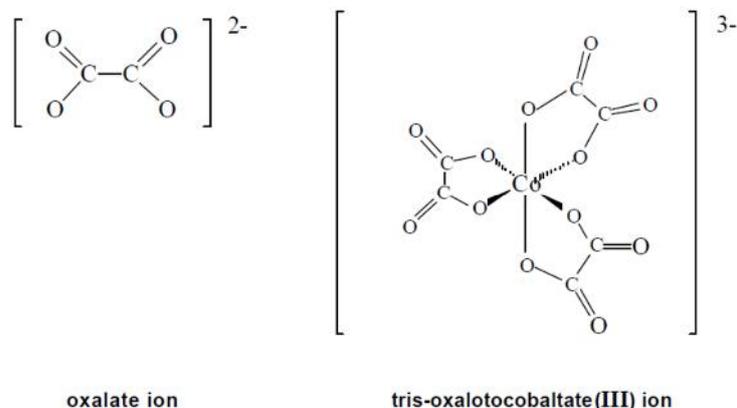
Scheme 3

2.0   OBJECTIVES

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

- To synthesize a coordination compound
- To examine some of the properties of transition metal ions

3.0   MAIN CONTENT

3.1   Preparation of potassium tris-oxalatoferrate(III)trihydrate: $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$

3.1.1 Materials

250 mL beaker, top-loading balance, iron(III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$, Bunsen burner. deionized water, potassium hydrogen oxalate   monohydrate, $KHC_2O_4 \cdot H_2O$, potassium hydroxide, KOH,

3.1.2 Method

- Place a clean, dry 250 mL beaker on the top-loading balance, record its mass and weigh by difference about 8.1 g (record actual mass used) of iron(III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$, into it.
- Add 20 mL of deionized water and a few boiling granules to the beaker and heat it gently using a Bunsen burner.

- Do not allow the solution to boil. Weigh by difference about 7.7 g (record actual mass used) of potassium hydrogen oxalate monohydrate, $KHC_2O_4 \cdot H_2O$ into a clean, dry weighing vial and add it, with stirring, to the beaker when all the $Fe(NO_3)_3 \cdot 9H_2O$ has dissolved.

- Heat the mixture gently until all the solid dissolves, then, stirring carefully, add 10 mL of 6.0 mol L^{-1} KOH. Stir the mixture until all of the brown precipitate which forms initially has dissolved. If the brown solid fails to dissolve you have made an error in your weighings and must begin again.

- Filter the hot solution through a glass funnel fitted with a fluted filter paper into a 250 mL conical flask. Slowly, with swirling, add 2 mL of 95% ethanol to the filtrate. Allow the solution to cool without disturbing it for at least 30 minutes to induce crystal growth. If the crystals have not appeared at this time add 3 more mL of 95% ethanol. Shake the flask vigorously and then allow it to stand undisturbed for a further 10 minutes to complete the crystallization.

- When crystallization is complete, collect the product by suction filtration in a Buchner funnel.

- Wash the crystals twice with 10 mL portions of acetone. Break the suction before each addition by pulling the hose off the aspirator or loosening the funnel.

- Warning: acetone and ethanol are flammable solvents. All flames must be extinguished in the lab before removing these solvents from the fumehood.

- Allow the crystals to dry for 5 minutes under suction. Then spread them out on a clean piece of smooth paper to air dry while you prepare the sample vial and label.

- Transfer the crystals to a pre-weighed vial and weigh the vial plus crystals. Record the yield, product formula and your name and bench # on the product label. Immediately wrap the vial in aluminum foil to protect your product from exposure to light and leave the product at your bench to be collected along with your report.

3.2   In-text questions and answers

ITQ 1.
Write out the balanced molecular equation for the formation of potassium tris-   oxalatoferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$
    ITA 1.

$$Fe(NO_3)_3 \cdot 9H_2O + 3KHC_2O_4 \cdot H_2O + 3KOH$$

$$K_3[Fe(C_2O_4)_3] \cdot 3H_2O(s) + 3KNO_3 + 12H_2O$$

 SELF-ASSESSMENT EXERCISE

Tabulate the results of your experiment using the format Show calculations in detail with full identification of the terms, paying attention to units and significant figures.

Measurement	Amount in grams
Mass of $KHC_2O_4 \cdot H_2O$ + Vial + Lid = Mass of emptied vial + Lid = Mass of $KHC_2O_4 \cdot H_2O$ =	
Mass of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ + vial + Lid = Mass of vial + lid = Mass of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O(s)$ =	

1. Calculate molar masses and the number of moles for all reagents and your product.
2. Using the balanced equation for the reaction you carried out, calculate the limiting reagent.
3. Calculate the theoretical yield of your product, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$.
4. Calculate the percentage yield of the product.
5. From the UV-vis spectral analysis, state the wavelength at max and calculate the energy equivalent in cm^{-1}
6. From your IR spectral analysis, identify the major functional groups present in the product.

4.0   CONCLUSION

A typical coordination compound- potassium tris-oxalatoferrate(III)trihydrate has been prepared by reacting potassium hydrogen oxalate monohydrate, $KHC_2O_4 \cdot H_2O$ with iron(III) nitrate, $Fe(NO_3)_3 \cdot 9H_2O$

5.0   SUMMARY

A complex is formed when the ion of a metal is surrounded by ligands. These ligands are either negatively charged ions, or molecules, and in both cases contain a lone pair of electrons which is used to make a coordinate bond to the central metal.

6.0   TUTOR-MARKED ASSIGNMENT

1.   Calculate molar masses and the number of moles for all reagents and your product.
2.   Using the balanced equation for the reaction you carried out, calculate the limiting reagent.
3.   Calculate the theoretical yield of your product, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$.

7.0   REFERENCES /FURTHER READING

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UNIT 2   COLOURS ASSOCIATED WITH LIGAND CHANGES IN SOME CO-ORDINATION COMPOUNDS OF COPPER(II).

CONTENTS

1.0   Introduction
2.0   Objectives
3.0   Main Content
        3.1   Basic principle
        3.2   Method
        3.3   In-text questions and answers
4.0   Conclusion
5.0   Summary
6.0   Tutor-Marked Assignment
7.0   References/Further Reading

1.0   INTRODUCTION

Many transition metal ions are coloured because the energies required for the electronic transitions within their partially-filled d-subshells lie in the visible region of the electromagnetic spectrum. That is, visible light passing through their crystals or solutions is sufficiently energetic to raise a d-electron from the ground state to a higher energy level within the d-subshell. Light passing through the crystal or solution will have certain wavelengths absorbed. The colour you observe will be composed of the remaining visible wavelengths. For example, octahedral copper(II) complexes such as $[Cu(H_2O)_6]^{2+}$ are typically light blue. This means that the blue and possibly some adjacent green and violet wavelengths pass through the crystal while the lower energy red and yellow wavelengths are absorbed. The wavelength of light absorbed by the crystal and hence its colour will vary both with co-ordination number and ligand type, resulting in a change in colour of the solution when a new ligand is added. The copper(II) ion readily forms coordination complexes with a variety of coordination numbers and geometries. These include four coordinate, square-planar complexes and five- and six-coordinate derivatives of the sp^3d^2 hybridized octahedral structure.

2.0   OBJECTIVE

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

•   To identify the colours associated with ligand changes in some co-ordination compounds of Copper(II).

3.0   MAIN CONTENT

3.1   Basic principle

Copper is element with atomic number 29 in the periodic table. It has an electronic configuration of $[Ar] 4s^2 3d^9$, but, perhaps surprisingly, its most common oxidation state is +2. Copper sulfate pentahydrate, $CuSO_4.5H_2O$, is probably the most well-known of all the compounds encountered in chemistry education. It is bright blue crystalline compound which loses water of crystallisation on heating to form the white anhydrous salt. This is a reversible reaction and addition of water caused a release of energy and the blue hydrated copper sulphate is regenerated.

$$CuSO_4 \qquad .5H_2O \qquad = \qquad CuSO_4 \qquad + \qquad 5H_2O$$

Water is a common ligand that we usually encounter during complex formation. For example, the water in hydrated salts is often part of a complex ion: $Cu(H_2O)_4^{2+}$ occurs in hydrated copper sulphate. Copper salts dissociate in aqueous solution and the metal ions are complexed by the water molecules:
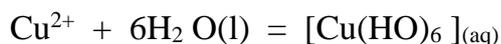
$$Cu^{2+} + 6H_2O(l) = [Cu(HO)_6]_{(aq)}$$
The octahedral hexaaquacopper(II) complex ions are blue in solution. This is the species that is produced by all copper salts when dissolved.

Addition of concentrated hydrochloric acid
Hydrochloric acid contains a high concentration of chloride ions. These undergo a ligand replacement reaction with the water ligands in the hexaaquacopper(II) complex.
$$[Cu(H_2O)_6]^{2+} \qquad + \quad 4Cl^- \quad = \quad [CuCl_4]^{2-} \quad + \quad 6H_2O(l)$$
The complex changes coordination number from 6 to 4 (the chloride ions cannot fit around the central atom in an octahedral arrangement) and the solution changes from blue to bright green.

Addition of potassium iodide solution
This is a redox reaction with the copper(II) complex being reduced to copper(I) while the iodide ions get oxidised to iodine. The colour change is from a blue solution to a white suspension of copper(I) sulfate mixed with the brownish iodine. $2Cu^{2+} + 2I^- = 2Cu^+ + I_2$ This reaction may be used to determine copper solutions. The iodine released can be titrated against sodium thiosulfate using starch solution as an indicator. $2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$
When the blue-black colour of the starch indicator disappears the end-point has been reached.

Addition of sodium hydroxide solution

Sodium hydroxide provides hydroxide ions that replace abstract protons from the water ligands around the copper ion. Once two protons have been removed the copper complex becomes neutral and precipitates from solution. This can be represented in a simple format: Cu^{2+} (aq) + 2OH⁻ (aq) = $2Cu(OH)_2$ (s)There is no further change on addition of excess hydroxide ions.

Addition of ammonia solution

Ammonia is also able to abstract hydrogen ions from the water molecule ligands around the central copper(II) ion: $[Cu(H_2O)_6]^{2+}$ (aq) + $2NH_3$ (aq) = $[Cu(H_2O)(OH)_2$](s) + $2NH_4^+$ (aq)

However, in this case, addition of more ammonia causes the blue precipitate to redissolves as the ammonia molecules replace the water (and hydroxide) ligands around the central copper(II) ion. The final complex contains four ammmonia ligands arranged in a square planar arrangement (the equatorial positions of an octahedral structure) with two axial water ligands.
$[Cu(H_2O)(OH)_2$]$_{(s)}$ + $4NH_3$ (aq) = $[Cu(NH_3)_4 (H_2O)_2]_{(aq)}$ + $2H_2O(l)$ + 2OH⁻ (aq)

The final solution is the deep blue tetraamminediaquacopper(II) ion solution. In many cases this is shortened to the tetraamminecopper(II) complex.

$[Cu(HO)_6$] $Cu(OH)_2$ $[Cu(H_2O)(OH)_2$ $Cu(NH_3)_4]$

3.2   Method

• Take 1 cm³ of the $[Cu(H_2O)_6]^{2+}$(aq) solution in a large test tube. Add one drop of 6 mol L^{-1} ammonia solution and note any change. Continue addition of the ammonia dropwise noting further changes, until any precipitate that forms finally dissolve. Record your observations.
• Take some quantity out for UV-vis measurements.
• To the same solution add 6 mol L^{-1} HCl dropwise, mixing at each addition, until no further changes occur. Record your observations.
• Run UV-vis measurements.

Table 4 Changes associated with addition of NH_3 and HCl to aqueous Cu^{2+} ions

$[Cu(H_2O)_6]^{2+}$(aq)	1 drop NH_3(aq)	Excess NH_3(aq)	Excess HCl(aq)

3.3   In-text questions and anwers

ITQ 1. What changes in colour, if any, would you expect to see when the following solutions are added to separate test tubes containing the complex hexaaquacopper(II) ions
i.   Conc HCl
ii.   NaOH(aq)
iii. NH_3 (aq)

ITA 1.
i.   The octahedral hexaaquacopper(II) complex ions are blue in solution. This is the species that is produced by all copper salts when dissolved. Cu^{2+} + $6H_2 O(l) = [Cu(HO)_6]_{(aq)}$ When HCl is added to $Cu(H_2O)_6]^{2+}$ solution, the chloride ions undergo a ligand   replacement reaction with the water ligands in the hexaaquacopper(II) complex. $[Cu(H_2O)_6]^{2+} + 4Cl^- = [CuCl_4]^{2-} + 6H O(l)$
     The complex changes coordination number from 6 to 4 (the chloride ions cannot fit around the central atom in an octahedral arrangement) and the solution changes from blue to bright green.
ii.   Sodium hydroxide provides hydroxide ions that replace abstract protons from the water ligands around the copper ion. Once two protons have been removed the copper complex becomes neutral and precipitates from solution. This can be represented in a simple format:
     Cu^{2+} (aq)   + $2OH^-$ (aq)   = $2Cu(OH)_2$ (s)

There is no further change on addition of excess hydroxide ions.

iii.   Ammonia is also able to abstract hydrogen ions from the water molecule ligands around the central copper(II) ion:
$[Cu(H_2O)_6]^{2+}_{(aq)} + 2NH_3 \ _{(aq)} = [Cu(H_2O)(OH)_2 \ ](s) + 2NH_4^+ \ (aq)$

However, in this case, addition of more ammonia causes the blue precipitate to redissolves as the ammonia molecules replace the water (and hydroxide) ligands around the central copper(II) ion. The final complex contains four ammmonia ligands arranged in a square planar arrangement (the equatorial positions of an octahedral structure) with two axial water ligands.
$[Cu(H_2O)(OH)_2 \ ]_{(s)} + 4NH_3 \ _{(aq)} = [Cu(NH_3)_4 \ (H_2O)_2]_{(aq)} + 2H_2O(l) + 2OH^-$ (aq)
The final solution is the deep blue tetraamminediaquacopper(II) ion solution. In many cases this is shortened to the tetraamminecopper(II) complex.

SELF-ASSESSMENT EXERCISE

i.   Solutions of copper(II) sulphate and potassium iodide react to form a white precipitate of copper(I) iodide and a brown solution of iodine.
ii.   Write the ionic equation for this reaction
iii.   Explain why this is classed as a redox reaction.
iv.   Suggest why the copper(I) iodide which forms is white, while copper(II) compounds are coloured.
v.   Write net ionic equations to represent the reactions you have observed in Table 4 and assign the various transitions responsible for the colour

4.0   CONCLUSION

In this experiment a solution of the six-coordinate complex ion $[Cu(H2O)_6]^{2+}(aq)$ will be converted to the four-coordinate complex ion $[Cu(NH_3)_4]^{2+}(aq)$ using aqueous ammonia then to the four-coordinate complex ion $[Cu(Cl)_4]^{2-}(aq)$ ion using aqueous HCl.

When a solution containing a different ligand is added to an aqueous solution containing hydrated copper (II) ions, an equilibrium is set up in which the water molecules are replaced by the new ligands. For example, the equilibrium in the presence of chloride ions would be:
$Cu(H_2O)_6^{2+} \ (aq) + 4Cl^-(aq) = CuCl_2(aq) + 4H_2O(l)$
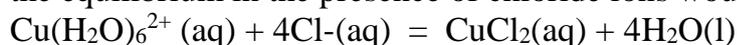
When excess ammonia is added to an aqueous solution of Cu(II) salts, a stepwise replacement of the coordinated water molecules by NH_3 will occur leading to the formation of aquo-ammine complex.

$$[Cu(OH_2)_6]^{2+} + 2NH_3 = [(Cu(H_2O)_4(NH_3)_2]^{2-} + 2H_2O$$
$$Cu(OH)_2 + 4NH_3 + 2H_2O = Cu(NH_3)_4(OH_2)_2]^{2+} + 2OH^-$$

5.0   SUMMARY

Copper as a transition element forms compounds in variable oxidation state viz +1, +2 and +3. In +1 oxidation state, copper has a $3d^{10}$ configuration and its compounds are therefore diamagnetic and colourless. Cu(I) is quite unstable in aqueous solution with respect to disproportionation.

$$2Cu^+ \rightleftharpoons CuO + Cu^{2+} \qquad E^o = 0.37V$$
$$\text{At } 25^oC, \quad K = [Cu^{2+}][Cu^+]^2 = 5.38 \pm 0.37 \times 10^5.$$

This equilibrium is displaced towards left in the presence of -acceptor ligands like CN^-, I^- ions. But in the presence of complexing ligands like SO_4^{2+}, ClO_4^- the equilibrium is displaced towards the right (i.e Cu^{2+} ions is favoured). The instability of copper (I) toward water is due to the high lattice and solvation energies as well as high formation constant for complexes of Cu^+ ion. The Cu(I) is stabilized in compounds of extremely low solubility in water and -acceptor ligands.

In +2 oxidation state copper has a d^9 configuration. A number of stable salts and complexes formed are paramagnetic and coloured. The maximum coordination number of Cu(II) is six corresponding to octahedral geometry which often undergoes tetragonal distortion. The distortion is due to Jahn-Teller effect arising from unequal distribution of electrons in the e_g set (d_z^2, $d_x^2 \cdot d_y^2$) in an octahedral ligand field (Ayi, 2019, see chapter 9 for details). Apart from coordination number of six, copper(II) complexes with 4 coordination are known and both tetrahedral and square planar geometry have been suggested. The most common being square planar geometry.

Cu(II) forms both cationic and anionic complexes. When Cu(II) salts dissolves in water the blue aquo ion $[Cu(H_2O)_6]^{2+}$ is obtained. Most of the hydrated salts of the oxo acids ($CuSO_4.5H_2O$ (blue vitriol), $Cu(NO_3).6H_2O$) are similarly coloured. The blue copper(II) sulphate is prepared by reacting Cu_2O with dilute H_2SO_4 or by direct addition of H_2SO_4 to copper turnings in the presence of oxygen:

$$Cu_2O + H_2SO_4 \text{ (dilute)} = 2CuSO_4 + Cu + H_2O$$
$$Cu + H_2SO_4 \text{ (dilute)} + O_2 = 2CuSO_4 + H_2O$$
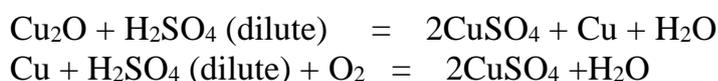
The blue crystalline efflorescent solid readily absorbs water molecules to form the pentahydrate. In the crystal structure of $CuSO_4.5H_2O$, four water molecules are coordinated in the plane around Cu(II) with two SO_4^{2-} groups occupying the axial position. The fifth water molecule provides hydrogen bonding interaction, which bridges the coordinated water molecule and the SO_4^{2-} group (Ayi, 2019).

There is a stepwise loss of water of crystallization on heating $CuSO_4.5H_2O$ depending on temperature.

50-70°C	100-150°C	200°C	700°C	
$CuSO_4.5H_2O$	$CuSO_4.3H_2O$	$CuSO_4.H_2O$	$CuSO_4$	CuO $+ SO_3$
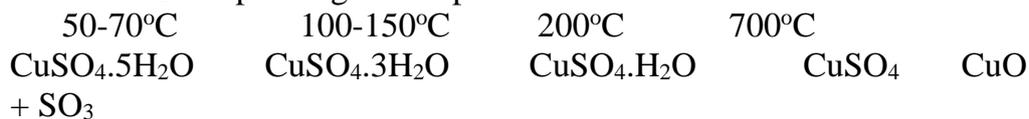
At higher temperature, decomposition takes place leading to the formation of CuO and SO_3. Copper sulphate on reacting with alkali sulphate gives double salts of the type $M_2Cu(SO_4)_2.6H_2O$ which contain $[Cu(H_2O)_6]^{2+}$.

6.0   TUTOR-MARKED ASSIGNMENT

1.   Solutions of copper(II) sulphate and potassium iodide react to form a white precipitate of copper(I) iodide and a brown solution of iodine.
2.   Write the ionic equation for this reaction
3.   Explain why this is classed as a redox reaction.
4.   Suggest why the copper(I) iodide which forms is white, while copper(II) compounds are coloured.

7.0   REFERENCES/ FURTHER READING

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AQA A level experimental chemistry - The chemistry of transition metal compounds   May 6, 2019

UNIT 3   PREPARATION   AND   ANALYSIS   OF CHLOROPENTAAMINE   COBALT   (III) CHLORIDE, [CO(NH$_3$)$_5$CL]CL$_2$.

CONTENTS

1.0   INTRODUCTION

Cobalt has two relatively stable oxidation states, the 2+ and 3+ states. The 2+ state is kinetically labile with respect to ligand substitution, which means that ligand exchange for Co(II) is rapid. The 3+ state is inert with respect to ligand substitution. Therefore, complexes of Co(III) are easy to handle and can be dissolved in water without a rapid change in composition. We take advantage of these properties to synthesize Co(III) compounds. A solution of Co(II) is prepared with a high concentration of the ions or molecules that we wish to introduce as ligands. The solution is then treated with an oxidizing agent, such as O$_2$ or H$_2$O$_2$, to convert the Co(II) to Co(III). This usually results in a compound with five of the six ligands that we want on Co(III). The solution is then acidified and heated to force the sixth ligand onto the Co(III).

2.0   OBJECTIVES

•   In   this   experiment   you   will   prepare hloropentaaminecobalt(III)chloride, [Co(NH$_3$)$_5$Cl]Cl$_2$.
•   In this experiment, we will be determining the % Co in the compound prepared and, by an indirect method we will determine the charge on the Co(III) ion.

3.0   MAIN CONTENT

3.1   Principle

The compound is prepared by dissolving $CoCl_2 \cdot 6H_2O$ in water and adding concentrated ammonia solution.

$Co(H_2O)_6^{2+} + 6NH_3 \quad Co(NH_3)_5OH^+ + NH_4^+ + 5H_2O$ (1)

The Co(II) is then oxidized with hydrogen peroxide.

$Co(NH_3)_5OH^+ + 1/2H_2O_2 \quad Co(NH_3)_5OH_2^+ + OH^-$ (2)

The solution is acidified and heated to complete the conversion to the desired product.

$[Co(NH_3)_5OH_2]^+ + H^+ \quad Co(NH_3)_5OH_2^{3+}$ (3)

$[Co(NH_3)_5OH_2]^{3+} + Cl^- \quad [Co(NH_3)_5Cl_2]^+ + H_2O$ (4)

$[Co(NH_3)_5Cl_2]^+ + 2Cl^- \quad [Co(NH_3)_5Cl]Cl_2 \text{ (solid)}$ (5)
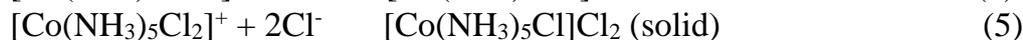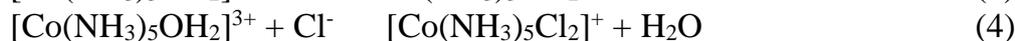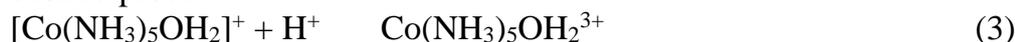
One of the most common methods of purifying a compound that has been prepared is to re-crystallize it. This means that the compound is brought into solution in a minimum amount of solvent, usually at a high temperature, and then allowed to crystallize slowly. This improves the compound's purity because the impurities remain in solution when the new crystals of the compound form slowly. This method of purification will be used on the compound that you prepare.

The Co will be analyzed by a technique called atomic absorption spectroscopy, AAS.

In this method a solution of the metal ion that is to be analyzed is aspirated into a flame. While in the flame, the compound decomposes into gas phase metal atoms, Co(g). At the same time a beam of radiation of the exact wavelength that Co(g) absorbs is passed through the flame. The Co(g) atoms absorb some of this radiation and this change in intensity is measured by a detector.

This change, which is called the absorbance, is proportional to the concentration of Co in the solution. By comparing the absorbance of the solution which you prepare with the absorbance of a series of standards, you can determine the concentration of Co(III) complex in your solution.

The positive charge on an ion can be determined by using "ion-exchange chromatography." A cation exchange resin is a polymeric material which has some sulfonic acid,$-SO_3H$, functional groups added to it. The H^+ in this group is exchangeable with other positive ions. If we begin with the ion-exchange resin in the H^+ ion form, we can exchange the H^+ for some cation in solution. The solution which comes off the ion-exchange resin will now have one mole of H^+ for each mole of positive charge which was

on the original cation. We can now titrate the acid, as you have done before, and calculate the units of positive charge on the complex ion.

3.2   Synthesis of $[Co(NH_3)_5Cl]Cl_2$

*   Accurately weigh 4.0 g of powdered cobalt chloride 6-hydrate in a 125mL Erlenmeyer flask.
*   Working in the hood, dissolve 2.0 g of ammonium chloride in 12mL of concentrated ammonia in a beaker. Add the mixture to the flask of $CoCl_2$ and swirl to dissolve. Some brown and/or purple solid will remain in suspension. (see equation 1.)
*   Add 4 mL of 30% hydrogen peroxide solution, in 1 mL increments. Swirl the flask between each addition to stir the mixture and allow the effervescence to cease. When all the hydrogen peroxide has been added, allow 5 minutes for the reaction to be completed. (see equation 2.)
*   Then slowly, with swirling, add 12 mL of concentrated hydrochloric acid. Considerable heat will be generated by this reaction.
*   Heat the mixture (in a hood) at 85°C for 20 minutes, using a 400 mL beaker on a hotplate as a heating bath. Do not allow the temperature to rise above 90°C. (see equations 3., 4.)
*   Allow the mixture to cool to near room temperature. Once a considerable amount of solid has formed, the cooling can be speeded by using an ice bath. (see equation 5.)

3.2.1 Isolation of the $[Co(NH_3)_5Cl]Cl_2$

*   Assemble the filter flask, trap and filter funnel.
*   Pour the solution through the funnel until only a small amount remains. Then swirl the flask to bring the solid into suspension and quickly pour all of the contents of the flask into the funnel. Allow the vacuum to draw the solution away from the precipitate.
*   Use 10 mL of ice-cold de-ionized water to transfer any solid remaining in the flask into the funnel.

3.2.2 The washing technique

*   Add just enough ice-cold water to the funnel to cover the precipitate, allow to set a   few seconds to wet all of the solid thoroughly, and then draw the wash solution through into the filter flask. Washing once with ice-cold water is sufficient.

*   Turn off the vacuum, and add 20 mL of ice cold methanol to the product on the filter paper. Let this set for a few seconds, and

apply the vacuum. When the methanol has been drawn through the solid product, turn the vacuum off, and rinse again with a 20 mL portion of methanol.

* After this second rinsing with methanol, leave the vacuum on, and draw air through the solid until it is dry.

* Place the solid product in a beaker, and put the beaker into your storage drawer. Go home!

3.3   Analysis of $[Co(NH_3)_5Cl]Cl_2$

3.3.1 Preparation of Solid Sample

- Accurately weigh the purified $[Co(NH_3)_5Cl]Cl_2$ that has been in your storage drawer for a week. Use the mass obtained to calculate %yield.

- Weigh out accurately 0.15 - 0.20 g of pure solid, into a clean, dry 250 mL beaker. Add about 60 mL of de-ionized water to the beaker, and swirl to dissolve the compound.

- Quantitatively transfer it to a 100 cm^3 volumetric flask, and dilute to the mark with de-ionized water.

3.3.2 Determination of percentage (%) of Co using AAS.

- Clean a 5.00 mL volumetric pipet, and rinse it with a small portion of the solution in the 100mL flask.

- Pipet 5.00 mL of the solution in the 100 mL volumetric flask into a clean 500 mL volumetric flask, and dilute to the mark with de-ionized water. Invert several times to mix the solution.

- This solution will be used for analysis for Co by AAS.

- Take your solution to be analyzed and your lab notebook with you as directed by your instructor.

- Calculate the mass percent Co in your compound. Compare to the expected value by calculating % absolute error.

3.3.3 Analysis for ion charge

- Set up the ion-exchange column and rinse it with de-ionized water until the effluent is colorless and has a pH of 6 (as the pH of the de-ionized water in the laboratory).

- Test for pH by allowing a drop of effluent to touch a small strip of pH paper: this may take as much as a hundred mL of water. At least half of the bottom part of the resin column should be a pale yellow color. Allow the water to drain from the column until the water level is just above the resin bed. Never permit the water level to drop below the top of the resin bed.

- Clean, rinse, and fill a 25.00 mL pipet with the sample solution in the 100 mL flask and add that 25.00 mL of sample solution to the column. Allow the resin to settle back in the column and then open the stopcock so that the effluent flows out at a rapid drip rate.
- Collect all of the effluent and the rinse effluent to follow in a clean 250 mL Erlenmeyer flask.
- As the solution in the column drains just to the top of the resin bed, add 20 mL of de-ionized water from your wash bottle to the column. After this 20 mL of wash has gone through the column and been collected, add more de-ionized water and begin testing the effluent with pH paper. When the effluent has a pH of 6, close the stop cock: the effluent collected should be colorless.
- Fill a buret with standard NaOH solution (record its molarity in your notebook).
- Add 2-4 drops of phenolphthalein indicator to the flask with the effluent and titrate with a standardized NaOH solution, to a faint pink color.
- Repeat the ion exchange process and analysis twice to obtain triplicate determinations.

3.2   In-text questions and answers

ITQ 1. Cobalt forms a complex compound of formula $[Co(NH_3)_4Cl_2]^+Cl^-$
i.   What is the oxidation state of cobalt in this compound?
ii.   What is the coordination number of cobalt in this compound?
iii.   Give the name of the complex ion in this compound
iv.   How many moles of silver chloride would be immediately precipitated from one mole of this compound in aqueous solution by the addition of an excess of silver nitrate?
ITA 1.
i.   The oxidation state of cobalt in $[Co(NH_3)_4Cl_2]^+Cl^-$ is +3
ii.   The coordination number of cobalt in $[Co(NH_3)_4Cl_2]^+Cl^-$ is 6
iii.   The name of the complex ion is tetraaminedichloridocobalt(III) chloride
iv. $[Co(NH_3)_4Cl_2]^+Cl^- + excess\ AgNO_3 = [Co(NH_3)_4Cl_2]^+NO_3^- + AgCl$
        Only one mole of silver chloride will be precipitated as shown in the equation.

SELF-ASSESSMENT EXERCISE

i.   Determine the actual mass of cobalt chloride hexahydrate you started with and the mass of the pure product you isolated.
ii.   Calculate the mass percent Co in your compound. Compare to the expected value by calculating % absolute error.

iii.   Calculate the charge on the Co(III) complex ion. Calculate the average of the three determinations, the standard deviation, and the % absolute error.
iv.   Discuss your overall confidence with synthesis and specific beliefs about intermediates.

4.0   CONCLUSION

In this experiment cloropentaaminecobalt(III)chloride, $[Co(NH_3)_5Cl]Cl_2$ has been prepared.

The Co(III) in this compound has a coordination number of six: five NH_3 molecules and one Cl- ion, in an octahedral geometry around Co(III), the central metal, to give an ion with a +2 charge. The compound has two Cl-anions to balance that charge.

5.0   SUMMARY

Cobalt(II) has d^7 configuration and forms numerous complexes with coordination number of six and four corresponding to octahedral and tetrahedral geometry respectively. The crystal field stabilization energy CFSE) for a d^7 ion of Co(II) favours a tetrahedral geometry than octahedral. Thus aqueous solution of cobalt(II) containing $[Co(H_2O)_6]^{2+}$ ion exists in equilibrium wit h small amounts of tetrahedral $[Co(H_2O)_4]^{2+}$ ion.

$$[Co(H_2O)_6]Cl_2 \leftrightharpoons [Co(H_2O)_4]Cl_2 + 2H_2O$$
Octahedral- pink   Tetrahedral-blue
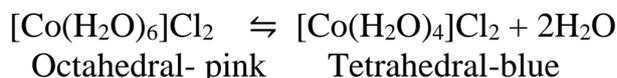
Compounds of Co(II) in the presence of strong field ligands are reducing and are easily oxidized   to the +3 state.

$$[Co(CN)_6]^{3+} + e^- = [Co(CN)_6]_4 \qquad E^o = 0.83\ V$$
$$[CoINH_3)_6]^{3+}\ e^- = [Co(NH_3)_6]^{2+}, \qquad E^o = 0.1\ V$$
$$[Co(H_2O)_6]^{3+} + e^- = [Co(H_2O)_6]^{2+} \qquad E^o = +1.82\ V$$
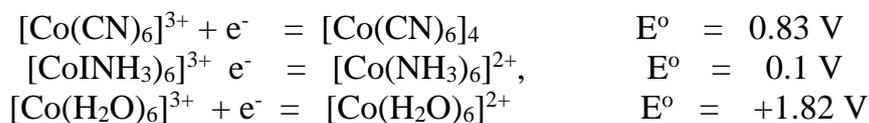
The +3 oxidation state of cobalt has d^6 configuration and with strong complexing ligands in an octahedral field, a stable low spin complexes with t_{2g}^6 configuration are formed and are kinetically inert. The aquo complexes of Co(III) are powerfully oxidizing, and oxidizes even water liberating O_2.

$$[Co(H_2O)_6]^{3+} + e^- = [Co(OH_2)_6]^{2+} \qquad E^o = 1.81 V$$
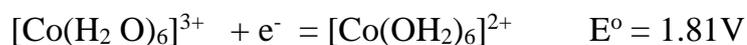
Small non-oxidizable anions however, form stable complexes e.g paramagnetic CoF_6^{3-}.

6.0 TUTOR-MARKED ASSIGNMENT

v.   Determine the actual mass of cobalt chloride hexahydrate you started with and the mass of the pure product you isolated.
vi.   Calculate the mass percent Co in your compound. Compare to the expected value by calculating % absolute error.
vii. Calculate the charge on the Co(III) complex ion. Calculate the average of the three determinations, the standard deviation, and the % absolute error.
viii. Discuss your overall confidence with synthesis and specific beliefs about intermediates.

7.0   REFERENCES /FURTHER READING

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