BSCCH- 304

B. Sc. III YEAR

LABORATORY COURSE III

DEPARTMENT OF CHEMISTRY
SCHOOL OF SCIENCES
UTTARAKHAND OPEN UNIVERSITY

BSCCH-304

LABORATORY COURCES-III

SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

Phone No. 05946-261122, 261123
Toll free No. 18001804025
Fax No. 05946-264232, E. mail info@uou.ac.in
htpp://uou.ac.in

Expert Committee

Board of Studies

Programme Coordinator

Unit Written By	Unit No.
Dr. Nandan Singh Karki Assistant Professor Department of Chemistry LSMGPGC, Pithoragarh	**01**
Dr. Manisha Bisht Assistant Professor Department of Chemistry LSMGPGC, Pithoragarh	**02**
Dr. Tanuja Bisht Assistant Professor Department of Chemistry Girls P.G.College, Haldwani	**03**
Dr. Pushpa Negi Assistant Professor Department of Chemistry Graphic Era Hill University, Bhimtal	**04 & 05**
Dr. Jyoti Singh Associate Professor Department of Applied Sciences Amrapali Institute of Technology and Sciences Lamachaur, Haldwani	**06 & 07**

Course Editor

Dr. Geeta Tiwari
Associate Professor
Department of Chemistry
D.S.B. Campus Nainital

Title : Laboratory Courses-III
ISBN No. : 978-93-90845-13-2
Copyright : Uttarakhand Open University
Edition : 2021

CONTENTS

BLOCK-1 INORGANIC CHEMISTRY

BLOCK-2 ORGANIC CHEMISTRY

BLOCK-3 PHYSICAL CHEMISTRY

UNIT-1 – INTRODUCTION TO LAB TECHNIQUES: INORGANIC CHEMISTRY

CONTENTS

1.1 INTRODUCTION

It is essential that the beginner should become familiar with basic laboratory apparatus or instruments and procedures. Moreover, inculcation of information or understanding to keep the laboratory clean and put the things back in right place after every laboratory exercise is essential. Routine habit to wear lab apron and maintaining laboratory note book is also equally important. Each must have to read or follow laboratory safety guidelines or Material Safety Data Sheet (MSDS).

Here are some important points to be followed by each student, as such;

- Always wear the laboratory coat, goggles and gloves while working with reagents or chemicals in the laboratory and make it habit.
- To keep the working benches clean and always use bench-cloth to remove or absorb any spill of solvent or reagent.
- Always put the reagent bottles back to self or locker immediately after use.
- Maintaining the habit of entering log book prior or after use of each instrument is important.
- Most of the sophisticated instruments are interfaced with computer and operated through software. Therefore, either the print out of the analysis report should be taken or results should be noted in the note book and it should be considered in routine practice.
- Some reagents are toxic. So, while using them, always use safety guidelines.

Here in this unit, the basic information about laboratory glasswares, general laboratory techniques, instruments and procedures are described for the students.

1.2 OBJECTIVES

After completing this unit, the students should;

I. Get familiar with the basic laboratory apparatus and instruments.
II. Learn basic laboratory procedures or methods.
III. Learn laboratory safety procedures or precautions.
IV. Learned how to clean the working benches and after completion of laboratory exercise how to manage the apparatuses.

1.3 COMMON LAB GLASSWARES AND APPARATUS

1.3.1 Cooling baths

Some chemical reactions required constant temperature to proceed and give better yield, which we can up to some extent achieved by using ice liquid ammonia or mixture of ethylene glycol and ethanol in simple beakers. However, few chemical reactions required a more accurate constant temperature to proceed. The simplest and most commonly used apparatus to achieve constant temperature is water bath. The simplest model of a water bath is shown in Figure 1.1.

Actually, water bath is laboratory equipment used to keep water at a constant temperature for incubating samples in a laboratory. Water bath always has electrical circuit with manual temperature control. The application range of water bath includes reagents warming, substrates melting as well as used to enable certain chemical reactions to occur at high temperature. Once the correct temperature is reached, the laboratory water bath turns on and off to maintain a constant temperature. There are different types of water baths such as; water bath with circulating system, non-circulating water bath, water bath with shaking system and non shaking water bath. Circulating water bath required for the reactions those proceed at constant temperature whereas non-shaking water baths are less accurate in sense of maintaining constant temperature throughout the water bath. Therefore, the type of water bath required depends on the type of application or more appropriately how much accurate temperature required to maintain.

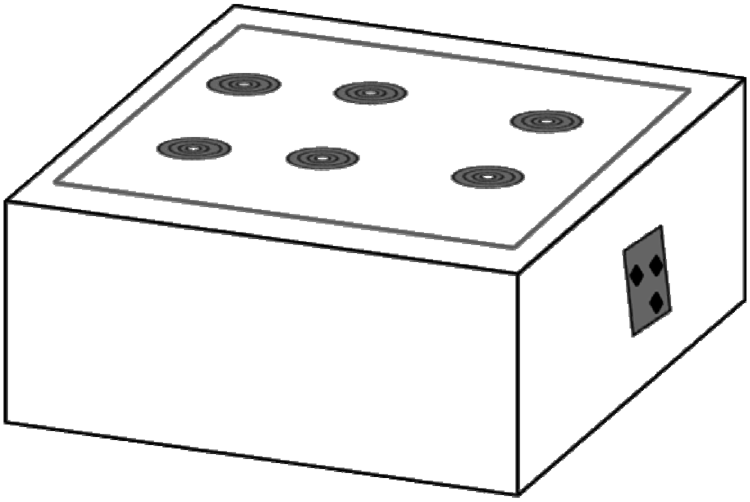


Figure 1.1 A simple model of water bath

1.3.2 Distillation assembly

Distillation process is used to separate the two different organic compounds having different boiling points. In this process, a homogenous mixture of different liquids heated to convert it into vapour and the liquid which one has lower boiling point converted into vapour first followed by liquid having higher boiling point. After this, these vapours are condensed into liquid by passing cold water into distillation assembly. Repeating the process on the collected liquid to improve the purity of the product is called double distillation. Distillation is used for many commercial processes, such as the production of gasoline, distilled water, xylene, alcohol, paraffin, kerosene, and many other liquids. Gas may be liquefied and separated. For example: nitrogen, oxygen, and argon are distilled from air. Diagrammatic representation of general distillation assembly is shown in Figure 1.2.

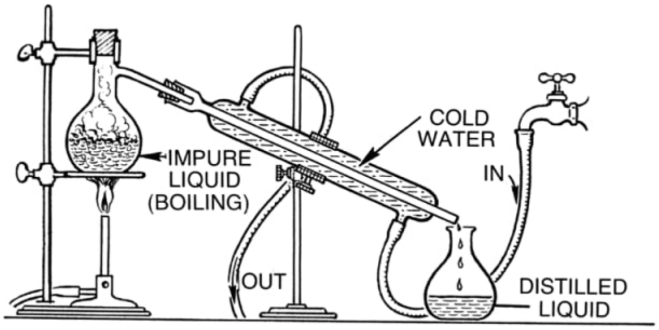


Figure 1.2. General distillation assembly

There are different types of distillation processes or assemblies such as;

1.3.2.1 Simple distillation , 1.3.2.2 Steam distillation, 1.3.2.3 Fractional distillation, 1.3.2.4 vapor distillation

1.3.2.1 Simple distillation

Simple distillation is mainly used to separate liquids having quiet significance difference in their boiling points especially to separate liquids from solids or non-volatile compounds.

1.3.2.2 Steam distillation

Steam distillation is used to separate heat-sensitive components. Steam is added to the mixture, causing some of it to vaporize. This vapour is cooled and condensed into two liquid fractions.

1.3.2.3 Fractional distillation

Fractional distillation is used when the boiling points of the components of a mixture are close to each other, as determined using Raoult's law. A fractionating column is used to separate the components in a series of distillations called rectification. In fractional distillation, a mixture is heated so that vapour rises and enters into the fractionating column. As the vapour cools, it condenses on the packing material of the column. The heat of rising vapour causes this liquid to vaporize again, moving it along the column and eventually yielding a higher purity sample of the more volatile component of the mixture.

1.3.2.4 Vacuum distillation

Vacuum distillation is used to separate components that have high boiling points. Lowering the pressure of the apparatus also lowers boiling points. Otherwise, the process is similar to other forms of distillation. Vacuum distillation is particularly useful when the normal boiling point exceeds the decomposition temperature of a compound.

1.3.3 Spectrophotometer

Spectrophotometer is an optical instrument used in lab for both qualitative and quantitative analysis. In this instrument, the U.V/visible light is passed through the sample and a detector is used to confirm the absorbance range. If the wavelength of the absorbing compound is known, one can do both qualitative and quantitative analysis. Now-a-days, it is very frequently used as basic laboratories experiments. Spectrophotometer comes in both single and double beam mode. Double beam is quiet common where there are two cuvette holders; one for reference and another one for the sample or test solution. Spectrophotometer works on Beer and Lambert's law principle where absorbance is directly proportional to the concentration of test compound. A simple spectrophotometer model is represented in Figure 1.3.

Figure 1.3. General spectrophotometer

1.3.4 Hot-air oven

To sterilize or to dry glasswares, hot air oven is used. It is recommended always to use clean and dry glasswares in chemistry laboratory. The drying oven is designed on the principle of recirculation and convection mode of heat transfer, to achieve uniform temperature inside the oven. Air at high speed is spread inside the oven at set temperature with the help of high performance centrifugal blower. Hot air after the heat transfer to material is taken to suction of the blower which is passed over the heater coil to gain fresh heat to continue cycle of recirculation. Oven is represented in Figure 1.4 a & b.

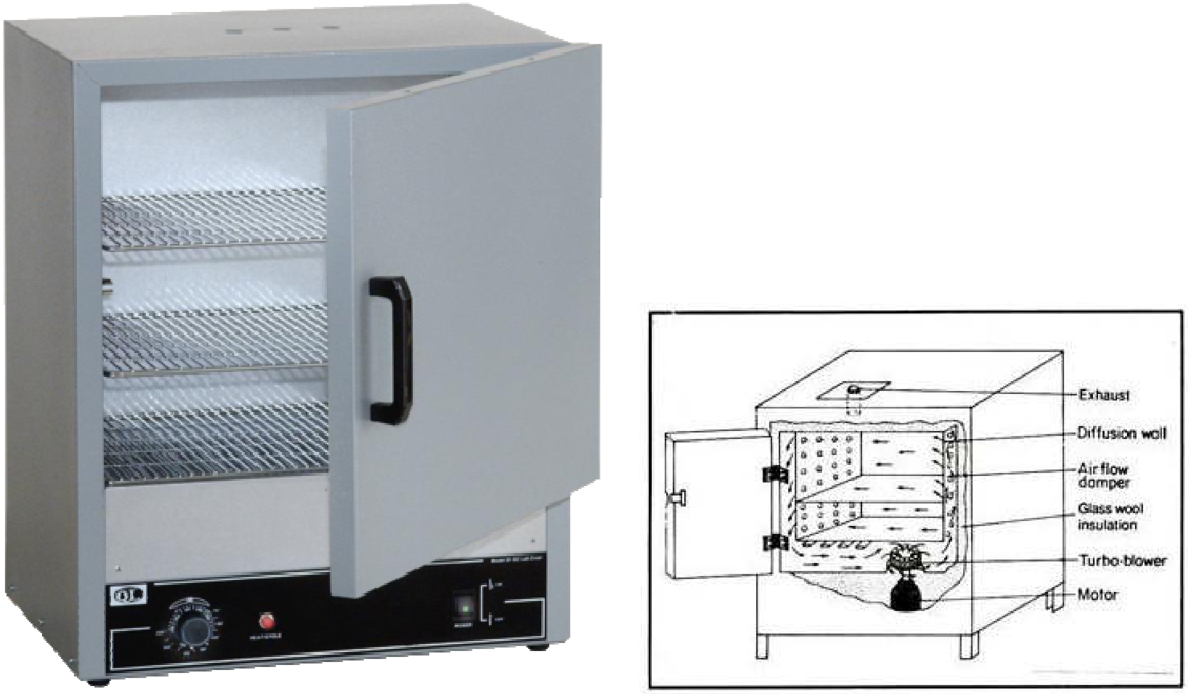


Figure 1.4. a) Hot air oven picture b) different parts of hot air oven

1.3.5 Weighing balance

Weighing balance in a laboratory is a very important and basic instrument. There are different types of balances available in market depending upon the sensitivity or range of weight. However, the most expensive are those which can measure the lowest weight. Now-a-days, analytical balance in laboratories is very crucial. In analytical balances, the measurement is easy, fast and accurate compared to two pan balance system. The general representation of balance is shown in Figure 1.5.

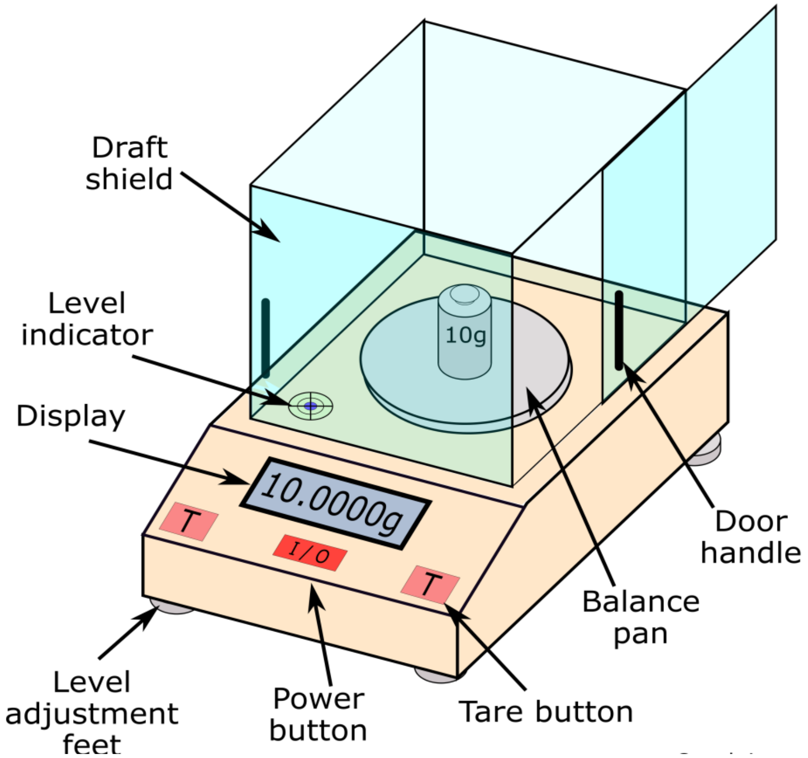


Figure 1.5. Analytical balance

1.3.6 Desiccator

A desiccator is a chamber or box that is used to store the hygroscopic materials. A traditional desiccator is a glass bowl and lid, each with thick glass rims that permit a seal when greased (Figure 1.6). Desiccant (a hygroscopic chemical that absorbs water out of the air) is placed beneath the perforated ceramic disk. If the compound is hygroscopic then it is always suggested to keep it in desiccator on the disk. Some common desiccants are $CaSO_4$, silica gel, $MgSO_4$, and P_2O_5.

Figure 1.6 A classical desiccators

1.3.7 Melting point measurement instrument

Melting point is the physical property that is used in characterization of the solid organic compound. A pure solid organic compound having the melting point in the small range (less than $1^{o}C$) while impurity containing solid organic compound having the melting point in the large range. So, melting point can also be used to check the purity of an organic compound.

Apparatus used for the measurement of melting point of the solid organic compound called melting point measurement apparatus. The simple melting point measurement apparatus is represented in Figure 1.7.

Figure 1.7 Melting point measurement apparatus

1.3.8 Commonly used glasswares

1.3.8.1 Glassware for qualitative use

A. Beakers

I. Beakers are cylindrical in shape and may or may not have a volume mark (Figure 1.8). They are available in the range from minimum 5-10 mL to 4-5 L. These are used to hold solid and liquid both. In lab, beakers are used to hold solvents for heating, carrying and storing. Their graduations are approximate, but very useful when exact volumes are not needed.

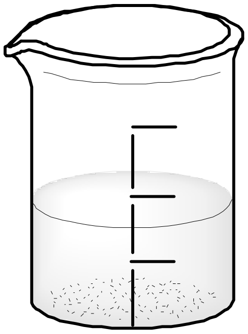


Figure 1.8 Beaker

B. Flasks

I. Flasks are designed so that the contents can be swirled without spilling. They are also easily fitted with stoppers and often have the stopper size written directly on the flask.

II. Erlenmeyer Flask

The most common of all flasks is the Erlenmeyer flask (Figure 1.9). This flask is having a wide base, narrow neck, and conical form, convenient in laboratory experimentation for swirling liquids by hand. The flat bottom allows the Erlenmeyer flask to be directly heated and used in simple reflux (boiling) and condensation procedures.

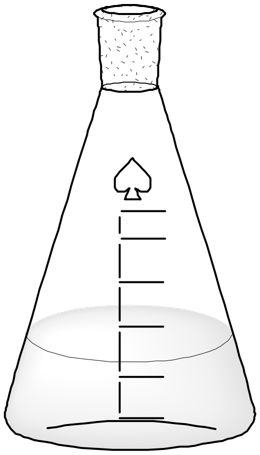


Figure 1.9 Erlenmeyer flask

III. Florence flask

The florence flask is a hybrid between the round bottom and the Erlenmeyer flask and ranges from a few hundred milliliters to a few liters in size (Figure 1.10). Florence flasks can have either a flat bottom or a round bottom. So, applications vary from direct heating to using a heating mantle. It does not have a ground glass joint, so a stopper is used to seal the container. The rounded shape is better for applications that involve boiling.

Figure 1.10 Florence flask

C. Test tubes

Test tubes are relatively small cylindrical vessels used to store, heat, and mix chemicals (Figure 1.11). While the test tube comes in specific sizes, it's typically used in qualitative observational procedures.

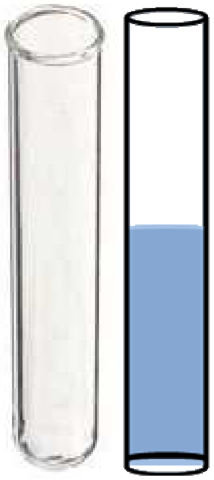


Figure 1.11 Test tube

D. Watch glass

The watch glass is used when a high surface area is needed for a small volume of liquid (Figure 1.12). This is common for crystallization and evaporation, as well as other qualitative procedures. Watch glasses can also be used as cover for beakers, but not flasks.

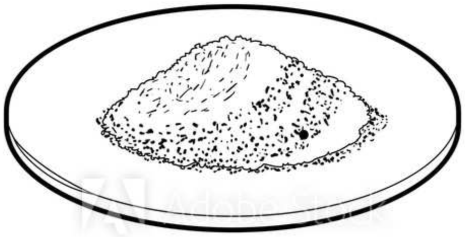


Figure 1.12 Watch glass

E. Crystallization dish

The crystallization dish is a hybrid between a watch glass and the Petri dish (common in biological procedures) (Figure 1.13). It has a low height-to-width ratio, which means the sides are very low compared to the width of the vessel. This allows high surface area for evaporation, but the crystallization dish is more commonly used as a short-term container for liquids in a variety of bath processes (water, acid, or oil).

Figure 1.13 Crystallization dish

1.3.8.2 Glassware for measuring

A. Graduated cylinder

The graduated cylinder is used to measure a semi-precise volume of liquid (Figure 1.14). While it is not as precise as volumetric glassware, it is much more accurate and precise than a beaker or flask (to within 1%). Volumes are measured to the bottom of the meniscus for aqueous solutions and the top of the meniscus for non-aqueous hydrophobic solutions. Graduated cylinders are general-use pieces of "To Deliver (TD)" glassware, where the delivery volume is important. Higher levels of accuracy require volumetric glassware.

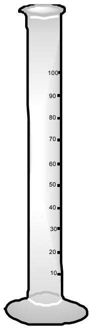


Figure 1.14 Graduated cylinder

B. Volumetric glassware

I. Volumetric flask

Volumetric flasks are used for making standardized (high precision) solutions, where precision is known to four significant figures (Figure 1.15). Since volumes are not necessarily additive, the volumetric flask is used to make solutions of precise volumes. The etched mark on the neck of the glassware signifies the volume to high precision at the specified temperature. A solution is prepared by adding enough solvent to dissolve the solute, and then the solute is added and dissolved. The solution is then diluted to the mark using the solvent. The solution is mixed throughout the dilution process and sometimes requires being placed in an ice bath in the case of exothermic dissolution (typically strong acids or bases). Volumetric flasks range in size from 1 mL to 4,000 mL and larger.

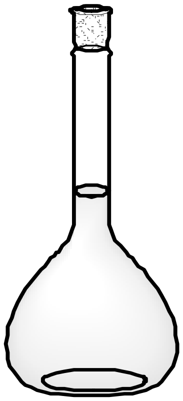


Figure 1.15 Volumetric flask

II. Pipettes

Volumetric pipettes are known for high precision, like volumetric flasks, but are used to dispense liquids, typically in the preparation of solutions in a volumetric flask (Figure 1.16). The pipette also has an etched mark denoting a precise volume, and the solution is drawn into the pipette using a pipette bulb, never by mouth.

Figure 1.16 Volumetric pipette

III. Micropipettes

Micropipettes are a specialized class of volumetric pipettes used for very small volumes from 1 µl to 1,000 µL. The micropipette uses plastic disposable tips, but these can be re-used under appropriate situations (Figure 1.17). Most micropipettes have an adjustable range of volumes using separate withdraw and dispense actions on the pipette body. The mechanism for adjusting, determining volume limits, and ejecting disposable tips varies by manufacturer.

Figure 1.17 Micropipette

IV. Burettes

The burette is an analytical piece of glassware used to dispense variable (but precise) volumes of liquids (Figure 1.18). Commonly found in analytical chemistry, this burette is used in a variety of titration experiments.

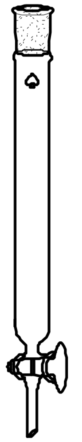


Figure 1.18 Burette

1.3.8.3 Procedural glassware

A. Round-bottom (Boiling) flasks

Round-bottom flasks, or boiling flasks, are typically found in synthesis experiments, since the round shape allows for even heating and stirring. The neck typically has a female ground-glass joint and can be attached to condensers and other pieces of glassware. To prevent spills, the solution volume should not exceed 50% of the flask volume. Sizes are available from a range of 50 mL to 20,000 mL.

B. Separatory funnel

While most common to the organic chemistry lab, the separatory funnel is used to separate liquids of different densities and solubilities (Figure 1.19). The bottom of the separatory funnel is very narrow and leads to a stopcock, allowing for precise separations of liquids, while the top is very wide for ease in shaking and mixing.

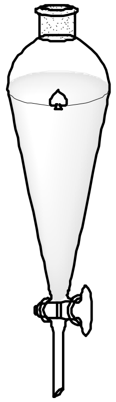


Figure 1.19 Separatory funnel

C. Filter (Büchner) flask (used for vacuum filtration)

The filter flask looks like an Erlenmeyer flask, but has a hose barb near the top to attach a vacuum hose (Figure 1.20). The flask typically has thicker walls than an Erlenmeyer due to the reduced pressure (vacuum) used with the flask. Vacuum (Büchner) funnels fit into the neck of the flask using a rubber collar or a 1-hole rubber stopper.

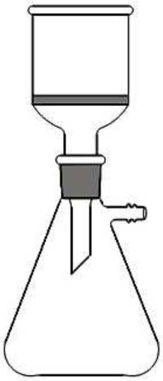


Figure 1.20 Büchner funnel

D. Funnels (used for filtering and transferring)

Traditional funnels used for gravity filtration have a wide cone-shaped body, for adding and filtering solutions, and a long narrow stem, for delivery into a flask (Figure 1.21). Filter paper is folded into a cone shape, inserted into the funnel, and wetted with a solvent (typically water). The powder funnel has a wider stem designed for dispensing solids and viscous liquids. Filter paper is only used in conjunction with the filter funnel.

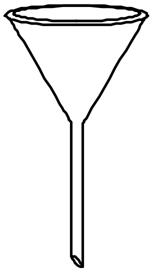


Figure 1.21 Funnel

E. Ceramics

1. Büchner funnel

The ceramic Büchner funnel fits into the filter (Büchner) flask using a rubber cone or 1-hole rubber stopper (Figure 1.22). The funnel is typically made of ceramic with pin-sized holes in the flat bottom. Filter paper is placed on top of the holes and wetted with solvent (water) to prevent solids from getting under the filter paper.

Figure 1.22 Büchner funnel

2. Crucible

A crucible is made of ceramic and holds small amounts of chemicals during heating at high temperatures (Figure 1.23). Depending on the specific type, the crucible can withstand temperatures above 1,000°C and is used in conjunction with a Bunsen burner or furnace. Common uses include heating a hydrated solid to remove water or combusting a compound to determine organic content.

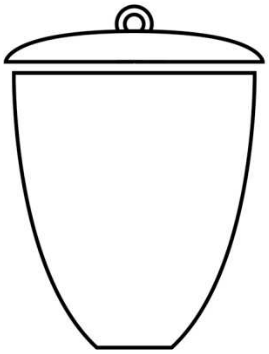


Figure 1.23 Crucible

3. Mortar and pestle

While the mortar and pestle originated in chemistry (and alchemy) laboratories, it is more common in pharmacology, biology, and culinary applications. Made of ceramic or stone, materials are placed in the bowl-shaped mortar and ground and crushed using the pestle (Figure 1.24).

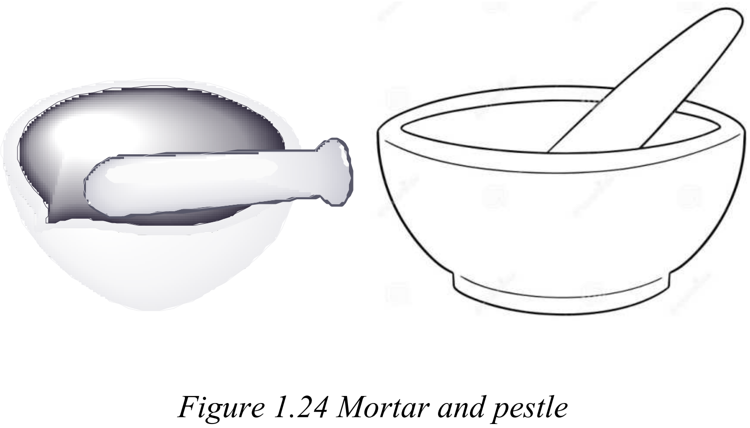


Figure 1.24 Mortar and pestle

1.3.9 Some sophisticated instruments

Two major categories of methods involving sophisticated instruments are spectroscopic and chromatographic methods. Spectroscopic methods are based on interaction of electromagnetic spectra (ranging from U.V-light to X-ray and radio-wave) with material. Spectroscopic methods are mainly used to characterize the materials. The most important spectroscopic methods are:

- Atomic Absorption Spectroscopy, Flame Photometry, Atomic Fluorescence Spectroscopy
- Emission Spectroscopy
- Raman Spectroscopy
- Microwave Spectroscopy
- U.V. Absorption Spectrophotometer
- Infrared Spectrophotometry
- Fluorophotometry - Phosphorimetry
- Turbidometry – Nephelometry
- Refractometry - Interferometry
- Raman Spectroscopy
- X-ray: Absorption, Emission, Diffraction
- Nuclear Magnetic Resonance Spectroscopy – Electron Spin Resonance Spectroscopy
- Gamma-ray Spectroscopy – Mossbauer Spectroscopy

Whereas chromatographic methods mainly used to separate the different compounds or molecules based on their affinity or interaction with stationary and mobile phase. Chromatographic technique is a modern technique for the separation of individual component present in the mixture. The chromatographic technique is based on the rate at which the component of a mixture move through the porous medium (stationary phase) under the influence of some solvent or gas (mobile phase).

Based on the nature of stationary phase and mobile phase, chromatography can be different types such as;

1-Partition chromatography, eg; Paper chromatography

2-Adsorption chromatography, eg; Thin layer chromatography (TLC)

3-Ion exchange chromatography, eg; Column chromatography

1.4 BASIC TECHNIQUES AND PROCEDURES

1.4.1 Titration

A titration is a technique where a solution of known concentration is used to determine the concentration of an unknown solution. Typically, the titrant (the know solution) is added from a burette to a known quantity of the analyte (the unknown solution) until the reaction is complete, which is often indicated by a colour change. There are four major classes of titration;

- Acid base titration (HCl v/s NaOH)
- Redox titration (FAS v/s $KMnO_4$)
- Precipitation titration (NaCl v/s $AgNO_3$)
- Complexometric titration (EDTA v/s water sample)

1.4.2 Filtration

Filtration is a very basic and routinely applied method in laboratories. This method is used to sieve the solutions having solid particles such as precipitates and for solutions those are heat sensitive cannot be separated through distillation process. For the simple precipitate filtration process, we commonly use Whatman filter papers (usually come in different grades). However for sophisticated instrument such as HPLC we commonly use 0.2μm filter paper.

1.4.3 Calibration of glasswares

1.4.3.1 Calibration of volumetric flask

For the calibration of volumetric flask, at first the weight of cleaned and dried flask is accurately determined by using the robust balance. Now air free distilled water is filled in the flask up to the fixed mark on the neck and determine the weight of water containing flask. Finally with the help of these two weights volume of volumetric flask is obtained.

1.4.3.2 Calibration of pipettes

Calibration of pipette is carried out by weighing the delivered water from the fixed mark. For this purpose, at first the pipette is washed and dried then after this air free distilled water is sucked up to the mark into the pipette. Now determine the weight of water delivered in the previously weighted flask. From the weight of water calculate the true volume of pipette.

1.5 SUMMARY

This is a basic introductory exercise where general description about common laboratory apparatuses and instruments is given. A brief account of different types of glasswares and their applications are provided for beginning students. Different precautions and safety procedures are also described.

1.6 GLOSSARY

- **Beaker** – Used to hold and heat liquids. Multipurpose and essential in the lab.
- **Bunsen burner** – Used for heating and exposing items to flame. They have more uses than a hot plate but do not replace a hot plate.
- **Crucible** – Used to heat small quantities to a very high temperature.
- **Erlenmeyer flask** – Used to heat and store liquids. The bottom is wider than the top so it will heat quicker because of the greater surface area.
- **Evaporating dish** – Used to heat and evaporate liquids.
- **Funnel** – Used to target liquids into any container so they will not be lost or spilled.
- **Micro spatula** – Used for moving small amounts of solid from place to place.

- **Mortar and pestle** – Used to crush solids into powder for experiments.
- **Pipette** – Used for moving small amounts of liquids from place to place.
- **Ring stand** - Used to hold items being heated. Clamps or rings can be used so that items may be placed above the lab table for heating by Bunsen burners or other items.
- **Stirring rod** – Used to stir things. Made of glass they will break easily. They are very useful in the lab.
- **Stopper** – These come in many different sizes and are used to seal containers. They can also have holes in them for thermometers and other probes.
- **Test tube holder** – Used to hold test tubes when they are hot and untouchable.
- **Test tube rack** – Used to hold test tubes while reactions happen in them or when they are not needed.
- **Tongs** – Used to hold many different thi9ngs such as flasks, crucibles, and evaporating dishes when they are hot.
- **Pipestem triangle** – Used to hold crucibles when they are being heated. They usually sit on a ring stand.
- **Watch glass** – Used to cover beakers so a reaction can be observed safely.
- **Wire gauze** – Used to place items on for heating. They usually sit on a ring stand.

1.7 SELF ASSESSMENT QUESTIONS

Q 1. Give the name of burner used in the laboratory and also give the name of gas used in the burner

Ans: Bunsen burner is used in the laboratory and LPG is used for burning in the Bunsen burner, which is the mixture of lower alkanes mainly propane and isobutene.

Q 2. Which chemicals are used for cleaning the glass apparatus in the laboratory?

Ans: Mixture of concentrated H_2SO_4 and HNO_3 or chromic acid solution can be used for cleaning the glass apparatus in the laboratory

Q 3. Which substance is used to prepare the filter paper?

Ans: Cellulose is used to prepare the filter paper.

Q 4. Why we use the chemical balance instead of electronic balance in the laboratory?

Ans: Chemical balance gives the more précised results in compare to the electronic balance due to which we use the chemical balance instead of electronic balance in the laboratory.

Q 5. Which chemical is used the desiccators?

Ans: Anhydrous $CaCl_2$ is used in the desiccator.

Q 6. Which chemical is used when skin is burnt by acid?

Ans: When skin is burnt by dilute acid then washing with NH_4OH can be used but when skin is burnt by concentrated H_2SO_4 then washing by $BaCl_2$ solution can be used.

Q 7. Why silica crucible is heated before weighing it during gravimetric experiments?

Ans: Silica crucible having the strong tendency to adsorb the moisture by which its accurate weight cannot be obtained which cause the non-accuracy in the results during the various experiments due to this reason silica crucible is heated before weighing it during gravimetric experiments.

Q 8. Give the name of apparatus used to prepare H_2S gas in laboratory and also give the method to prepare it.

Ans: Kipp's apparatus is used to prepare the H_2S gas in the laboratory and it is prepared by the reaction of dilute H_2SO_4 with ferrous sulphide (FeS) according to the following reaction.

$$FeS + \text{dil. } H_2SO_4 \rightarrow FeSO_4 + H_2S \uparrow$$

Q 9. What substance is used in making the centre of wire gauge?

Ans: Centre of wire gauge is constructed by the Asbestos.

Q 10. What is the necessary condition for the fractional distillation during the separation of the two volatile liquids from the mixture

Ans: There should be the difference of boiling points about 40°C for the fractional distillation during the separation of the two volatile liquids from the mixture.

1.8 REFERENCES

1. R. Sarkar. (2007). General and Inorganic Chemistry Part II, New Central Book Agency (Pt) Ltd.
2. Satya Prakash, G.D. Tuli, S.K. Basu and R.D. Madan. Advanced Inorganic Chemistry .Vol. I, S, S. Chand & Com. Ltd.

3. J. E. Huheey, E. A. Keiter and R. L. Keiter (1993). Inorganic Chemistry: Principles of Structure and Reactivity, 4th ed. Harper-Collins, New York.
4. N. N. Greenwood and A. Earnshaw. (1997). Chemistry of the Elements, 2nd ed.Pergamon.
5. F. A. Cotton and G. W. Wilkinson. (1989). Advanced Inorganic Chemistry, 5th ed. John-Wiley & Sons.
6. J. E. House. (2009). Inorganic Chemistry, 1st ed. Academic Press.
7. Shriver and Atkins. (2006). Inorganic Chemistry, 4th ed. Oxford Univ. Press.
8. Fred Basolo and Ralph G. Pearson. (1967). Mechanisms of Inorganic Reactions, 2nd ed. John Wiley and Sons.
9. A. Skoog, D.A. West, F.J. Holler and S.R. Crouch. (1990). Analytical Chemistry, an Introduction, 7th ed.
10. JoVE Science Education Database. (2019). General Chemistry. Common Lab Glassware and Uses. JoVE, Cambridge, MA,.
11. Fifield, F. W., & Kealey, D. (2000). Principles and practice of analytical chemistry. Oxford: Blackwell Science.
12. Douglas A. Skoog, Stanley R. Crouch and F. James Holler. (2007). Principles of Instrumental Analysis. Belmont, CA.
13. Arikawa Yoshiko. (2001). Basic Education in Analytical Chemistry (pdf). Analytical Sciences. The Japan Society for Analytical Chemistry. 17 (Supplement): i571–i573. Retrieved 10 January 2014.
14. Gary D. Christian. (2004). Analytical Chemistry, 6th ed. Wiley, Hoboken, N.J.
15. B.K. Sharma. (2018). Analytical Chemistry, 1st ed. Krishna Prakashan Media (P) Ltd. India.
16. G. R. Chatwal and Madhu Arora. (2015). Pharmaceutical Chemistry, Himalaya Publishing House, India.
17. A.L. Gupta. (2015). Modern Analytical Chemistry, Pragati Prakashan, India.
18. R.M. Verma. (2015). Analytical Chemistry, CBS Publishers & Distributors, India.
19. S. M. Khopkar. (2007). Analytical Chemistry: Problems and Solutions, New Age International (P) Limited, India.

1.9 SUGGESTED READINGS

1. Douglas A. Skoog, Stanley R. Crouch and F. James Holler. (2007). Principles of Instrumental Analysis. Belmont, CA.
2. A. I. Vogel and J. Mendham (2000). Vogel's Textbook of Quantitative Chemical Analysis, 6th ed. Harlow, Prentice Hall.
3. R.A. Day and A.L. Underwood. (2006). Quantitative Analysis, 6th ed.Prentice- Hall India.
4. J.N. Miller and J. C. Miller. (2005). Statistics and Chemometrics for Analytical Chemistry, 5th ed. Pearson/Prentice Hall.
5. Willard, Merritt, Dean and Settle. (2004). Instrumental Methods of Analysis, 7th ed. CBS Publication.
6. Robert L. Grob and Eugene F. Barry. (2004). Modern Practice of Gas Chromatography, 4th ed. John Wiley & Sons, Inc Pub.
7. C. N. Banwell. (1994). Fundamentals of Molecular Spectroscopy, 4th ed. McGraw-Hill.
8. F. J Holler, S.R Crouch D.M, West and D. A. Skoog. (2014). Fundamentals of Analytical Chemistry. Fort Worth, Tex Saunders College Pub.

1.10 TERMINAL QUESTIONS

Q 1**.** Give a brief account about different safety procedure used in chemistry laboratory.

Q 2. Describe the different types of glasswares used in chemistry laboratory and their applications.

Q 3. Describe the different types of titrations.

Q 4. What are the common chemistry lab instruments? Explain their applications.

Q 5. Describe the general procedure of glassware calibration

UNIT-2 –SYNTHESIS AND ANALYSIS

CONTENTS

2.1 INTRODUCTION

Inorganic compounds are generally formed by non-living natural processes or by laboratory preparation methods as they do not formed from living things. There are two important classes of inorganic compounds: Double salts and Coordination compounds.

A double salt is a substance that can be prepared by combining two different salts which crystallize together into a single substance but when dissolved in water, the double salt ionize into its constituent ions. Alums (isomorphous crystalline solids that are soluble in water) such as potash alum, chrome alum, ferric alum are the common examples of double salts.

Coordination or complex compounds can be prepared by a large number of transition metals in which the metal atom is bonded to neutral molecules or to negatively charged species (ligands). The ligands can donate electrons to the metal atoms to form a ligand-metal coordinate bond. When dissolved in water, the coordination compounds do not ionize into its constituent ions. Tetraamine cupric sulphate complex, nickel dimethylglyoxime complex and *cis* and *trans* potassium-dioxalato diaquo chromate complexes are the example of complex compounds.

2.2 OBJECTIVES

After completing this unit, you will understand;

- Basic understanding of inorganic compound synthesis.
- How to synthesize sodium ferrioxalate complex, tetraamine cupric sulphate complex, nickel dimethyl glyoximate complex and *cis* and *trans* potassium-bis (oxalate) diaquo chromate.
- How to prepare double salts such as ferric alum and chrome alum.

2.3 PREPARATION OF COORDINATION COMPOUNDS

2.3.1 Sodium tris (oxalato) ferrate (III) complex; $Na_3[Fe(C_2O_4)_3]$

2.3.1.1 Objective

To prepare sodium tris (oxalato) ferrate (III) complex.

2.3.1.2 Theory

Mixing of $FeCl_3$ and KOH in minimum amount of water forms hydrated ferric oxide slurry. And when this slurry is added to the hot solution of sodium oxalate, a greenish-brown solution of Iron (III) oxalate obtained, which on slow evaporation gives greenish crystals of sodium tris (oxalato) ferrate (III).

$$FeCl_3 + 3\,NaOH \longrightarrow Fe(OH)_3 + 3NaCl$$

$$Fe(OH)_3 + 3H_2C_2O_4 + 3NaOH \longrightarrow Na_3[Fe(C_2O_4)_3] + 6H_2O$$

2.3.1.3 Requirements

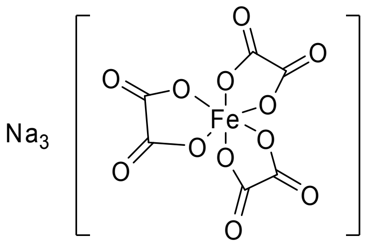
Apparatus: Electronic weighing machine, beaker 500 mL, beaker 250 mL, Bunsen burner, desiccator, filtration apparatus, conical flask, funnel, glass rod, pair of tongs, tripod stand, watch glass, water bath, wire guaze.

Required chemicals:	Ferric chloride	2.50 g
	Sodium hydroxide	2.75 g
	Oxalic acid	3.00 g

2.3.1.4 Procedure

I. Preparation of ferric hydroxide: Separately dissolve 2.5 g of $FeCl_3$ and 1.75 g of sodium hydroxide in 1-2 mL of water. Now add dodium hydroxide solution to ferric chloride solution to make brown colour slurry with stirring. This slurry is the precipitate of $Fe(OH)_3$. Filter the precipitate of ferric hydroxide in Bruckner funnel and wash it with small amount of hot water 2and 3 times.

II. Preparation of sodium tris (oxalato) ferrate (III)**:** Dissolve 3g of oxalic acid in 10-15 mL of hot water then add 1 g of NaOH. Transfer ferric hydroxide in this hot solution with constant stirring. Dissolve $Fe(OH)_3$ in hot solution, taking 3 moles of oxalic acid per 1 mole of $Fe(OH)_3$. This will produce dark greenish-brown solution of iron (III) oxalate. Filter the solution and concentrate the green filtrate on water bath and obtain green crystal of sodium tris (oxalato) ferrate (III).



Structure of sodium tris (oxalato) ferrate (III)

2.3.1.5. Result

The yield of sodium tris (oxalato) ferrate (III) is …………………….g.

2.3.2 Nickel dimethylglyoxime

2.3.2.1 Objective

To prepare nickel dimethylglyoxime.

2.3.2.2 Requirements

Apparatus: Electronic weighing machine, beaker 500 mL, beaker 250 mL, Bunsen burner, desiccator, filtration apparatus, conical flask, funnel, glass rod, pair of tongs, tripod stand, wash bottle, watch glass, water bath, wire guaze, sintered glass crucible (G-3).

Chemicals required: Nickel ammonium sulphate 9 g
1 %alcoholic DMG solution
Ammonical solution

Reagent preparation

Preparation of nickel ammonium sulphate solution: This solution is prepared by dissolving 9 g of nickel ammonium sulphate in distilled water and few mL of dil. hydrochloric acid in 500 mL measuring flask.

Preparation of 1% alcoholic DMG solution-This solution is prepared by dissolving 0.5 g of HDMG in 50 mL of distilled water.

Preparation of 1:1 ammonical solution-This can be prepared by dissolving 25 mL of liquor ammonia with 25 mL of distilled water.

2.3.2.3 Theory

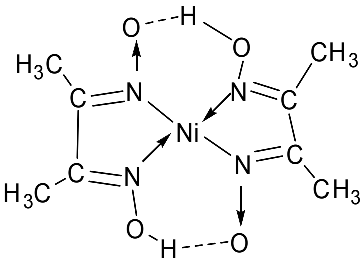
Nickel dimethylglyoxime [Ni(DMG)$_2$] complex obtained by the reaction of nickel ammonium sulphate with 1 %alcoholic dimethylglyoxime in ammonical medium,

$$NiSO_4\,(NH_4)_2SO_4.6H_2O \rightarrow NiSO_4 + (NH_4)_2SO_4 + 6H_2O$$

$$NiSO_4 + 2HDMG + 2NH_4OH \rightarrow \underset{\text{ppt}}{[Ni(DMG)_2]} + (NH_4)_2SO_4 + 2H_2O$$

2.3.2.4 Procedure

Prepared 1% alcoholic DMG solution is added in prepared nickel ammonium sulphate solution. Now add ammonia solution slowly with constant stirring until the smell of ammonia come out, a scarlet red precipitate of DMG is formed. The precipitate is digested on a water bath for about half an hour. The solution is filtered in a previously washed dried and weighted sintered glass crucible (G-3). Now dry it at 120°C in an electric oven. This precipitate is cooled in a desiccator and weighted.



Structure of nickel dimethylglyoxime complex

2.3.2.5 Result

The yield of nickel dimethylglyoxime is ………………………….g.

2.3.3 Tetraamine cupric sulphate complex $[Cu(NH_3)_4]SO_4.H_2O$

2.3.3.1 Objective

To prepare tetraammine cupric sulphate complex

2.3.3.2 Requirements

Chemicals:

Copper sulphate	2.5 grams
Liquid ammonia	5 mL
Ethyl alcohol	7.5 mL

Apparatus: Electronic weighing machine, beaker 500 mL, beaker 250 mL, filtration apparatus, flask conical, funnel, desiccator, glass rod, tongs, tripod stand, watch glass, water bath.

2.3.3.3 Theory

Hydrated tetraammine cupric sulphate is obtained by addition of liquid ammonia in the solution of copper sulphate followed by the addition of ethyl alcohol in the solution.

$$CuSO_4 + 4NH_3 + H_2O \longrightarrow [Cu(NH_3)_4]SO_4.H_2O$$

2.3.3.4 Procedure

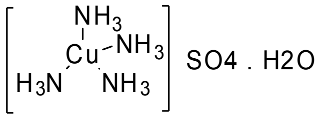
The four steps involve during the formation of hydrated tetraammine cupric sulphate complex given as

Step I Firstly dissolve 2.5 g of crystalline $CuSO_4.5H_2O$ in minimum amount of H_2O in 250 mL beaker. Now add few drop of conc. H_2SO_4 to clear up the solution if necessary.

Step II Add liquor ammonia to copper sulphate solution from dropping funnel with constant stirring until the blue precipitate formed is dissolved to give a deep solution.

Step III Now add 20 mL of ethyl alcohol slowly with constant stirring to the deep blue solution. And allow it to stand to slow evaporation which gives long needle shaped brilliant dark blue-violet crystal of tetraamine cupric sulphate complex.

Step IV Filter and wash it with ethyl alcohol and dry in a desiccator.



Structure of tetraamine cupric sulphate complex

2.3.3.5 Result

The yield of tetraamine cupric sulphate is …………………g.

2.3.4 C*is* and *trans* potassium-dioxalato diaquo chromate (III) $K[Cr(C_2O_4)_2(H_2O)_2].2H_2O$

2.3.4.1 Objective

To prepare *cis* and *trans* potassium-dioxalato diaquo chromate complex.

2.3.4.2 Requirements

Chemicals:	Oxalic acid crystal	3 g
	$K_2Cr_2O_7$	1 g
	C_2H_5OH	20 mL

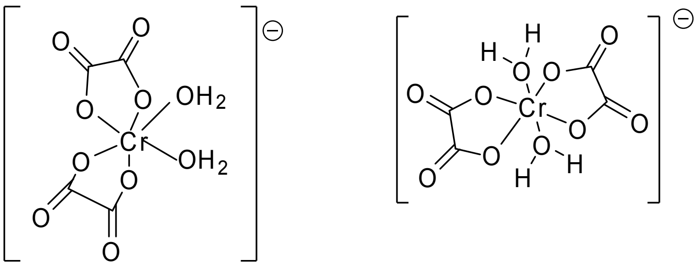
Apparatus: Electronic weighing machine, beaker 500 mL, beaker 250 mL, Bunsen burner, desiccator, filtration apparatus, conical flask, Funnel, Glass rod, Pair of tongs, Tripod stand, Watch glass, Water bath, Wire guaze.

2.3.4.3 Theory

Cis and *trans* potassium dioxalato diaquo chromate (III) ionize in the following fashion:

$$K[Cr(C_2O_4)_2(H_2O)_2].2H_2O \longrightarrow K^+ + [Cr(C_2O_4)_2(H_2O)_2]^- + 2H_2O$$

The complex ion obtained from above ionization process exists in the *cis* and *trans* geometrical isomeric forms which can be represented as:

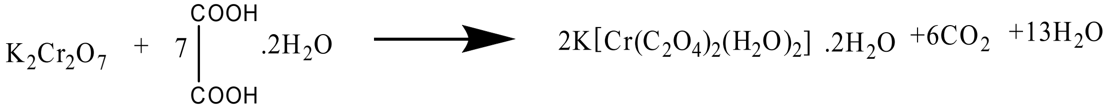

Cis isomer

Trans isomer

Structure of *cis* and *trans* dioxalato diaquo chromate complex ions

A. *Cis* potassium dioxalato diaquo chromate (III) complex K $[Cr(C_2O_4)_2(H_2O)_2]2H_2O$

This isomer is prepared by the reaction of $K_2Cr_2O_7$ according to the following reaction:



$$K_2Cr_2O_7 + 7\,(COOH)_2.2H_2O \longrightarrow 2K[Cr(C_2O_4)_2(H_2O)_2]\ .2H_2O + 6CO_2 + 13H_2O$$

B. *Trans* potassium dioxalato diaquo chromate (III) complex $K[Cr(C_2O_4)_2(H_2O)_2].2H_2O$

This isomer is prepared by the reaction of $K_2Cr_2O_7$ according to the following reaction.

$$K[Cr(C_2O_4)_2(H_2O)_2].2H_2O \longrightarrow K^+ + [Cr(C_2O_4)_2(H_2O)_2]^- + 2H_2O$$

2.3.4.4 Procedure

A. *Cis* potassium dioxalato diaquo chromate (III) complex

Preparation of the *cis* isomer involves the following steps:

Step I At first, 3g of oxalic acid and 1g of $K_2Cr_2O_7$ are mixed with each other and grinded to obtain the powder form.

Step II Take this mixture in the china dish and heat the content in china dish gently on a low flame by which a vigorous reaction will occur with the evolution of CO_2 and water vapour. Finally the mixture will become deep colored liquid.

Step III Now without cooling the liquid, 20 mL C_2H_5OH is added over this liquid and triturate the content by metallic spatula until the solid mass is formed.

Step IV Now warm the content until the product cannot be obtained in the form of granular crystals. The crystals of *cis* potassium dioxalato diaquo (III) complex look black in the diffused day light which are finally weigh.

B. *Trans* potassium dioxalato diaquo chromate (III) complex

Preparation of the *trans* isomer involve the following steps:

Step I Take 3g of oxalic acid crystal in a beaker and add small amount of water and heat to dissolve the oxalic acid crystal in water.

Step II Take 1g of $K_2Cr_2O_7$ and small amount of water in a boiling tube and heat to dissolve the $K_2Cr_2O_7$ in water.

Step III Now introduce the content of boiling tube in the beaker containing oxalic acid solution and cover the beaker by watch glass.

Step IV Now cool the dark coloured content of beaker and transfer it to a china dish. The content of china dish is kept in air for 36-48 hours by which volume is reduced to one third of the original volume.

Step V Now the crystals of *trans* isomer get deposited and filter by regular filter paper with the help of funnel which are washed by water and ethyl alcohol and finally weigh the crystals of trans isomer.

2.3.4.5 Result

A. The yield of *cis* potassium dioxalato diaquo chromate (III) complex is …………..g.

B. The yield of t*rans* potassium dioxalato diaquo chromate (III) complex is ………g.

2.4 PREPARATION OF DOUBLE SALTS

2.4.1 Ferric alum

2.4.1.1 Objective

To prepare ferric alum (ferrous ammonium sulphate); $FeSO_4.(NH_4)_2SO_4.6H_2O$

2.4.1.2 Requirements

Required chemicals:	Ferrous sulphate	5 g
	Ammonium sulphate	2.5 g
	Dilute sulphuric acid	1 to 2 mL

Apparatus: Electronic weighing machine, Beaker 500 mL, Beaker 250 mL, water bath, glass rod etc.

2.4.1.3 Theory

When equimolar quantity of ferrous sulphate $FeSO_4.7H_2O$ and ammonium sulphate $(NH_4)_2SO_4$ are dissolved in water and the solution is evaporater, light blue coloured crystals of ferrous ammonium sulphate is separate out.

$$FeSO_4.7H_2O + (NH_4)_2SO_4 \rightarrow FeSO_4.(NH_4)_2SO_4\,.6H_2O + H_2O$$

2.4.1.4 Procedure

To prepare the double salt ferrous ammonium sulphate (Mohar salt), at first few drop of dilute H_2SO_4 should be added in the ferrous sulphate (to prevent the hydrolysis of ferrous sulphate) and dissolve it in a 5 mL of water in a beaker. Now dissolve ammonium sulphate in minimum amount of water (2 to 3 mL) in a test tube. Now the ammonium sulphate solution should be added in ferrous sulphate solution and solution is boiled to 2 to 3 mL and allowed to cool, as a result of which crystals of ferrous ammonium sulphate are obtained. These should be dried in air and weighed.

2.4.1.5 Result

The yield of ferric alum is …………………g.

2.4.2 Chrome alum

2.4.2.1 Objective

To prepare chrome alum; $K_2SO_4.Cr_2(SO_4)_3 .24 H2O$

2.4.2.2 Requirements

Chemicals:	Potassium dichromate ($K_2Cr_2O_7$)	5 g
	Ethyl alcohol (C_2H_5OH)	4 mL
	Concentrated H_2SO_4	4 mL

Apparatus: Electronic weighing machine, beaker 500 mL, beaker 250 mL, water bath, glass rod etc.

2.4.2.3 Theory

The crystals of chrome alum may be prepared by reducing the acidified solution of $K_2Cr_2O_7$. Reduction can be carried out by using the ethyl alcohol or starch solution.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5OH \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3CH_3CHO$$

$$K_2SO_4 + Cr_2(SO_4)_3 + 24H_2O \rightarrow \underset{\text{Chrome alum}}{K_2SO_4.Cr_2(SO_4)_3.24H_2O}$$

2.4.2.4 Procedure

Five gram of $K_2Cr_2O_7$ should be taken in a 100 mL beaker and 20 mL of water should be added into it. Now 4 mL of concentrated H_2SO_4 should be added drop wise with constant stirring. The content of beaker should be now placed in the water bath and finally 3 to 4 mL of ethyl alcohol (C_2H_5OH) is to added drop wise with constant stirring. The content of beaker should now be placed overnight, when the crystals of chrome alum are prepared. The crystals should be washed with small amount of water, dried between the fold of filter paper and weighed.

2.4.2.5 Result

The yield of chrome alum is ………………..g.

2.5 SUMMARY

In this exercise, the synthesis of sodium ferrioxalate, tetraamine cupric sulphate, nickel dimethyl glyoxime and *cis-trans* potassium-dioxalato diaquo chromate (III) complexes along with two double salts namely ferric and chrome alum were explained in a simple way for the better understanding of beginner students. All these compuonds were synthesized by using common laboratory apparatus.

2.6 GLOSSARY

Complex: When center metal is surrounded by ligand (molecule or ions) is called complex.
Crystallization: It process is used for the separation of the solid substance from the saturated solution prepared at high temperature, by cooling it to room temperature.
Triturate: Grind to a fine powder

2.7 SELF ASSESSMENT QUESTIONS

Q 1. Explain why during the formation of *cis*-potassium dioxalato diaqua chromate (III), gentle heating is required instead of strong heating ?

Ans: During the formation of cis-potassium dioxalato diaqua chromate (III) gentle heating is required otherwise the reaction may go out of control and cause explosion.

Q 2. What do you understand by crystallization process ?

Ans: Crystallization process is used for the separation of the solid substance from the saturated solution prepared at high temperature ,by cooling it to room temperature.

Q 3. What is mother liquor?

Ans: The liquid remaining after the separation of crystal of substance from the saturated solution is known as mother liquor.

Q 4. What will be the structure of $[Cu(NH_3)_4]SO_4$ complex?

Ans: According the concept of VBT structure of $[Cu(NH_3)_4]SO_4$ complex will be tetrahedral.

Q 5. What will be the coordination no of Ni in $[Ni(DMG)_2]$ complex compound?

Ans: Coordination no of Ni in $[Ni(DMG)_2]$ complex compound will be 4.

Q 6. What is the difference between double salt and complex salt?

Ans: Double salt on dissolving in any solvent retain the test of all the ions of individual constituent salts while on the other hand complex salt on dissolving in any solvent cannot retain the test of all the ions of individual constituent salts .

Q 7. Give the IUPAC name of $[Cr(C_2O_4)_2(H_2O)_2]^-$ complex ion?

Ans: IUPAC name of $[Cr(C_2O_4)_2(H_2O)_2]^-$ complex ion is dioxalato diaqua chromate (III) ion .

Q 8. What will be the magnetic behavior of $[Ni(DMG)_2]$ complex compound?

Ans: Due to the absence of unpaired electron at the central metal atom (Ni) in this complex the magnetic behavior of $[Ni(DMG)_2]$ complex compound will be diamagnetic.

Q. 9. Whether the complex $K[Cr(C_2O_4)_2(H_2O)_2].2H_2O$ will behave as a double salt or complex salt?

Ans: The complex K[Cr(C_2O_4)$_2$(H_2O)$_2$].2H_2O will behave as a complex salt because this complex cannot retain the test of all the ions of constituent salts on dissolving in any solvent .

Q.10. Why the hot saturated solution should not cooled suddenly?

Ans: When the hot saturated solution are cooled suddenly then small size crystals of the substance are obtained but on slow cooling large size crystals are obtained due to which the hot saturated solution are not cooled suddenly .

Q. 11. What do you know about the term seeding?

Ans: Sometime crystals of the substance cannot be prepared on cooling the saturated solution .A crystal of same substance is placed in the saturated solution which induces crystallization. This process is known as seeding.

2.8 REFERENCES

1. A. Skoog, D.A. West, F.J. Holler and S.R. (2000). Crouch. Analytical Chemistry, an Introduction, 7th Edition.
2. Modern Inorganic Synthetic Chemistry. Second Edition (2017), edited by Ruren Xu Yan Xu Elsevier.
3. L.W. Jolly. (1991). The Synthesis and Characterization of Inorganic Compounds. Waveland Pr. Inc.
4. P.J. van der Put. (1998). Synthesis of Inorganic Materials. *In*: The Inorganic Chemistry of Materials. Springer, Boston, MA.
5. C.N.R. Rao and Kanishka Biswas. (2015). Essentials of Inorganic Materials Synthesis. John Wiley & Sons, Inc.
6. G. Pass. (1979). Practical Inorganic Chemistry: Preparations, Reactions and Instrumental Methods (Science Paperbacks). Springer.

2.9 SUGGESTED READINGS

- G. Raj. (2016). Advanced Practical Inorganic Chemistry. 16th ed. GOEL publishing house Meerut, India.
- I.R. Siddiqui, J. Singh, J. Srivastava, L. D. S. Yadav, R.K.P. Singh and J. Singh. (2008*).* Advance Practical Chemistry. Pragati Prakashan, Meerut, India.
- R. J. Angelici. (1991). Synthesis and Technique in Inorganic Chemistry. 2nd ed. University Science Books, U.S.

2.10 TERMINAL QUESTIONS

Q 1**.** What do you understand by complex?

Q 2. How to synthesis nickel dimethyl glyoxime?

Q 3. How to synthesis tetraamine cupric sulphate complex?

Q 4. Give the synthesis of any *cis* and *trans* complexes.

UNIT-3 -GRAVIMETRIC ESTIMATION

CONTENTS

3.1 INTRODUCTION

Gravimetric analysis is one of the most accurate and precise analytical methods for quantitative analysis of analyte. Gravimetric methods are quantitative methods that are based on measuring the mass of a pure compound to which the analyte is chemically related. In this method, the solution of pure compound is converted into insoluble form of a compound from which analyte mass is accurately measured.

There are three most common methods used for gravimetric analysis are:

- Precipitation gravimetry
- Volatilization gravimetry
- Electrogravimetry method

Precipitation gravimetry: As we discussed in previous paragraph, in this method, the analyte of interest is separated from a solution by precipitation with appropriate reagent followed to conversion into a compound of known composition that can be weighed.

Volatilization gravimetry: In this method, the interested analyte is separated from other a sample by converting it into another form of a gaseous compound followed by weight.

Electrogravimetric method: In this method, the analyte of interest is separated by electrochemical method. The analyte to be separated is deposited on an electrode by electrolysis. The mass of this product then should be used to calculate the analyte concentration.

In this exercise, we will discuss in detail only about precipitation gravimetric method. In precipitation gravimetry, the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed to be free of impurities, converted to a product of known composition by suitable heat treatment, and weighed.

3.2 OBJECTIVES

Determination of nickel and copper in a given mixture by precipitative gravimetric analysis method. In the following exercise, the precipitation of copper (Cu^+) and nickel (Ni^{2+}) from the solution should be done by adding ammonium thiocyanate and dimethyl glyoxime respectively.

After completing this exercise students should learn;

- The basic understanding of gravimetric analysis.
- Different steps to be followed in the gravimetric analysis.
- How to choose appropriate precipitating agent to avoid contamination of non-essential analytes.
- Optimization of the precipitation conditions in order to obtain a desirable precipitate.
- Basic calculations related to gravimetric analysis.

3.3 GRAVIMETRIC ESTIMATION OF COPPER AND NICKEL

3.3.1 Requirements

3.3.1.1 Objective

To estimate copper and nickel in the given solution of cupper and nickel ios gravimetrically

3.3.1.2 Apparatus

Electronic weighing machine, beaker 500 mL, beaker 250 mL, Bunsen burner, desiccator, filtration apparatus, conical flask, funnel, glass rod, pair of tongs, sintered glass crucible (G-3), sintered glass crucible (G-4), tripod stand, wash bottle, watch glass, water bath, wire guaze.

3.3.1.3 Chemicals

10% Ammonium thiocyanate, aqueous ammonia, copper(II) sulphate, dimethylglyoxime, ethanol Hydrochloric acid (conc.), nickel(II) sulphate, nitric acid (conc.), ammonium hydrogen sulphite solution

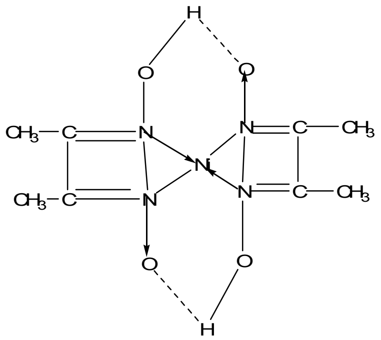
3.3.2 Theory

During the gravimetric estimation of copper and nickel, copper is estimated first as cuprous thiocyanate (CuSCN) and in the filtrate, nickel is estimated as nickel dimethylglyoxime [Ni(DMG)$_2$]. The given solution is first treated with ammonium thiocyanate solution precipitating cuprous thiocyanate leaving behind nickel in the solution. During precipitation of cuprous thiocyanate, sulphurous acid is added to reduce Cu(II) to Cu(I).

$$\begin{array}{c} 2Cu^{2+}_{(aq)} + HSO_3^-{}_{(aq)} + H_2O_{(l)} \rightarrow 2Cu^+_{(aq)} + HSO_4^-{}_{(aq)} + 2H^+_{(aq)} \\ 2Cu^+_{(aq)} + SCN^-_{(aq)} \rightarrow 2CuSCN_{(s)} \\ \hline 2Cu^{2+}_{(aq)} + HSO_3^-{}_{(aq)} + 2SCN^-_{(aq)} + H_2O_{(l)} \rightarrow 2CuSCN_{(s)} + HSO_4^-{}_{(aq)} + 2H^+_{(aq)} \end{array}$$

After precipitating CuSCN, solution of dimethylglyoxime is added in the filtrate to precipitate nickel as scarlet red coloured nickel dimethylglyoxime.

$$Ni^{2+}_{(aq)} + 2H_2DMG_{(aq)} \rightarrow \underset{\text{Nickel dimethylglyoxime}}{Ni(HDMG)_{2(s)}} + 2H^+_{(aq)}$$



Nickel dimethylglyoxime

3.3.3 Procedure

Following steps are involved in gravimetric analysis

3.3.3.1 Preparation of the solution

A. Estimation of copper

3.3.3.2 Precipitation

3.3.3.3 Digestion

3.3.3.4 Filtration

3.3.3.5 Washing

3.3.3.6 Drying or igniting

3.3.3.7 Weighing and finally calculation

B Estimation of nickel

3.3.3.8 Precipitation

3.3.3.9 Digestion

3.3.3.10 Filtration

3.3.3.11 Washing

3.3.3.12 Drying and weighing

3.3.1 Preparation of the solution

a) **$CuSO_4.5H_2O$ solution:** 60.0 grams of $CuSO_4.5H_2O$ is dissolved in 1000 mL distilled water.

b) **Nickel ammonium sulphate solution:** 40.0 grams of nickel ammonium sulphate is dissolved in 1000 mL distilled water.

c) 40 mL $CuSO_4.5H_2O$ and 40 mL of nickel ammonium sulphate solutions are mixed in 250 mL beaker and make up the volume up to the mark by the addition of distilled water. This solution is named as solution A.

Now by using the 50 mL of solution "**A**" (test solution) gravimetric estimation of Cu and Ni can be done.

B. Estimation of copper

3.3.3.2 Precipitation

a) Pipette out 50 mL of test solution in a 500 mL beaker. Add into it 2-3 mL dilute HCl and 40-50 mL of freshly prepared ammonium hydrogen sulphite or sulphurous acid solution and ensure that smell of SO_2 continuously coming out. This solution is diluted by 100 mL of distilled water.

b) Boil the contents of the beaker gently on a water bath. Remove the flame and add 10% ammonium thiocyanatesolution (25 mL) in this solution with constant stirring. Keep stirring the precipitate with a glass rod intermittently.

3.3.3.3Digestion

Now keep the solution along with precipitate in the beaker in water bath for 30 minutes. This process is called digestion. Digestion involves dissolution of small particles and re-precipitation on larger ones resulting in particle growth and better precipitate characteristics. This process is called Ostwald ripening.

3.3.3.4Filtration

Weigh an empty and cleaned sintered glass crucible (G-4) and note it’s mass. Filter the precipitate through this crucible first by draining off the supernatant liquid and then the precipitate with minimum quantity of liquid. This procedure of filtration keeps the precipitate away from clogging the pores of the crucible.

3.3.3.5 Washing

Wash the precipitate with 2-3% NH_4SCN solution. Wait and check the filtrate. If any precipitate appears then filter the precipitate again through the same weighed crucible. Preserve the filtrate for estimation of nickel. Finally wash the precipitate several times with 20% ethanol until the precipitate is free from 'SCN^-ions.

3.3.3.6 Drying

Now heat the sintered glass crucible at a temperature of 100 - 120°C in a hot air oven for at least an hour.

3.3.3.7 Weighing and calculation

Cool the crucible in a desiccator and then weigh. Repeat the process of heating, cooling and weighing till the constant mass of the crucible with precipitate is obtained.

B Estimation of nickel (Ni^{2+})

3.3.3.8 Evaporation

The filtrate and washing left after the estimation of Cu is placed in an evaporating dish and evaporate the solution nearly to 80-100 mL on a water bath. Now add 35 mL concentrated nitric acid and 15 mL concentrated HCl and heat to dryness on a water bath or sand bath in a fume hood.

3.3.3.9 Precipitation

To the residue, obtained, add 100 mL of distilled water and dissolve the contents by shaking. Add 2-3 drops of methyl red indicator and then add 10% aqueous ammonia solution till smell of ammonia prevails and the colour of the methyl red changes to yellow. Now add 40-50 mL of dimethylglyoxime solution with adequate stirring with a glass rod. Again add ammonia solution till the colour becomes yellow.

3.3.3.10 Digestion

Digest the precipitates of $[Ni(DMG)_2]$ complex on a water bath at least for 30 minutes.

3.3.3.11 Filtration

After digestion, cool the solution for 1 to 2 hours and filter by using previously weighted sintered crucible (G-3). Drain out the supernatant liquid first and then the precipitate with minimum quantity of liquid.

3.3.3.12 Washing

Now wash the precipitate 2-3 times with 2-3% dimethylglyoxime solution. If any precipitate appears in the filtrate, then filter it again through the crucible. Wash the precipitate with 2-3% aqueous ammonia solution. Finally wash the precipitate with hot water.

3.3.3.13 Weighing

Heat the crucible and precipitate at temperature range 100-120°C in a hot air oven. Cool the crucible in a desiccator and then weigh it. Repeat heating, cooling and weighing till a constant mass of the crucible with precipitate is obtained.

3.3.4 Observations

I. Observe the empty mass of sintered crucible (G-4) at least 2-3 times and took the average of constant readings = w_1 g

II. Observe the mass of sintered crucible (G-4) and CuSCN precipitates together 2-3 times and took the average of constant readings = w_2 g

III. Similarly observe the empty mass of sintered crucible (G-3) at least 2-3 times and took the average of constant readings = w_3 g

IV. Again observe the mass of sintered crucible (G-3) and $Ni(DMG)_2$ precipitates together 2-3 times and took the average of constant readings = w_4 g

3.3.5 Calculations

3.3.5.1 Calculations for copper

I. First we should measure the weight of CuSCN as follow

Mass of sintered crucible (G-4) + CuSCN precipitates (w_1) - mass of empty sintered crucible (G-4) (w_2) as shown in observation section.

II. Now we should use the stoichiometry for CuSCN formation

$$\underset{\text{(Mol Wt. 63.57 g)}}{Cu} \equiv \underset{\text{(Mol Wt. 121.62 g)}}{CuSCN}$$

Suppose constant weight of cuprous thiocyanate be x g.

121.62 gram of cuprous thiocyanate contain copper = 63.57g

So, x gram of cuprous thiocyanate will contain copper $= \frac{63.57 \times x}{121.62}$ g

Since 50 mL of solution contain Cu $= \frac{63.57 \times x}{121.62}$ g

So 1000 mL of solution will contain Cu $= \frac{63.57 \times x}{121.62} \times \frac{1000}{50}$ g/L

Concentration of copper $= \frac{63.57 \times Mass\ of\ CuSCN \times 1000}{121.62 \times Volume\ of\ test\ solution\ taken}$ g/L

3.3.5.2 Calculation for nickel

I. First we should measure the weight of $Ni(DMG)_2$ as follow

Mass of (sintered crucible (G-3) + $Ni(DMG)_2$ precipitates) (w_4)- (mass of empty sintered crucible (G-3) (w_3) as shown in observation section.

II. Now we should use the stoichiometry for $Ni(DMG)_2$ formation

Suppose the weight of nickel dimethylglyoxime complex = y g

$$[Ni(DMG)_2] \equiv Ni$$

(Mol Wt. 288.91 g) (Mol Wt. 58.69g)

Since, 288.91 gram of $[Ni(DMG)_2]$ complex contain nickel =58.69 g

So, y gram of $[Ni(DMG)_2]$ will contain nickel = $\frac{58.69 \times y}{288.91}$g

Since 50 mL of given solution contain nickel = $\frac{58.69 \times y}{288.91}$ g

So 1000 ml of given solution will contain nickel = $\frac{58.69 \times y}{288.91} \times \frac{1000}{50}$ g/L

Concentration of Nickel= $\frac{58.69 \times Mass of Ni(DMG)2 \times 1000}{288.91 \times Volume of test solution taken}$ g/L

Note: Gravimetric factor = $\frac{nMwt. of analyte}{mMolwt. ppt}$, where n= moles of analyte, m= moles of ppt. compound based on stochiometry.

3.3.6 Results

Mention the results as:

Concentration of copper in the test solution = g/L

Concentration of Nickel in the test solution = g/L

3.4 SUMMARY

In this exercise, precipitation gravimetric analysis is performed for the determination of concentration of copper and nickel in a given test solution. For the determination of copper (II) sulphate in a test solution, copper is precipitated as copper (I) thiocyanate (CuSCN) that is filtrated and weighed. Similarly, nickel (II) sulphate concentration determined by precipitating nickel as nickel dimethylglyoxime [Ni(DMG)$_2$] followed by filtration and weighing.

3.5 GLOSSARY

Precipitation: It is a process of particle aggregation to form small nuclei those later combined together to form large particles or nucleus.

Analyte: It is compound of interest that is determined or analyze in a given sample

Digestion: Digestion involves dissolution of small particles and re-precipitation of larger ones resulting in particle growth and better precipitate characteristics.

Filtration: It is a physical process used to sieve or separate particles or precipitates from solution.

Drying: It is also a physical process where solvent is heated up at about 120-150^{o}C in a hot air oven to remove the moisture or concentrate the solvent.

Desiccator: This is sealable enclosure containing desiccants used for preserving moisture-sensitive items. A common use of desiccator is to protect chemicals which are hygroscopic or which react with water from humidity**.**

Sintered glass crucible: Special glass crucible having specific pore size is used in the laboratory to contain chemical compounds when heated to extremely high temperatures. Crucibles are available in several sizes and typically come with a correspondingly-sized lid

Water bath: A water bath is laboratory equipment made from a container filled with heated water. It is used to incubate samples in water at a constant temperature over a long period of time.

3.6 SELF ASSESSMENT QUESTION

Q 1.Draw the structure of Ni(DMG)$_2$.

Q2. Describe the process of precipitation.

Q 3. What do you understand by nucleation process in precipitation?

Q 4. Describe the digestion process in precipitation.

Q 5. Describe the threshold concentration of precipitating agent used in precipitation process to obtained maximum precipitation.

Q 6. Describe the Von-Weimarn ratio in precipitation process.

Q 7. Describe the gravimetric factor

Q 8. Orthophosphate (PO_4^{3-}) is determined by weighing as ammonium phosphomolybdate, $(NH_4)PO_4.12MoO_3$. Calculate the percent P in the sample and the percent P_2O_5 if 1.1682g precipitate were obtained from a 0.2711 g sample?

Ans. 7.11 %, 16.30%

Q 9. An ore is analyzed for the manganese content by converting the manganese to Mn_3O_4 and weighing it. If a 1.52 g sample yields Mn_3O_4 weighing 0.126g, what would be the percent Mn and Mn_2O_3 in the sample?

Ans. 8.58 % , 5.97 %

Q 10. What is the role of pH in precipitation process?

3.7 REFERENCES

1. A. Skoog, D.A. West, F.J. Holler and S.R. (2000). Crouch. Analytical Chemistry, an Introduction, 7th Edition.
2. F. W. Fifield and D. Kealey. (2000). Principles and Practice of Analytical Chemistry. Oxford, Blackwell Science.
3. Douglas A. Skoog, F. James Holler and Stanley R. Crouch. (2007). Principles of Instrumental Analysis. Belmont, CA.
4. Yoshiko Arikawa. (2001). Basic Education in Analytical Chemistry. (pdf). Analytical Sciences. The Japan Society for Analytical Chemistry. 17 (Supplement): i571–i573. Retrieved 10 January 2014.
5. Gary D. Christian (2004). Analytical Chemistry, 6th ed. Wiley, Hoboken, N.J.
6. B. K. Sharma. (2018). Analytical Chemistry, 1st ed. Krishna Prakashan Media (P) Ltd. India.
7. G. R. Chatwal and Madhu Arora. (2015). Analytical Chemistry. Himalya Publishing House, India.
8. A. L. Gupta. (2015). Modern Analytical Chemistry. Pragati Prakashan, India.

9. R.M. Verma. (2015). Analytical Chemistry. CBS Publishers & Distributors, India.
10. S. M. Khopkar. (2007). Analytical Chemistry: Problems and Solutions, New Age International (P) Limited, India.

3.8 SUGGESTED READINGS

1. A. I. Vogel and J. Mendham. (2000). Vogel's Textbook of Quantitative Chemical Analysis. 6th ed. Harlow, Prentice Hall.
2. J. N. Miller and J. C. Miller. (2005). Statistics and Chemometrics for Analytical Chemistry. 5th ed. Pearson/Prentice Hall.
3. Daniel C. Harris. (2002). Quantitative Chemical Analysis. 6th Ed. W. H. Freeman.

3.9 TERMINAL QUESTIONS

Q 1**.** What do you understand by gravimetric analysis?

Q 2. Briefly describe the precipitation mechanism

Q 3. Describe the precipitation gravimetric method of analysis

Q 4. Write short note on the following

(a) Electrogravimetric method (b) Volatilization gravimetry

Q 5. Describe the relationship between concentration of precipitating agent and precipitates obtained.

UNIT 4: QUALITATIVE ANALYSIS

CONTENTS

4.1 INTRODUCTION

Separation, identification and structure determination of an unknown substances is an important aspect of organic chemistry. Different spectroscopic techniques such as Infra-red spectroscopy (IR), Ultra-Visible (UV) spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy are helpful in elucidation of the structure of organic compounds, but these spectroscopic techniques must be supplemented with other information such as physical state, solubility, elements present, melting or boiling point and functional groups about the unknown compound. Formation of a solid derivative of unknown compound with known melting point provides final confirmation of structure. This unit is provides the information regarding the separation and qualitative analysis of unknown organic compounds. Qualitative analysis of organic compounds involves a study of various chemical characteristics of a given compound and then a careful correlation of the observed data.

4.2 OBJECTIVES

By studying this unit, the students will be able to understand:

- Qualitative analysis
- Methods of separation of mixture of organic compounds.
- Systematic identification of organic compounds
- Special elements and their identification

4.3 SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUND

It involves the systematic identification of an unknown organic compound. The identification of an unknown organic compound includes the following steps-

4.3.11 Physical examination of the compound

4.3.12 Tests for unsaturation (presence of multiple bonds which can be involved in addition reactions)

4.3.13 Solubility test

4.3.14 Ignition test
4.3.15 Detection of elements
4.3.16 Detection of functional groups
4.3.17 Determination of melting / boiling point of the compound
4.3.18 Confirmatory test for the suspected organic compound and preparation of suitable derivatives.
4.3.19 Result
4.3.20 Structural formula

4.3.1 Physical examination of the compound

The following physical characters are helpful in identifying the given organic compound-

(i) Physical state: This physical test indicates the physical state of the compound (liquid/solid).

(ii) Colour: Each organic compound has a characteristic colour due to the presence of a group known as chromophore and can be suspected by observing its colour as shown below-

- (a) Pale yellow-Nitro compounds, Iodoform
- (b) Orange- Ortho Nitroaniline, phenanthroquinone, azo compounds
- (c) Red-1,2 Napthaquinone

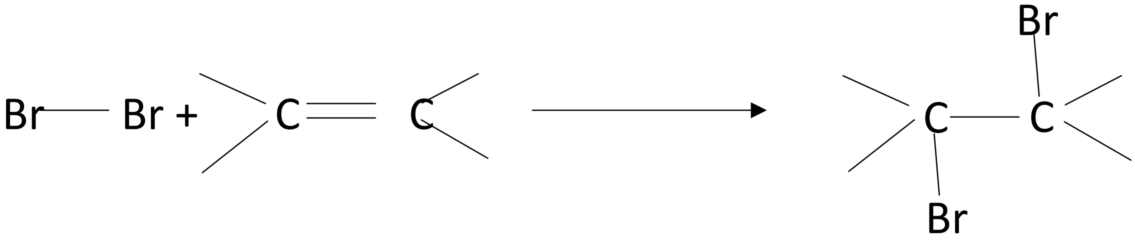
(iii)Odour: The presence of a characteristics odour is an indication of a particular class of organic compound.

- (a) Pleasant- Esters, ethers, lower aliphatic alcohols, Chloroform
- (b) Pungent- Acetic acid, acetyl chloride, acetic anhydride, benzoyl chloride, benzyl chloride, formic acid and pyridine
- (c) Bitter almonds- Nitrobenzene, benzaldehyde
- (d) Phenolic-Phenols, naphthols, some derivatives of salicylic acid
- (e) Moth balls-Napthalene
- (f) Fishy-Amines
- (g) Rotten eggs-Sulphur containing compounds

4.3.2 Tests for unsaturation

Positive test of organic compounds for Bromine solution and Baeyer's reagent (1% $KMnO_4$, w/v) shows the presence of unsaturated compound

(i) Bromine solution test- Take solution of compound in a test tube and add the bromine solution dropwise with shaking. Disappearance of reddish brown colour of bromine solution indicates the presence of unsaturation.



(ii) Baeyer test- Add Baeyer's reagent (1%w/v $KMnO_4$) dropwise to a solution of organic compound prepared in water or ethanol. Shake it continuously and disappearance of purple colour indicates the presence of unsaturated compound.

4.3.3 Solubility tests

Solubility behaviour of organic compound in H_2O, NaOH, $NaHCO_3$ and HCl provides valuable information for the presence of certain classes of organic compounds. Therefore, careful observation is important for identification of organic compounds.

The solubility test is performed in a sequential manner which is as follows-

(i) Dissolve 0.5 g organic compound in 2 mL water with shaking.

(ii) If the compound is insoluble in water then observe its solubility in 2M or 5% (w/v) NaOH solution.

(iii)The compound insoluble in NaOH solution is further checked for its solubility in 1.5M HCl

(iv) An organic compound, insoluble in H_2O, NaOH and HCl solution, contains no nitrogen and again can be tested for its solubility in 2M H_2SO_4 solution.

Solubility flow chart (Figure 4.1) will give you an idea about the presence of various classes of organic compounds which thereby will support the identification of given organic compound.

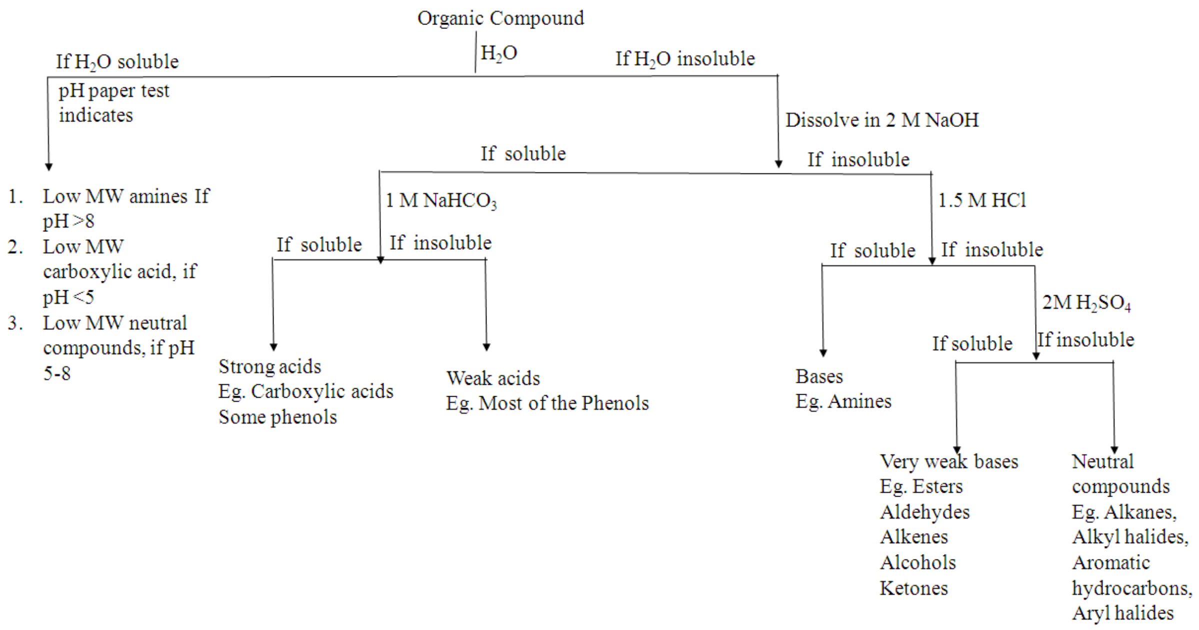


Figure 4.1. Solubility flow chart

4.3.4 Ignition

Take a small amount of compound on metal spatula or water bath ring and burn in a flame, if it burns

i. With non-sooty flame- Aliphatic compound suspected
ii. With a sooty flame-Aromatic compound suspected
iii. Non ignition- polyhalogenated compound suspected
iv. With charring- Carbohydrate, tartaric acid and its salts, suiphonic acids
v. Violet vapours- Iodoform

4.3.5 Detection of additional (special) elements

Organic compounds are composed of two or more elements. All organic compounds contain carbon and hydrogen in their basic skeleton but the presence of nitrogen, sulphur and halogens is determined in certain compounds.

Oxidative or reductive mineralization (ionization) of an unknown organic compound gives the test for the presence of an additional element using the method of Lassaigne's. Since the organic compounds are non-ionic in nature therefore, they are fused with sodium metal for detection of these elements to convert them into water soluble inorganic compounds. Based on this fact, the most effective method Lassaigne's test was developed by J. L. Lassaigne. In this test, the organic compounds on fusion with alkali metals are first converted into ions *i.e.* nitrogen in presence of carbon is converted to cyanide ion (CN^-) whereas sulphur and halogen are converted to sulphide (S^{--}) and halide ions (Cl^-) respectively.

4.3.5.1 Fusion with sodium (Lassaigne's Test)

Place 20-22 mg of the solid or 1 mL of liquid organic sample in an ignition tube. Cut a small piece of sodium metal, dry it with filter paper so as to remove the adhering liquid that is kerosene oil and then slide it along the side of the ignition tube to its bottom. Add 5-10 mg of compound more so that the sodium is now sandwiched between the organic sample. Heat the ignition tube in a Bunsen flame till sodium melts and then strongly till it becomes red hot. There is an alternative method of organic compound fusion with sodium. In this method first take dried sodium piece in a dried ignition tube and slightly heat the ignition tube over a Bunsen burner so that the sodium piece melt into a shiny liquid. Take a pinch of organic compound with the help of a spatula into the fusion tube till it becomes red hot. Plunge the red hot ignition tube immediately into a porcelain dish containing 50 mL distilled water. This breaks the ignition tube. Plunge two or three ignition tubes into water in the same way. If the ignition tube does not break, crush the tube with the help of a glass rod. Boil the mixture for 2-3 minutes and then filter. This filtrate is known as a sodium extract. The filtrate should be clear and alkaline. If it is dark in colour, it indicates incomplete fusion and so the process should be repeated with fresh ignition tube. In this process nitrogen is converted into water soluble inorganic cyanide while the halogens and sulphur formed water soluble halides and sulphide respectively.

$$Na + C + N \rightarrow NaCN \text{ when nitrogen is present}$$

$$2Na + X_2 \rightarrow 2\,NaX \text{ when halogens are present}$$

$$(X = Cl^-, Br^-, I^-)$$

$$2Na + S \rightarrow Na_2S \quad \text{when sulphur is present}$$

$$2Na + C + N + S \rightarrow NaCNS \quad \text{when nitrogen and sulphur both are present}$$

The above sodium extract is alkaline in nature due to the formation of sodium hydroxide.

$$Na + 2H_2O \rightarrow 2NaOH + H_2$$

4.3.5.2 Test for Nitrogen

- In a test tube, place 1 mL of sodium or Lassaigne's extract, add 1 mL of freshly prepared ferrous sulphate solution. A dark green or grey precipitate of ferrous hydroxide is formed. Heat the tube over a Bunsen burner. Ferrous sulphate reacts with sodium cyanide to form sodium ferro cyanide. Add a few drops of ferric chloride solution in to the test tube and again add small amount of conc. HCl to acidify the solution. Appearance of prussian blue colour or precipitate indicates the presence of nitrogen.

$$FeSO_4 + 2NaOH \rightarrow \underset{\text{Ferrous hydroxide}}{Fe(OH)_2\downarrow} + Na_2SO_4$$

$$Fe(OH)_2 + 2NaCN \rightarrow \underset{\text{Ferrous cyanide}}{Fe(CN)_2} + 2NaOH$$

$$Fe(CN)_2 + 4NaCN \rightarrow Na_4[Fe(CN)_6]$$

(Final reaction)

$$FeSO_4 + 6NaCN \rightarrow \underset{\text{Sodium ferrocyanide}}{2Na_4[Fe(CN)_6]} + Na_2SO_4$$

In the presence of hydrochloric acid, ferric chloride reacts with sodium ferrocyanide to give Prussian blue (blue green) colour of ferric ferro cyanide.

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \rightarrow \underset{\text{Ferric ferro cyanide}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

- Acidify 2 mL of sodium extract with glacial acetic acid, add 1-2 drops of freshly prepared 1% solution of benzidine in 50% acetic acid and then stir the solution. Add 1 drop of 1% $CuSO_4$ solution. A blue coloured solution or precipitate indicates the presence of nitrogen.

4.3.5.3 Test for halogens

In a test tube place 5 mL sodium extract, add dilute HNO_3 solution and then boil the solution to expel H_2S or HCN, if present. Add few drops of $AgNO_3$ solution.

(i) White precipitate indicates the presence of chloride in the organic compound.

(ii) Pale yellow precipitate, sparingly soluble but completely soluble in excess of NH_4OH, shows the presence of bromide.

(iii)Yellow precipitate, insoluble in NH_4OH, confirms the presence of iodide.

$$NaX + AgNO_3 \xrightarrow{\text{dil } HNO_3} AgX\downarrow + NaNO_3$$

Silver halide ($X = Cl^-, Br^-, I^-$)

$$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]^+ Cl^- + 2H_2O$$

White Precipitate   Ammonium solution   Silver aminochloride (soluble)

$$AgBr + 2NH_4OH \rightarrow [Ag(NH_3)_2]^+ Br^- + 2H_2O$$

$$AgI + NH_4OH \rightarrow \text{No reaction}$$

4.3.6 Detection of functional groups

The correct determination of elements in an unknown organic compound gives the idea of functional group present. Once the functional group present in the organic compound is known, one is able to find out the name of the probable compound with the help of melting point or boiling point. After having the idea of functional group, the next procedure is to study some specific reactions of the compound and then to confirm its name by preparing suitable derivatives. Test for element carbon, hydrogen and oxygen are not required. This means that if no other element is present, functional group containing carbon, hydrogen and oxygen are determined. The test for functional group should be performed in the following sequence-

4.3.6.1 Compounds containing C and H with or without oxygen

(A) Carboxylic acid (-COOH)

(i) Litmus Test- Take a small amount of given organic compound (0.5 g) and make its solution with water in a test tube. Dip a blue litmus paper in the solution. If the litmus paper turns red, it shows the presence of carboxylic group (phenols being acidic in nature also give this test).

(ii) Sodium bicarbonate test- Take 0.5 g of given organic compound in a test tube and 5 mL of cold 50% aqueous solution of $NaHCO_3$ and shake gently. Effervescence indicates presence of carboxylic group in the given compound.

(B) Phenols (Phenolic-OH, O~~H~~ directly attached to an aromatic nucleus)

(i) Take water solution of given organic compound in a test tube and dip the blue litmus paper in to it. If blue litmus changes to red but no effervescence with $NaHCO_3$ indicates the presence of phenolic group.

(ii) $FeCl_3$ Test- Take 1 mL of aqueous or alcoholic solution of given organic compound in a test tube. Add 2-3 drops of neutral or very dilute solution (aqueous) of ferric chloride. A blue, green, red or violet colour indicates presence of phenolic group (Ar- OH).

(iii) Libermann's Test- All phenols in which para position is free always gives this test. Take 0.5 g of given organic compound and few crystals of $NaNO_2$ in a dry test tube and heat gently for a minute. Cool the mixture and add 1 mL of conc. H_2SO_4 and shake thoroughly. A deep green or blue colour appears which on further dilution with water turns red. Now add excess of dil. NaOH to the above red coloured solution which again becomes deep green or blue. It indicates the presence of phenolic group.

(iv) Phthalein Test-Take 0.5 g of given organic compound and 0.5 g of phthalic anhydride in a dry test tube, add 1.0 mL of conc. H_2SO_4 and heat for a minute in Bunsen flame. Cool it and make it alkaline in with dil. NaOH solution. Pour a few drops of this solution in 20 mL water taken in a beaker. Following characteristics colours shows the presence of phenolic group-

Pink colour- Phenol, *o*-Cresol
Blue colour- Catechol, *m*-Cresol
Fluorescent green - Resorcinol
No colouration- *p*-Cresol

(C) Carbohydrate

(i) Molisch's Test- Take 2 mL aqueous solution of given organic compound in a test tube and add 1 mL of Molisch's reagent (dissolve 10 g α- naphthol in 100mL alcohol or 10 g β-naphthol in 100 mL chloroform) and shake well. Now take 2 mL of conc. H_2SO_4 in a separate test tube and add it to the tube containing organic compound with Molisch's reagent from side wall. Allow to stand for 5 minutes. A reddish violet ring at the junction of two liquids shows the presence of carbohydrate.

(ii) Reaction with H_2SO_4- Take 0.5 g of given organic compound in test tube and add 1 mL conc. H_2SO_4. An immediate charring and blackening of the solution shows the presence of carbohydrate.

(D) Aldehydes (-CHO)

(i) Schiff Test- Take 1 mL alcoholic or aqueous solution of given organic compound in a test tube and add 2 mL of Schiff reagent (Dissolve 1 g p-rosaniline in 50 mL water with gentle warming. Cool, saturate with SO_2 and filter) and shake. A deep red or violet colour shows the presence of aldehydic group (Never heat during this process).

(ii) Tollen's Test- Take 2 mL Tollen's reagent (Take 5 mL $AgNO_3$ solution and add 2-3 drops of dilute *i.e* 1% NaOH aqueous solution. A white ppt. is obtained. Now add NH_4OH drop by drop till the ppt. just dissolves. The reagent should be prepared fresh when required) and add 0.5 g of given organic compound in a boiling test tube. Heat the mixture on water bath. Formation of silver mirror or blackish precipitate indicates the presence of aldehydic group (reducing sugars also gives this test).

(iv) Fehling Solution Test-Take a test tube with 1 mL Fehling solution A and further add 1mL Fehling solution B in it until a blue precipitate first formed is redissolved to give a deep blue solution. Now Add 0.5 g of given organic compound and heat for 2 minutes. Reddish brown precipitate shows the presence of aldehydic group. This test is also given by reducing sugars. (**Fehling's solution**- consists of two parts, A and B; Solution A: Dissolve 35 g crystalline $CuSO_4.5H_2O$ in 500 mL water. Add few drops of conc. H_2SO_4. Solution B: Dissolve 173 g sodium potassium-tartarate (Rochelle salt) and 60 g of NaOH in 500 mL water. Equal volume of A and B are mixed before use.)

(E) Ketones ($>$ CO)

(i) **Schiff reagent**- No colour

(ii) **2,4 Dinitrophenylhydarzine Test-** Take 2 mL of Brady's reagent in a test tube and add 2-3 drops of given organic compound. Shake it vigorously. Heat and cool the solution. A red, yellow or orange coloured precipitate indicates the presence of ketonic group. (**Brady's reagent**- Mix 4 g 2,4 -dinitrophenyl hydrazine with 8 mL conc. H_2SO_4. To this solution, add gradually 70 mL CH_3OH with shaking and cooling. Now warm the solution and make up the solution to 100 mL by adding water).

(F) Esters ($R—COOR^1$)

(i) Fruity smell- All the esters have fruity smell.

(ii) Phenolphthalein Test

Take 100 mg of given organic compound in a test tube and add 3 mL of dilute NaOH solution and 1 mL of phenolphthalein solution. A pink colour is obtained due to the presence of NaOH which is discharged on heating the solution. Ester is hydrolysed into an acid and alcohol. The acid neutralizes the NaOH and hence pink colour is disappeared.

$$RCOOR^1 + H2O \xrightarrow{NaOH} RCOOH + R^1OH$$

(iii) Hydroxamic acid Test

Take 40 mg of given organic compound and 1 mL of hydroxylamine HCl solution in ethanol with 0.2 mL, 6M NaOH solution in a boiling test tube. Acidify the above solution with HCl solution and then cool it. Add 1-2 drops of $FeCl_3$ solution. Appearance of red-violet colour indicates the presence of ester.

Esters react with hydroxylamine HCl to yield a compound which can make complex with ferric chloride to give coloured compound.

$$\underset{}{R\text{-}COOR^1} + H_2NOH \rightarrow \underset{\text{Hydroxamic acid}}{RCONHOH} + R^1\text{-}OH$$

$$3R\text{-}CONHOH + FeCl_3 \rightarrow \underset{\substack{\text{Ferric Hydroxamate complex} \\ \text{Red-violet colour}}}{[RCOHNO]_3\,Fe} + 3HCl$$

(G) Alcohols (—OH)

(i) Take 2 mL of given organic compound in a dry test tube and add 1 g of anhydrous Na_2SO_4 and filter. To the filtrate add a small piece of sodium. Effervescence due to the presence of H_2 shows the presence of an alcohol.

(ii) Take 1 mL of given organic compound or its aqueous solution in a test tube and add few drops of ceric ammonium nitrate. A pink colour or red colour shows the presence of an alcohol.

(H) **Hydrocarbons**

There is no specific group test for hydrocarbons. Hydrocarbons may be either saturated or unsaturated. Unsaturated hydrocarbons may be aliphatic or aromatic in nature. They are insoluble in water but soluble in many organic solvents. Since hydrocarbons are non-reactive, their identification is done on the basis of their results of preliminary tests (like test of unsaturation, detection of elements), determination of melting point/boiling point, specific test for particular hydrocarbons and preparation of their derivatives.

4.3.6.2 When nitrogen is present

(A) Amides (-CONH$_2$)

Take 0.2 g of given organic compound in a test tube and add 1 mL of aq. NaOH and heat, smell of ammonia shows the presence of an amide.

(B) Primary amines (-NH$_2$)

(i) Nitrous Acid Test-

Take 0.5 g of given organic compound in a test tube and add 4 mL of dil. HCl in to it and cool. Now add 10% aq. $NaNO_2$ solution. A brisk effervescence shows the presence of an aliphatic primary amine.

(ii) Carbylamine Test-

Take 0.5 g of given organic compound in a test tube and add 4 mL of alcoholic solution of KOH and 2 drops of chloroform ($CHCl_3$) to it. Shake and heat gently. An intolerable offensive odour of carbylamine shows the presence of primary amine.

(iii) Diazotisation Test- Take 0.2 g or 0.5 mL of given organic compound in a test tube and dissolve in 2-3 mL of dil. HCl and cool under tap water. Now add 2 mL of 2.5% aqueous $NaNO_2$ solution, cool again and add 0.5 mL of alkaline β-naphthol solution. An orange-red or a red dye shows the presence of aromatic primary amine.

(C) Secondary amines (>NH-)

(i) Secondary amines do not give carbylamine test.

(ii) Nitrous Acid Test-

Take 0.2 g or 0.5 mL of given organic compound in a test tube and add 2 mL of dil. HCl and cool test tube under tape water. Add 2 mL of 2.5% $NaNO_2$ solution. Yellow oily drops are obtained which shows the presence of secondary amine. This test is given by both aliphatic and aromatic secondary amines.

(iii) Libermann's Nitroso Reaction-

Take 0.5 g or 0.5mL of given organic compound in a test tube and add 4 mL of dil. HCl and cool the test tube under tap water. Now add 2.5% aqueous solution of $NaNO_2$ gradually with continuous shaking until yellow oil separates at the bottom. Decant off the aqueous layer. Take 2 drops of this oily nitroso compound in a dry test tube, add 0.5 g of phenol and warm gently for a few seconds. Cool and add 1 mL of conc. H_2SO_4. A greenish blue colour is obtained which changes red upon dilution with water. Greenish blue colour reappeared on adding excess of NaOH solution. This shows the presence of secondary amine.

(D)Tertiary amines ($\overset{\diagdown}{\underset{\diagup}{-}}$N:)

(i) Tertiary amines do not give carbylamine test

(ii) Take 0.2 g or 0.5 mL of given organic compound in a test tube and add 4-5 mL of dil. HCl. Cool the tube under tap water. Now add 2-5 mL of 2.5% aqueous soution of $NaNO_2$ gradually with shaking and observe:

(a)Production of green or brown coloured salt indicates the presence of aromatic tertiary amine.

(b) No reaction indicates the presence of aliphatic tertiary amine.

(E) Anilides (-NHCOR) (e.g. acetanilide, benzanilide)

All anilides are colourless, odourless crystalline solids. Acetanilides and benzanilides are both soluble in cold water but acetanilides have the greater solubility in hot water.

(i) **2,4 –Dinitrochlorobenzene Test-** Organic compound having anilide group gives intense colour on a paper soaked with 2,4-dinitrochlorobenzene.

(ii) **Tafel's Test-**Take 0.5 g of given organic compound in a test tube and add 3 mL concentrated H_2SO_4 and powdered $K_2Cr_2O_7$ into it. Shake the tube thoroughly. Red or violet colour changes to green shows the presence of anilide which do not contain any substituent in benzene ring.

(iii) **Hydrolysis Test-** Take 0.5 g of given organic compound in a boiling test tube and add 5 mL of dil. HCl. Boil and cool the tube. Now add 2 mL of 2.5% $NaNO_2$ solution, cool again and add 0.5 mL of alkaline β-naphthol solution. An orange –red dye shows the presence of an anilide (Anilides are hydrolysed on boiling with HCl and thus, liberates primary amino group which gives the dye-test).

(F) Nitro Compounds (-NO$_2$)

(i) Azo-Dye Test- Take 0.5 g/ 1mL of given organic compound in a boiling test tube, add 3 mL conc. HCl, 2 mL water and 1 g of solid stannous chloride (or tin granules). Heat the contents on water bath for few minutes. Filter and cool the filtrate. Now add 2.5% aq. $NaNO_2$ solution drop by drop to the filtrate to complete the diazotization. Cool again and add 1-2 mL of alkaline β-naphthol solution. An orange –red or red dye shows the presence of nitro group (The dye is formed due to liberation of primary amino group by reduction of nitro group) .

$$\mathbf{C_6H_5NO_2} \xrightarrow{\text{Sn, HCl}} \mathbf{C_6H_5NH_2}$$

(ii)Tollen's Reagent Test-

Take 0.5 g of given organic compound in a test tube and add 10 mL C_2H_5OH in to it. Shake the tube thoroughly and now add 0.5 g NH_4Cl and 0.5 g zinc dust with shaking. Heat the content on a water bath for 5 minutes. Cool the mixture, filter and add 1 mL ammonical silver nitrate solution (Tollen's reagent). Formation of silver mirror indicates the presence of nitro group.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{\text{Zn, }NH_4Cl} \underset{\text{Phenyl hydroxylamine}}{C_6H_5NHOH} + H_2O$$

$$C_6H_5NHOH + 2[Ag(NH_3)_2]\,OH \longrightarrow C_6H_5NO + \underset{\text{(Silver mirror)}}{2Ag} + 4NH_3 + 2H_2O$$

(ii) Ferrous Hydroxide Test-

Take 0.2 g of given organic compound in a test tube and add 2 mL of 5% Ferrous ammonium sulphate. Shake test tube content thoroughly. Now add 1 mL of 6N H_2SO_4 followed by 2 mL of 2N KOH solution prepared in CH_3OH. Formation of red brown precipitate indicates the presence of nitro group.

$$R\text{-}NO_2 + \underset{\text{Blue green}}{6Fe(OH)_2} + 4H_2O \longrightarrow \underset{\text{Red brown precipitate}}{6Fe(OH)_3} + R\text{-}NH_2$$

4.3.6.3 When nitrogen and sulphur are present

Thiourea (-NHCSNH-)

(i) Take 0.5 g of given organic compound in a test tube and add 1mL dil. NaOH in to it and shake the flask thoroughly. Smell of ammonia confirms the presence of thiourea.

(ii) Take 0.5 g of given organic compound in a test tube and add 1 mL dil. NaOH solution, cool and add lead acetate $[Pb(CH_3COO)_2]$. A brown or black colour of precipitate indicates the presence of thiourea.

4.3.6.4 When halogen is present

(A) Aliphatic halogen compounds (RX)-

Take 0.5 g of given organic compound in a test tube and add 5 mL of alcoholic NaOH solution in to it and boil the tube content for about 10 minutes. Cool and dilute the solution with water, add excess of dil. HNO_3 and then $AgNO_3$ solution. A precipitate of silver halide is obtained.

(B) Aromatic halogen compounds (ArX)-

When any one of the halogen atom like chlorine, bromine, iodine is present in aromatic ring then test depends on the type of the additional functional group.

4.3.7 Determination of melting point of the compound

A thin capillary of about 5 cm in length with uniform bore is sealed at one end by bringing it near to the flame. The pure, dry and fine powdered compound approximately 2 mg under identification is filled through open end of the capillary tube by gentle tapping the closed end. Melting point of unknown compound is determined by placing the capillary tube along with thermometer either in Kjeldahl's flask or digital melting point apparatus.

4.3.8 Confirmatory test for the suspected organic compound and preparation of suitable derivatives

4.3.8.1 Carboxylic acid (R-COOH)

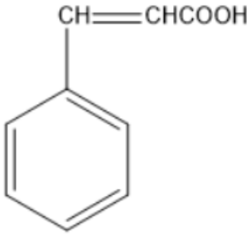
(a) Oxalic acid $(COOH)_2.2H_2O$ [m.p. 101^oC]

1. Oxalic acid is crystalline in nature and colorless in appearance with solubility in cold water.
2. Take aqueous solution of oxalic acid (2 mL) in a test tube and neutralize it with dilute NH_4OH solution. Now add aqueous $CaCl_2$ solution to the tube content; white precipitate, insoluble in acetic acid but soluble in dilute HCl is obtained. On adding $CaCl_2$ solution, white precipitate of calcium oxalate (CaC_2O_4) is formed.

3. Take aqueous solution of the compound and heat it with acidic potassium permanganate solution. Purple colour of the solution is discharged.

Anilide derivative: M.P. 245°C

(b) Cinnamic acid [M.P. 133°C]

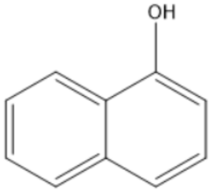


1. Cinnamic acid is crystalline in nature with pale yellow in colour and soluble in hot water.
2. Take a pinch of compound and add it to a solution of potassium permanganate, the pink colour is discharged and a brown precipitate with bitter almond smell of benzaldehyde is produced.
3. Add concentrated H_2SO_4 to the compound, heat gently; a green colouration changing to brownish red is produced.
4. Take 0.2 g of cinnamic acid and dissolve it in 5 mL Na_2CO_3 solution. Add bromine water drop by drop and note the separation of bromostyrene $C_6H_5CH{=}CHBr$ as colourless oil, having pleasant odour.

   Amide derivative: M.P. 142°C

4.3.8.2 Phenols (Ar—OH)

α-Naphthol [M.P. 94°C]



1. α-Naphthol is dark violet coloured crystal
2. It is insoluble in water.
3. It does not give colour with neutral aqueous ferric chloride but gives white precipitate.

4. Shake a small amount of the compound with a mixture having equal volume of iodine and potassium iodide (KI) and add excess of NaOH; violet colour appears which rapidly darkens followed by a precipitate formation.
5. Take 0.2 g of compound in a test tube and 2 mL NaOH solution, a drop of CCl_4 and a pinch of copper powder and warm the contents. Blue colour is formed.
6. It gives green colour with titanic acid and concentrated H_2SO_4.

2,4 Dibromo-derivative: M.P. 105^0C

Benzoate derivative: M.P. 56°C

4.3.8.3 Carbohydrates

α- Glucose [$CHO(CHOH)_4CH_2OH$] [M.P. 146°C]

1. Glucose is colourless and powered form soluble in cold water.
2. It reduces Fehling's solution, Tollen's reagent and Barfoed's reagent.
3. Take 2 mL of aqueous solution of compound in a test tube and add 1 g lead acetate $(CH_3COO)_2Pb$, boil and add 5 mL dilute ammonia solution. Continue boiling for 5 minutes. A rose pink colour confirms the presence of glucose.
4. Take 2 g compound in test tube and add 5 mL dilute NaOH solution, boil the content. The mixture turns yellow then brown and produces the colour of caramel.

Osazone derivative: M.P. 205°C

Acetate derivative: M.P. 110-111°C

4.3.8.4 Ketones ($>$CO)

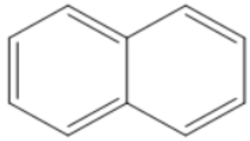
Benzophenone [$C_6H_5COC_6H_5$] [M.P. 48°C]

1. It is colourless crystalline solid with pleasant smell, insoluble in water.
2. Dissolve 2 g of compound in concentrated H_2SO_4, a yellow solution is obtained.
3. Fusion of the compound with sodium (Na) produces deep blue colour.
4. Take 0.2 g of compound in a test tube, add 1 g naphthalene and heat the content until completely molten. Add a small piece of sodium metal and heat again. The surface of the sodium metal becomes green.
5. It does not give iodoform test.

Derivative: 2,4-Dinitrophenylhydrazone: M.P. 238°C

4.3.8.5Hydrocarbons

Napthalene [M.P. 80°C]



1. It is colourless crystalline solid with characteristic odour like naphthalene balls and insoluble in water.
2. Take 2 g of the compound and dissolve in 5 mL chloroform ($CHCl_3$) and add anhydrous aluminium chloride ($AlCl_3$). A green colour appears.

Derivative: Picrate, M.P. 70°C

4.3.8.6 Amides ($RCONH_2$)

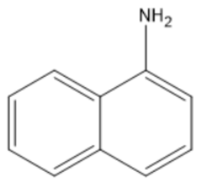
Urea [NH_2CONH_2][M.P 132°C]

1. It is white crystalline solid, soluble in water.
2. Take 2 gm of compound and dissolve in 5 mL dilute HCl, cool and add few drops of sodium nitrite ($NaNO_2$) solution to it. N_2 gas is evolved with effervescence.
3. Mix concentrated solution of oxalic acid and urea, white crystals of urea oxalate is formed.
4. Biuret test: Take 2 g of compound in a dry test tube and heat the content. The solid melts and NH_3 is evolved. Cool the tube when a white residue (biuret) is left in it. Dissolve it in 2 mL water, add a drop of copper sulphate ($CuSO_4$) solution and 2 mL sodium hydroxide (NaOH) solution when violet colour is produced.

$$\underset{\text{Urea}}{2NH_2CONH_2} \xrightarrow{\text{Heat}} \underset{\text{Biuret}}{NH_2CONHCONH_2} + NH_3$$

4.3.8.7 Primary amines

α-Naphthylamine [M.P. 50°C]

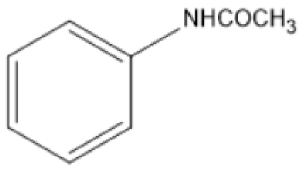


1. It is solid, colourless when freshly crystallized but turns brown on exposure in air.
2. Slightly soluble in hot water.
3. Dissolve 0.5 g of the compound in dil. HCl and add few drops of $FeCl_3$ solution. A blue precipitate is obtained.
4. It gives carbylamine reaction and dye test positive.

Derivative: Picrate M.P 161°C

4.3.8.8 Anilides (-NHCOR)

Acetanilide [M.P. 114°C]



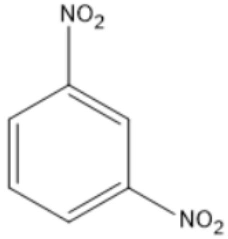
1. Colourless thin plate like crystals.
2. Acetanilide is sparingly soluble in cold water but has the greater solubility in hot water.
3. **Tafel's Test-** Take 0.5 g of compound in a test tube and add 0.3 g of $K_2Cr_2O_7$ crystals and 3 mL of concentrated H_2SO_4. Heat the content. Red or violet colour changing to green shows the presence of anilide which do not contain substituent in the benzene nucleus.
4. Gives carbylamine reaction test.

Derivative: ***p*-Bromoacetanilide, M.P.167°C**

***p*-Nitroacetanilide, M.P. 210°C**

4.3.8.9 Nitro Compounds (-NO_2)

m-Dinitrobenzene [M.P. 90°C]



1. It is Yellow crystalline solid.
2. It gives red-brown colour on boiling with NaOH.
3. Take 0.5 g of compound in test tube and add 2 mL acetone into it. Now add a drop of NaOH solution to it. A violet blue colour is produced which changes to violet red on adding acetic acid.
4. Dissolve 0.5g of compound in dilute NaOH and boil. To this, add a very small amount of glucose (or tin chloride). Violet colour is produced.

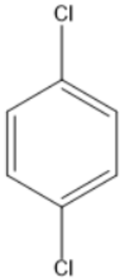
Derivative: m-phenylene diamine, M.P. 63°C

4.3.8.10 Thioureas (H_2NCSNH_2)[M.P. 180°C]

1. White crystalline solid soluble in hot water.
2. Take 0.5 g of compound in test tube and add 2 mL dilute NaOH solution. Boil the content, ammonia gas is evolved.
3. Take 0.2 g of compound in a dry test tube, cool and add few drops of $FeCl_3$ solution. A blood red colour is produced due to formation of ferric thiocyanate.
4. Take 0.2 g of compound in test tube and dissolve it by adding 2 mL dilute CH_3COOH, heat the content. Now add 2 mL potassium ferrocyanide solution to hot solution. A green colour changing to blue appears.
5. Add lead acetate solution to the compound dissolved in NaOH solution, black precipitate appears.

4.3.8.11 Aromatic Halogen Compound (Ar-X)

p-Dichlorobenzene [M.P.53°C]



Take 1 g of acid in boiling test tube and add 1 mL phosphorus pentachloride in it and shake the content till the vigorous reaction ceases. Warm the reaction gently and cool it. Now add 2 mL aniline and shake the reaction mixture vigorously. If necessary, warm and then cool. Filter off the anilide, wash it with cold water and crystallize from ethanol and dry it.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Aniline}}{H_2NC_6H_5} \longrightarrow \underset{\text{Anilinde}}{RCONHC_6H_5} + H_2O$$

1. It is white crystalline solid with characteristic smell.
2. It does not give white precipitate with $AgNO_3$ solution.
3. It can be readily nitrated.

Derivative: 2,5-Dichloronitrobenzene, M.P. 54°C

4.4 PREPARATION OF SOME IMPORTANT DERIVATIVES

4.4.1 Anilide derivative of carboxylic acids

Take 1 g of acid in boiling test tube and add 1 ml phosphorus pentachloride in it and shake the content till the vigorous reaction ceases. Warm the reaction gently and cool it. Now add 2 ml aniline and shake the reaction mixture vigorously. If necessary, warm and then cool. Filter off the anilide, wash it with cold water and crystallize from ethanol and dry it.

4.4.2 Amide derivative of carboxylic acids

Take 1 g of compound in 100 mL conical flask and add 3 mL of phosphorous pentachloride. Shake the content till the vigorous reaction ceases. Warm the reaction content gently for 25-30 minutes and cool it. Now add 10 mL concentrated ammonia solution carefully, stir with glass rod, cool and filter the produced acid amide. Wash the formed product with cold water, crystallize from water and dry it.

$$\mathrm{RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl}$$

Acid Acid Chloride

$$\mathrm{RCOCl + NH_4OH \rightarrow RCONH_2 + HCl + H_2O}$$

Amide

4.4.3 Benzoate derivative of phenols

Take 100 mL conical flask, dissolve 1 g α-naphthol in 5 mL acetone and add 2.5 mL benzoyl chloride to it. Add 10 mL aqueous NaOH gradually with cooling and shaking then further add 40 mL NaOH solution. Stopper the flask and shake vigorously till the odour of benzoyl chloride has disappeared. The final solution should be alkaline to the litmus paper. Filter the product, wash first with dilute HCl, then with cold water and re-crystallize from ethanol or acetone.

Alpha naphthol Alpha naphthyl benzoate

4.4.4 Osazone derivative of carbohydrates

Take 1 g of powdered sugar in a clean and dry test tube. In another test tube, dissolve 1 g phenylhydrazine hydrochloride and 1.2 g crystalline sodium acetate in 5 mL cold water and add this solution to tube which contains sugar. Loosely cork the test tube, immersed it in a boiling water bath with periodical shaking, and note the exact time required for the first appearance of a turbidity or precipitate of osazone. Cool the solution, filter the precipitate and re-crystallize from ethanol.

4.4.5 Picrate derivative of naphthalene

Make a concentrated solution of picric acid in acetone. Now take 2 mL of picric acid solution in a test tube and add 2 mL concentrated solution of naphthalene (concentrated solution of naphthalene is prepared in acetone). Shake the content thoroughly, warm and allow to stand for at least 30 minutes. A yellow precipitate of picrate is formed. Wash with water and dry it.

$$\underset{\text{Naphtalene}}{C_{10}H_8} + \underset{\text{Picric acid}}{C_6H_2(NO_2)_3OH} \rightarrow \underset{\text{Naphthalene picrate}}{C_{10}H_8C_6H_2(NO_2)_3OH}$$

4.5 SEPARATION AND SYSTEMATIC IDENTIFICATION OF COMPOUNDS PRESENT IN AN ORGANIC MIXTURE

The following steps should be followed by the students for separation and identification of organic mixture

1. **Objective:** To separate and identify the organic compounds in the given organic mixture.
2. **Separation of organic compounds from a mixture (A&B):** The mixture can be separated by water, $NaHCO_3$ or NaOH

Compound A

(i) Preliminary examinations

(ii) Solubility test
(iii)Ignition test
(iv)Test for unsaturation
(v) Element detection
(vi)Test for functional group
(vii) Melting point determination
(viii) Confirmatory test
(ix)Preparation of derivatives of organic compounds
(x) Structure of compounds

Compound B

(i) Preliminary examinations
(ii) Solubility test
(iii)Ignition test
(iv)Test for unsaturation
(v) Element detection
(vi)Test for functional group
(vii) Melting point determination
(viii) Confirmatory test
(ix)Preparation of derivatives of organic compounds
(x) Structure of compounds

3. Result: The given organic mixture is containing the following compounds:

A: …………………..; B: ………………….

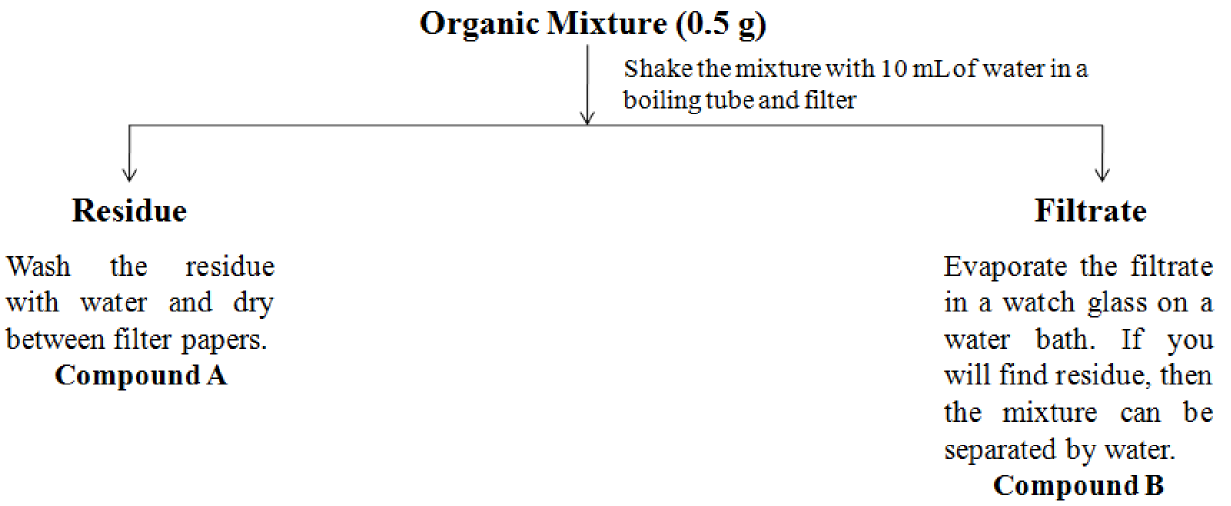
Methods of separation of organic mixture

Organic mixture can be separated by chemical and physical methods. Distillation, electrophoresis, counter current separation and chromatography are some common physical methods of separation of organic mixture. Chemical methods of separation may depend upon the chemical properties (polarity, solubility, acid or basic property) of the constituents of a mixture. Separation also depends upon the type of mixture (solid-solid, solid-liquid, liquid-liquid). Separation of a solid-solid mixture can be done on the basis of solubility and salt formation. On the basis of solubility, the solid-solid mixture can be separated by water separation method while on the basis of salt formation, $NaHCO_3$ or NaOH separation can be done for a solid-solid mixture.

4.5.1 Separation of solid-solid mixture on the basis of solubility

4.5.1.1 Water separation

The method is used when one of the components is soluble in water and other is not. The separation by water can be done by following the Scheme 4.1.



Shake the mixture with 10 mL of water in a boiling tube and filter

Wash the residue with water and dry between filter papers.

Evaporate the filtrate in a watch glass on a water bath. If you will find residue, then the mixture can be separated by water.

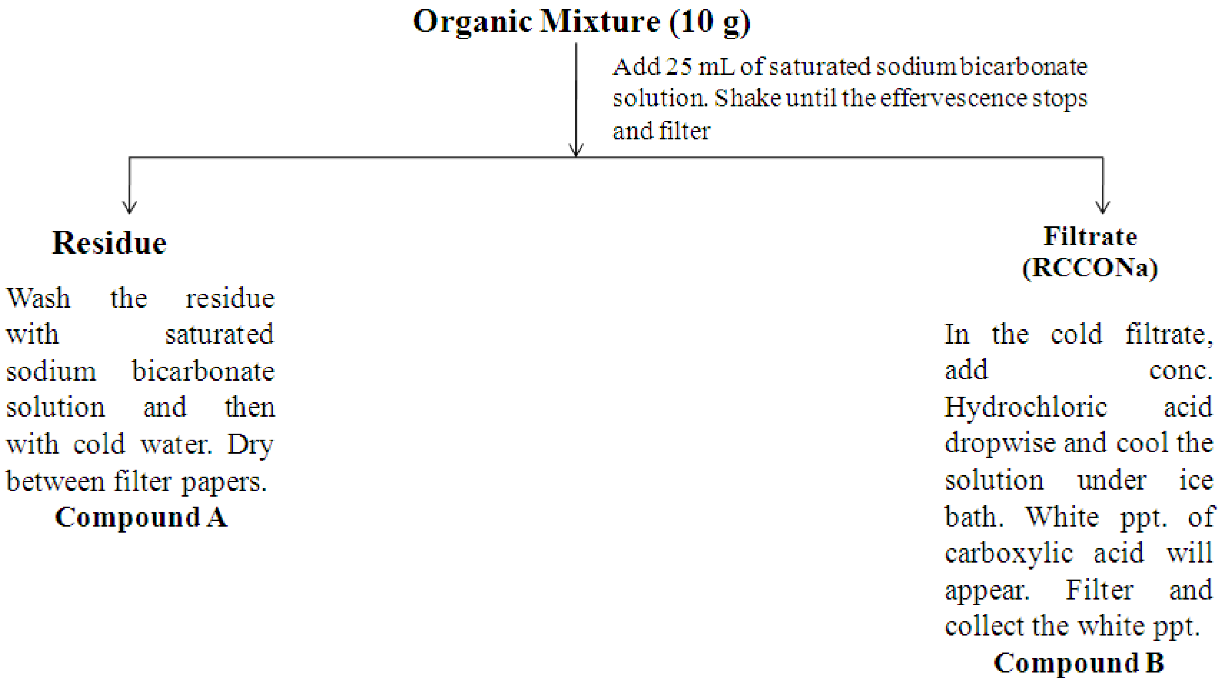
Scheme 4.1: Water separation of an organic binary mixture

4.5.2 Separation of solid-solid mixture on the basis of salt formation

Separation of organic mixture based on salt formation is used when one of the components is acidic or basic in nature or when both the components are insoluble in water.

4.5.2.1 NaHCO$_3$ separation

NaHCO$_3$ separation is used when one component is acidic and other component is either basic or neutral or phenolic (Scheme 2).



Organic Mixture (10 g)

Add 25 mL of saturated sodium bicarbonate solution. Shake until the effervescence stops and filter

Residue

Wash the residue with saturated sodium bicarbonate solution and then with cold water. Dry between filter papers.

Compound A

Filtrate (RCCONa)

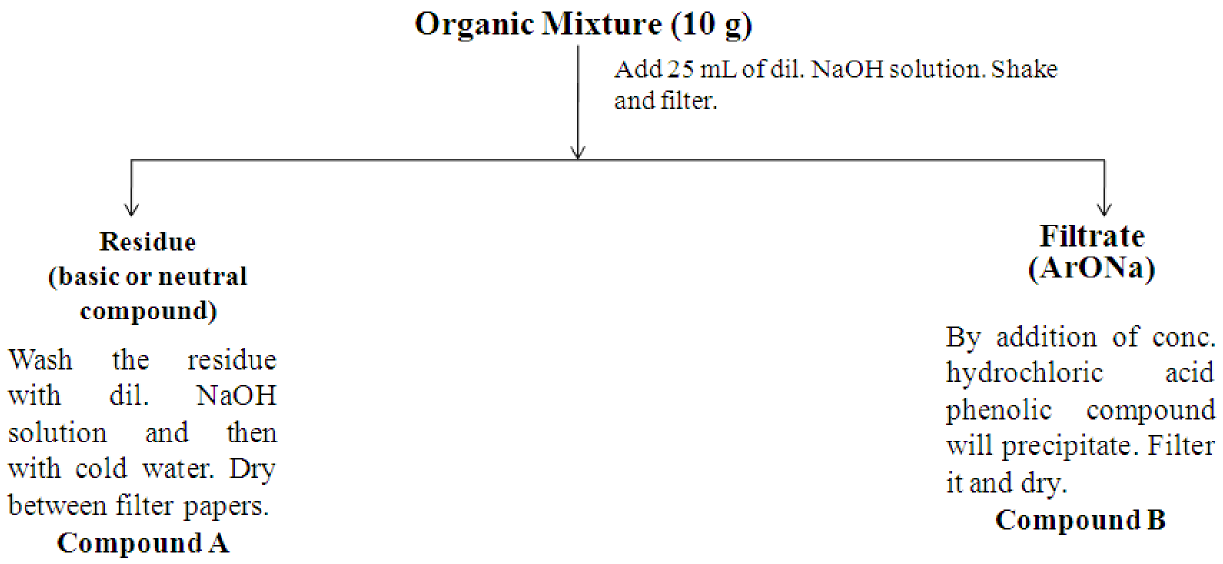
In the cold filtrate, add conc. Hydrochloric acid dropwise and cool the solution under ice bath. White ppt. of carboxylic acid will appear. Filter and collect the white ppt.

Compound B

Scheme 4.2: NaHCO$_3$ separation

4.5.2.2 NaOH separation

NaOH separation is used when one of the components is phenolic and the other either basic or neutral but not acidic (Scheme 4.3).



Organic Mixture (10 g)

Add 25 mL of dil. NaOH solution. Shake and filter.

Residue (basic or neutral compound)

Wash the residue with dil. NaOH solution and then with cold water. Dry between filter papers.

Compound A

Filtrate (ArONa)

By addition of conc. hydrochloric acid phenolic compound will precipitate. Filter it and dry.

Compound B

Scheme 4.3 NaOH separation

4.6 TERMINAL QUESTIONS

Q 1. What are organic compounds?

Q 2. What is the difference between qualitative and quantitative analysis?

Q 3. Write the steps involved in the systematic identification of an organic compound.

Q 4. Give the name of special elements that may be present in organic compound.

Q 5. How can we test the aliphatic and aromatic nature of an organic compound?

Q 6. What are unsaturated compounds? How can unsaturation be detected in organic compounds?

Q 7. What is sodium extract? Why one has to prepare sodium extract during systematic identification of an organic compound?

Q 8. What do you understand by functional group? If nitrogen is present in an organic compound, what will be the possible functional groups?

Q 10. Differentiate between primary and secondary amine.

Q 11. Which kind of organic mixture can be separated by $NaHCO_3$ solution?

4.7 SUGGESTED READINGS

1. O.P. Pandey, D.N. Bajpai and S.Giri. (2010). Practical Chemistry, S. Chand Publisher, New Delhi.
2. S. Goyal. (2017). Text Book B.Sc Chemistry Practical-II, Krishna Publication, Meerut.

UNIT 5: SYNTHESIS OF ORGANIC COMPOUNDS

CONTENTS

5.1 INTRODUCTION

Organic synthesis is the process of construction of complex compounds from simpler ones (feed stock). It plays an important role in chemistry, biochemistry, medicine, agriculture and other fields. Modern medicine, the dye industry, aromas and cosmetics, vitamins and nutritional goods, polymers and plastics, energy fuels and high-tech materials are some of its direct benefits that shaped the world as we know it today. The simplest synthesis of a molecule is one in which the target molecule can be obtained by submitting a readily available starting material to a single reaction that converts it to the desired target molecule. However, in most cases the synthesis is not that straightforward, in order to convert a chosen starting material to the target molecule, numerous steps that add, change, or remove functional groups, and steps that build up the carbon atom framework of the target molecule may need to be done. This unit will enlighten the simplest one or two steps synthesis reactions involved, methodology and careful characterization of synthesized organic compound.

5.2 OBJECTIVES

By studying this unit, students will be able to understand:

1. How to produce compounds in small scale in laboratory that do not form naturally for research purpose
2. Theoretical knowledge of reactions involved for synthesis of a particular compound.
3. Detailed procedure, techniques, equipment, feed stock and time engagement for the synthesis of finished form of compound
4. Characterization of a particular compound by its specific physical properties and its melting point.
5. The idea about yield of synthesized compound compared with starting material and relative ratio of feed stock which can be further utilized for up-scaling of synthesis of compound.

5.3 ACETYLATION OF SALICYLIC ACID, ANILINE AND BENZOYLATION OF ANILINE AND PHENOL

5.3.1 Acetylation of salicylic acid

5.3.1.1 Objective

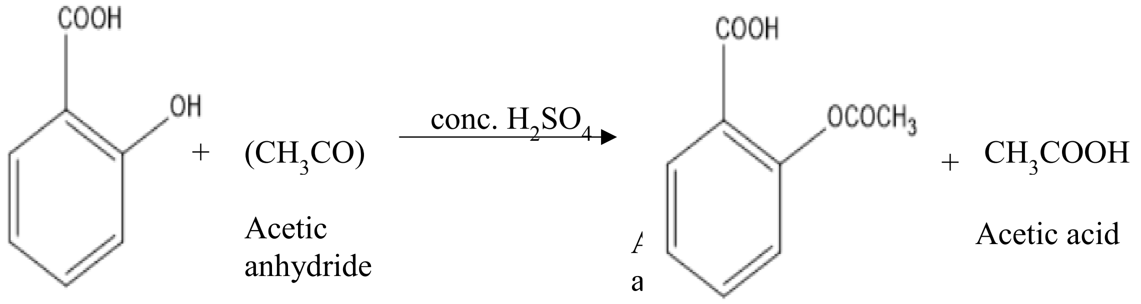
To prepare acetyl salicylic acid from salicylic acid and acetic anhydride

5.3.1.2 Requirements

Salicylic acid, acetic anhydride, conc. H_2SO_4, ethanol, hot water, ice cold water, conical flask (100mL.), water bath, glass rod, beaker, glass funnel, filter paper, etc.

5.3.1.3 Theory

Acetylation of salicylic acid with acetic anhydride in the presence of concentrated sulphuric acid (H_2SO_4) produces acetylsalicylic acid and a molecule of acetic acid. In this reaction, sulphuric acid acts as a catalyst which augments the process of detaching the acetate ion (CH_3COO^{-}) from acetic anhydride which thereby gets associated with H^+ ion from phenolic hydroxyl group in salicylic acid and a molecule of acetic acid is eliminated.



Acetyl salicylic acid is commonly known as aspirin and largely used in medicine as an analgesic (pain killer) and antipyretic (temperature lowering) agent.

5.3.1.4 Procedure

Take 5 g of salicylic acid and 9 g of acetic anhydride in a 100 mL conical flask. Add 3-5 drops of conc. H_2SO_4 and shake the flask thoroughly. Heat the flask on water bath for 10-15 minutes. Cool the flask at room temperature and then pour the reaction mixture with continuous stirring into a 200 mL beaker containing 50 mL ice water. Continuous stirring increases the process of rapid crystallisation. Collect the crude product on funnel with filter paper and wash it thoroughly with cold water and drain.

5.3.1.5 Recrystallization

Acetyl salicylic acid can be recrystallized using a mixture of equal volume of hot water and ethanol. Dissolve the obtained crude product in minimum amount of hot water (60^{o}C) and ethanol and then allow it to cool. Acetyl salicylic acid is obtained as colourless needle within few hours.

5.3.1.6 Characterization

The crude and recrystallized acetyl salicylic acid can be characterized by determining the melting point. Melting point of pure salicylic acid is 132-137°C. Melting point closer to this range shows the formation of desired compound.

5.3.1.7 Result

Acetyl salicylic acid (Aspirin) was synthesized by acetylation of salicylic acid.
Appearance : Colourless crystal
Yield : ....g

Melting point before recrystallization ....°C
Melting point after recrystallization ....°C
Molecular formula: $C_9H_8O_4$

5.3.2 Acetylation of aniline

5.3.2.1 Objective

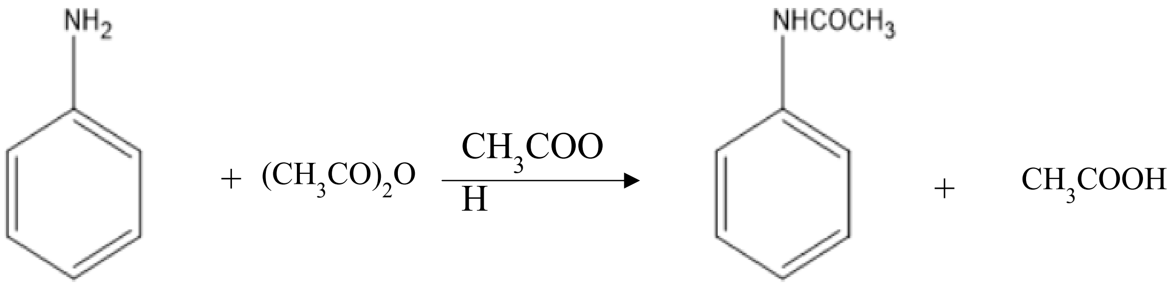
To prepare acetanilide from aniline and acetic anhydride

5.3.2.2 Requirements

Round bottom flask (100 mL), reflux condenser, aniline, glacial acetic acid, acetic anhydride, oil bath, glass rod, beaker (250 mL.), ice cold water, funnel, filter paper, boiling water, animal charcoal, cotton plug.

5.3.2.3 Theory

Acetylation of aniline involves the reaction between aniline and acetic ahydride in the presence of glacial acetic acid. In this reaction the hydrogen atom of NH_2 group in aniline is substituted by the acyl group (CH_3CO-) of acetic anhydride. The reaction is depicted as following:



Aniline Acetic anhydride Acetanilide Acetic acid

Acetanilide is medicinally important as it is used as febrifuge (antifebrin)

5.3.2.4 Procedure

Take 5 mL of aniline in a 100 mL round bottom flask fitted with a reflux condenser. Add 5 mL of acetic acid and 5 mL of acetic anhydride in to the flask containing aniline. Heat the mixture gently under reflux for 15-20 minutes on oil bath and then pour the contents while still hot with stirring into a 200 mL beaker containing 100 mL ice cold water. Stir the mixture vigorously to hydrolyse the excess acetic anhydride. After a time, acetanilide has precipitated, collect it on funnel with filter paper and wash with cold water.

5.3.2.5 Recrystallization

Acetanilide can be recrystallized with hot water. Dissolve the obtained crude product in minimum amount of hot water (60^{o}C). If the product is excessively coloured add a pinch of animal charcoal to hot water and then filter hot water containing product through cotton plug and then allow it to cool. Filter the obtained pure colourless crystals of Acetanilide.

5.3.2.6 Characterization

The pure colourless crystals of acetanilide are confirmed by its melting point. Melting point of pure acetanilide is 114^{o}C. Melting point closer to this point shows the formation of desired compound.

5.3.2.7 Result

Acetylation of aniline provides acetanilide
Appearance-: Colourless crystal
Yield: ....g
Melting point before recrystallization: ....^{o}C

Melting point after recrystallization: ....°C

Molecular formula: C_8H_9NO

5.3.3 Benzoylation of aniline

5.3.3.1 Objective

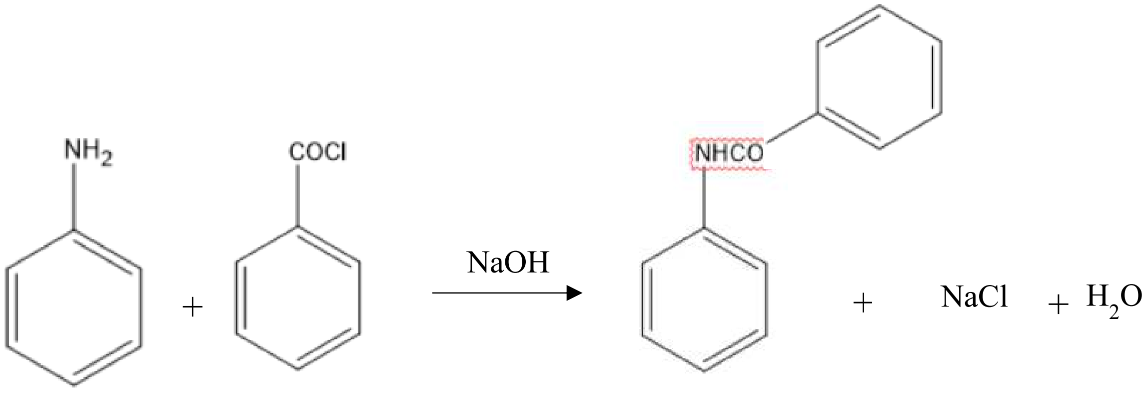
To prepare benzanilide from aniline.

5.3.3.2 Requirements

Aniline, 10%Na OH, benzoyl chloride, cold water, hot alcohol, conical flask, funnel, measuring cylinder, filter paper.

5.3.3.3 Theory

Benzoylation of aniline involves the insertion of benzoyl (C_6H_5CO) moiety in the presence of NaOH to the primary amino group of aniline. In this reaction, benzanilide is produced. NaOH neutralizes the liberated HCl and also catalyse the reaction. The reaction is as follows:



Aniline Benzoyl Chloride Benzanilide

Benzanilidesis used as fungicide and acaricide (pesticide that kills ticks and mites).

5.3.3.4 Procedure

Take 2 mL of aniline and 30 mL of 10% NaOH solution in a 250 mL conical flask, then add 3 mL of benzoyl chloride slowly with vigorous shaking. Cork the flask and shake for further 15-20 minutes or till the odour of benzoyl chloride can no longer be detected. Add 50 mL cold water and mix well. Collect the crude benzanilide on funnel with filter paper. Wash it again with cold water.

5.3.3.5 Recrystalization

Benzanilide can be recrystallized from hot alcohol (55-60°C). Dissolve the obtained crude product in minimum amount of hot alcohol and then filter the pure crystals of benzanilide**.**

5.3.3.6 Characterization

The pure colourless crystals of benzanilide are determined by its melting point. Melting point of pure benzanilide is 163^{o}C. Melting point closer to this point shows the formation of desired compound.

5.3.3.7 Result

Benzoylation of aniline provides benzanilide
Appearance: Colourless crystal
Yield: ....g
Melting point before recrystallization: ....°C
Melting point after recrystallization:...............................°C
Molecular formula: $C_{13}H_{11}NO$

5.3.4 Benzoylation of phenol

5.3.4.1 Objective

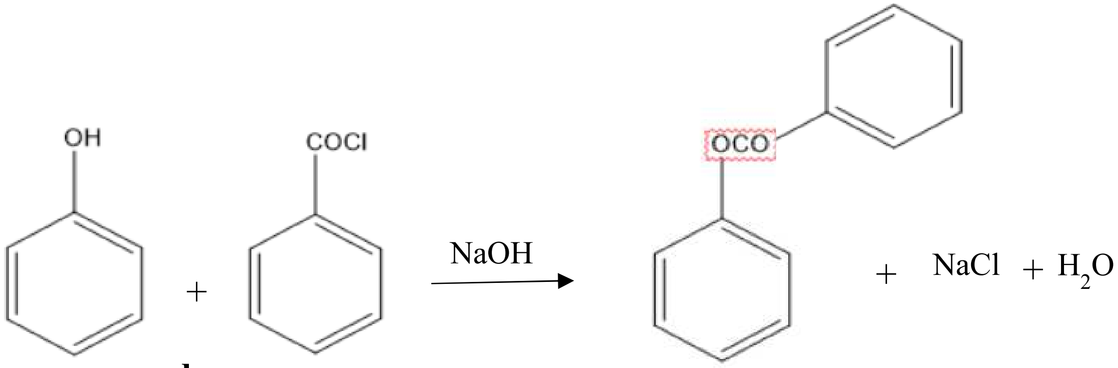
To prepare phenyl benzoate from phenol and benzoyl chloride.

5.3.4.2 Requirement

Phenol, benzoyl Chloride, NaOH, alcohol, 250 mL conical flask, beaker, volumetric flask, measuring cylinder, cold water, funnel, filter paper, melting point apparatus, thermometer.

5.3.4.3 Theory

Benzoylation of phenol involves the reaction of phenol with an aromatic acid chloride in the presence of excess of NaOH at room temperature to form an ester. The reaction is called Schotten Baumann reaction. If phenol is shaken with benzoyl chloride and excess amount of NaOH solution, it is benzoylated to give the ester, phenyl benzoate. In this reaction, phenol is first converted into the ionic compound sodium phenoxide (sodium phenate) by dissolving it in NaOH solution. The phenoxide ion reacts more rapidly with benzoyl chloride than the original phenol does, but even so you have to shake it with benzoyl chloride for about 15 minutes. Solid phenyl benzoate is formed.



5.3.4.4 Procedure

Take 2.5 gram phenol and dissolve it in 35 mL 10% NaOH in 100 mL beaker. Now add this phenol solution in to a 100 mL conical flask and then add 5 mL benzoyl chloride to it. Cork the flask properly and shake the mixture vigorously for 20 minutes or until the pungent smell of benzoyl chloride has disappeared. Filter off the formed crude product on funnel using filter paper. Wash it with cold water 2-3 times.

5.3.4.5 Recrystallization

Phenyl benzoate can be recrystallized from alcohol. Dissolved the obtained crude product in minimum amount of hot alcohol (55-60oC) and then filter the pure crystals of benzoyl chloride.

5.3.4.6 Characterization

The pure colourless needles of benzoyl chloride are determined by its melting point. Melting point of pure benzoyl chloride is 68-69^{o}C. Melting point closer to this point shows the formation of desired compound.

5.3.4.7 Result

Benzoylation of phenol provides phenyl benzoate.
Appearance: Colourless needle like crystals
Yield: ....g
Melting point before recrystallization: °C
Melting point after recrystallization: ....°C
Molecular formula: $C_{13}H_{10}O_2$

5.4 PREPARATION OF IDOFORM

5.4.1 Preparation of Iodoform from acetone

5.4.1.1 Objective

To prepare Iodoform from acetone in the presence of sodium hydroxide

5.4.1.2 Chemicals and equipment required

Ethanol, sodium hydroxide, iodine, distilled water, cold water, round bottom flask, funnel, filter paper, melting point apparatus, thermometer.

5.4.1 3 Theory

Iodoform is prepared when any α-H containing methyl group (ketone, secondary alcohol or acetaldehyde) reacts with iodine in the presence of base (NaOH, KOH, Na_2CO_3). When iodine reacts with acetone in the presence of NaOH, a pale yellow precipitate of triiodomethane (iodoform) is produced. The reactions involved in the process are as follows:

$$CH_3COCH_3 + 3NaClO + 3KI \quad \rightarrow \quad CH_3COONa + 2NaOH + 3KCl + CHI_3$$

5.4.1.4 Procedure

Take 2 mL acetone and 30 mL of 10% NaOH in a 250 mL conical flask. Add 70 mL of 2N-sodium hypochlorite solution (freshly prepared) in to the reaction mixture and shake it vigorously. Allow it to stand at room temperature for 2-3 minutes. Filter the yellow precipitate of iodoform using funnel. Wash it with water twice and crude iodoform is obtained.

5.4.1.5 Recrystalization

Pure iodoform can be recrystallize from alcohol. Take the crude material in a 150 mL round bottom flask fitted with a reflux water condenser. Add a small quantity of alcohol and heat to boiling on a water bath and then add more alcohol until all the iodoform is dissolved. Filter the solution through a filter paper directly into a 100 mL beaker and then cool in ice water. The iodoform rapidly crystallizes. Filter and dry it.

5.4.1.6 Characterization

The pure crystals of iodoform are determined by its melting point. Melting point of iodoform is 119-120^{o}C. Melting point closer to this point shows the formation of iodoform.

5.4.1.7 Result

Iodination of acetone gives Iodoform
Appearance: Yellow crystals
Yield:.................................g
Melting point before recrystallization:............................°C
Melting point after recrystallization:.................................°C
Molecular formula: CHI_3

5.4.2 Preparation of idoform from ethanol

5.4.2.1 Objective

To prepare Iodoform from ethanol and iodine.

5.4.2.2 Chemicals and equipment required

Ethanol, sodium carbonate, iodine, distilled water, cold water, round bottom flask, funnel, filter paper, melting point apparatus, thermometer.

5.4.2.3 Theory

Iodoform an analogous to chloroform, is also known as triiodomethane and belongs to the family of organic halogen compounds. Ethanol is the only primary alcohol to give the triiodomenthane reaction. Many ketones give this reaction but those that do all have a methyl group on one side of the carbon-oxygen double bond. These are also known as methyl ketones. Compounds that are easily oxidized to acetaldehyde and secondary alcohols that have the general formula CH_3CHOHR can be oxidized to methyl ketones. Methanol does not give iodoform.

When ethanol reacts with iodine in the presence of base, it first oxidised to ethanal and then gives iodoform. Reactions involved in the process are given below:

$$CH_3CH_2OH + 4I_2 + 3Na_2CO_3 \rightarrow CHI_3 + 5NaI + HCOONa + 3CO_2 + 2H_2O$$

Iodoform has antiseptic and disinfectant properties.

5.4.2.4 Procedure

Take 500 mL round bottom flask and add 20 mL water, 20 mL ethanol and 40 gm sodium carbonate into it. Heat the flask to about 70-80^oC on a water bath. To the warm solution, add small amount of iodine at a time with constant shaking. Add more iodine so that the reaction product should have a pale yellow colour. Allow the reaction mixture to stand for 5 minutes. Filter the crude Iodoform and wash it with cold water 2-3 times.

5.4.2.5 Recrystalization

Pure iodoform can be recrystallized from alcohol. Take the crude material in a 100 mL round bottom flask. Add a small quantity of alcohol and heat to boiling on a water bath and then add more alcohol until all the iodoform is dissolved. Once the crude iodoform completely dissolves, allow it to cool in ice cold water. The iodoform rapidly crystallises. Filter the solution through a filter paper directly into a 100 mL beaker. Wash it with cold water and allow to dry.

5.4.2.6 Characterization

The pure crystals of iodoform are determined by its melting point. Melting point of iodoform is 119-120^{o}C. Melting point closer to this point shows the formation of iodoform.

5.4.2.7 Result

Iodination of ethanol gives Iodoform.
Appearance: Yellow crystals
Yield:............................g
Melting point before recrystallization:..................................^{o}C
Melting point after recrystallization: ....^{o}C
Molecular formula: CHI_3

5.5 PREPARATION OF BENZOIC ACID

5.5.1 Preparation of benzoic acid from toluene

5.5.1.1 Objective

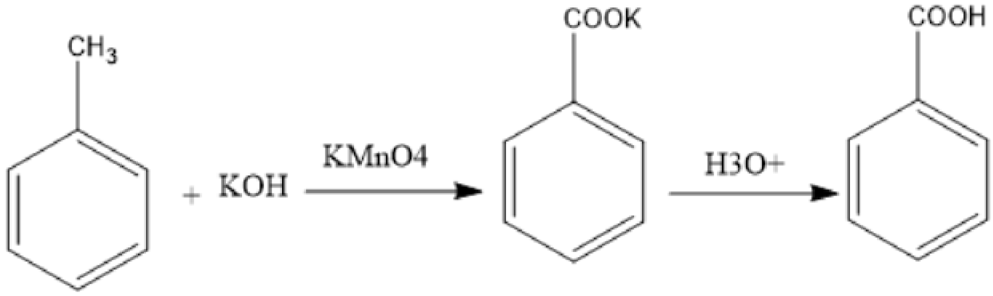
To prepare benzoic acid by oxidation of toluene.

5.5.1.2 Chemicals and equipment required

Toluene, potassium permanganate, potassium hydroxide (1M), distilled water, Sulphuric acid (1M).

5.5.1.3 Theory

Benzoic acid is the simplest aromatic carboxylic acid. It is prepared by oxidation of alkyl benzene *i.e* toluene with acidic potassium permanganate ($KMnO_4$) in the presence of potassium hydroxide. Reaction involved in the process is shown as follows:



Toluene Potassium benzoate Benzoic acid

Benzoic acid occurs naturally in many plants. It serves as an intermediate in the biosynthesis of many secondary metabolites. Salts of benzoic acid are used as food preservatives and benzoic acid is an important precursor for the industrial synthesis of many other organic substances.

5.5.1.4 Procedure

Take 10 g $KMnO_4$ in round bottom flask fitted with a reflux condenser and then add 130 mL distilled water. Mix it thoroughly. Now add 20 mL 1M KOH add 10 mL toluene slowly in to the reaction mixture. Finally reflux condenser should be attached to the flask and system is heated and refluxed on oil bath. Allow the reaction mixture to reflux for 3-4 hours until oily toluene disappears. Notice as the reaction proceeds, black coloured MnO_2 particles attached on the wall of flask. Once the reaction is finished, it is allowed to cool down to room temperature. Filter it on funnel and wash with hot (70°C) distilled water 2-3 times. The filtrate contains potassium benzoate. Add small amount of conc. sulphuric acid and mix it thoroughly. Check pH of the reaction mixture with pH paper, which should be in acidic range. Filter and dry crude benzoic acid.

5.5.1.5 Recrystallization

Benzoic acid is recrystallized with hot water. Take crude benzoic acid in a beaker and add hot water in to it. Mix thoroughly and allow to cool at 4^oC. After 8-10 minutes, colourless needle shaped crystals obtained. Filter the solution through funnel and dry it.

5.5.1.6 Characterization

The pure crystals of benzoic acid can be characterized by its melting point. Melting point of benoic acid is 122^oC. Melting point closer to this point shows the formation of benzoic acid.

5.5.1.7 Result

Oxidation of benzoic acid with $KMnO_4$ gives benzoic acid.
Appearance: Colourless crystals
Yield: ....g
Melting point before recrystallization: ....°C
Melting point after recrystallization: ....°C
Molecular formula: $C_7H_6O_2$

5.6 PREPARATION OF ANILINE

5.6.1 Preparation aniline from nitrobenzene

5.6.1.1 Objective

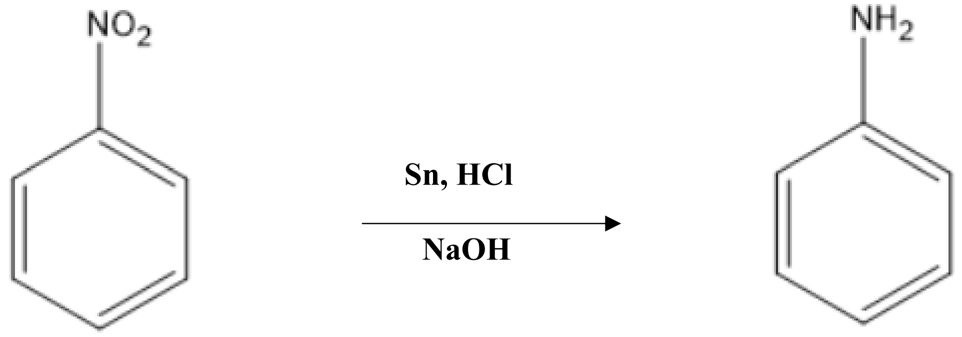
To prepare aniline from nitrobenzene by reduction

5.6.1.2 Chemicals and equipment required

Sn powder, nitrobenzene, HCl, NaOH, KOH, NaCl, dichloromethane (DCM), round bottom flask, hot plate, magnetic stirrer, separating funnel, conical flask

5.6.1.3 Theory

Aniline is an organic compound with the molecular formula $C_6H_5NH_2$ consisting of a phenyl group attached to an amino group. Aniline is the prototypical aromatic amine. It is used in the manufacture of precursors to polyurethane and other industrial chemicals. Reduction of nitrobenzene with Sn in presence of HCl and subsequently with NaOH yields Aniline. Reaction involved in the reaction is depicted in the following figure.



Nitro benzene Aniline

5.6.1.4 Procedure

Take 35 g of Sn powder in a round bottom flask. Pour 15 mL nitrobenzene in to the flask which contains Sn. Connect the flask to the condenser on hot plate and stir with magnetic stirrer. Add 15 mL of 32% HCl slowly into the flask. With time, color changes to dark brown. If reaction becomes vigorous, cool it down by cold water. Once the complete HCl is added, the reaction mixture is heated in water bath for 60 minutes. Now slowly add 60% NaOH to the reaction mixture in flask. If the reaction mixture becomes too hot, cool it on ice bath. In this process all the acid will be neutralized by NaOH and aniline will be formed. Mix the formed product thoroughly and cool it.

5.6.1.5 Distillation and separation of aniline

Set the above flask containing aniline for steam distillation. In distillation process, a yellow aniline water mixture will come out from the flask as a distillate. Collect initial 100 mL of clear distillate. Since aniline is soluble in water, add 20 gm NaCl to the 100 mL distillate and allow to mix it thoroughly and then transfer to a separating funnel. Allow to stand the separating flask with mixture for 5-10 minutes. A layer of aniline begins to form at the top. Collect the water layer and aniline layer from the separating funnel in a 100 mL beaker separately.

5.6.1.6 Extraction of aniline

Since aniline is soluble in water so the water layer may contain some amount of aniline. Therefore remaining aniline from water is extracted by using dichloromethane (DCM). Wash the aniline containing water sample with DCM. For this purpose, take 25 mL DCM and add to a beaker which contains aniline-water sample. Stir it with glass rod and transfer to a separating funnel. Shake it thoroughly and allow to stand for 5-10 minutes. Collect the water layer and aniline layer in separate beaker. Repeat this process three times with DCM (3X 25 mL DCM). Pool all the fractions of aniline and extracted solution is then dried using KOH. Store the solution with KOH for half an hour and then filter on a funnel with filter paper. The filtrate contains DCM which is removed by simple distillation process.

Set up a simple distillation assembly and discard everything collected below 120°C (boiling point of DCM is 40°C). Once the DCM has been removed, the collection flask is replaced with new 50 mL collection flask to facilitate the distillation. Collect the fraction between 180-184°C.

5.6.1.7 Characterization

The pure liquid aniline can be determined by its boiling point. Boiling point of aniline is 184°C. Boiling point closer to this point shows the formation of aniline.

5.6.1.8 Result

Reduction of nitrobenzene with Sn in acidic medium produces aniline.
Appearance: Yellow colored liquid with fishy odour.
Yield: ....mL
Boiling point before Extraction : ....°C
Boiling point after Extraction: ....°C
Molecular formula: $C_6H_6NO_2$

5.7 PREPARATION OF m-NITROANILINE

5.7.1 Preparation of m-nitroaniline from m-dinitrobenzene

5.7.1.1 Objective

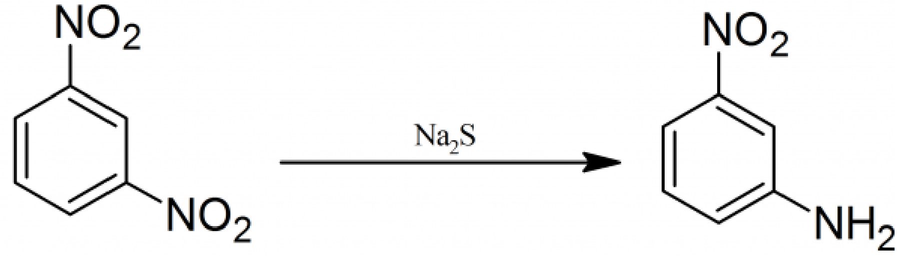
To prepare m-nitroaniline from m-dinitrobenzene through selective hydrogenation

5.7.1.2 Chemicals and equipment required

Conical flask, crystallised sodium sulphide, sodium bicarbonate, sodium sulphide, methanol, m-dinitrobenzene, 250 mL round bottom flask, reflux condenser, water.

5.7.1.3 Theory

Selective hydrogenation of one of the nitro group of m-dinitrobenzene with sodium sulphide in alkaline medium yields corresponding nitroaniline. In this reaction, first sodium sulphide gets converted into NaSH and then reacts with m-dinitrobenzene in alkaline medium. The reaction involved in the process is as follows:



5.7.1.4 Procedure

Take 50 mL water in a conical flask and dissolve 18 g crystallised sodium sulphide ($Na_2S.9H_2O$) in it. Add 6 g of finely powdered sodium bicarbonate ($NaHCO_3$) in sodium sulphide solution with constant stirring. When the sodium bicarbonate has dissolved completely, add 50 mL of methanol and cool it below 20°C. Filter the precipitated sodium carbonate on a funnel with filter paper. Wash the precipitate thrice with 8 mL methanol. Retain the filtrate and washings, these contain about 3.9 g of NaSH in solution and must be used for the selective reduction

Now dissolve 7 g of m-dinitrobenzene in 50 mL of hot methanol in a 250 mL round bottom flask and add with shaking, the previously prepared methanolic solution of sodium hydrogen sulphide. Attach the round bottom flask with a reflux condenser and boil the mixture for

20 min. Ignore any further sodium carbonate which may precipitate. Allow the reaction mixture to cool. Fit the condenser for distillation on a water bath and distil off most of the methanol (100-120 mL). Pour the liquid residue of round bottom flask into 200 mL of cold water with constant stirring. After 30-40 minutes, yellow crystals of m-nitroaniline appear. Filter the formed crystals on funnel with filter paper and wash with cold water.

5.7.1.5 Recrystalization

m-Nitroaniline is crystallized with methanol. Take crude m-nitroaniline in a beaker and add 75% aqueous methanol in to it. Mix thoroughly and allow to cool it to 4°C. After 15-20 minutes, bright yellow crystals obtained. Filter the solution through funnel and dry it.

5.7.1.6 Characterization

The pure crystals of m-nitro aniline can be characterized by its melting point. Melting point of m-nitroaniline is 114°C. Melting point closer to this point shows the formation of m-nitroaniline.

5.7.1.7 Result

Selective hydrogenation of m-dinitrobenzene yields nitroaniline
Appearance: Colourless crystals
Yield: …………………….g
Melting point before recrystallization: ……………………..°C
Melting point after recrystallization: ………………………..°C
Molecular formula: $C_6H_6N_2O_2$

5.8 TERMINAL QUESTIONS

Q1. Why synthesis of organic compound is important in laboratory?

Q2. Is this possible to synthesize 20 kg organic compound in laboratory?

Q3. What are the basic criteria to characterize a synthesized compound in laboratory?

Q4. What is the formula of acetic anhydride and acetyl salicylic acid?

Q5. What is the use of acetyl salicylic acid?

Q6. What is the role of separating funnel?

Q7. Is this possible to separate out two water miscible liquids by separating funnel?

Q8. What is the formula of iodoform?

Q9. What is the formula of m-nitroaniline?

Q10. What is the molecular formula of benzoic acid?

5.9 SUGGESTED READING

1. O.P.Pandey, D.N. Bajpai and S. Giri. (2010). Practical Chemistry, S. Chand Publisher, New Delhi.
2. S. Goyal. (2017). Text Book B.Sc Chemistry Practical-II, Krishna Publication, Meerut.
3. Arun Sethi. (2010). Systematic Lab Experiments in Organic Chemistry, New Age Publisher.

UNIT 6: MOLECULAR WEIGHT DETERMINATION

CONTENTS

6.1 INTRODUCTION

Molecular weight measurement is very important as it gives very useful information about the chemical compounds. The molecular weight is used to deduce possible molecular formulae. Mass spectrometry offers the most refined method for determination of the molecular weight of compounds which have vapour pressures higher than 0.1 mm Hg at 350°C. If the instruments of high resolving power are used then the molecular weight is obtained to an accuracy of 15 ppm.

In organic synthesis, the characterisation of an organic compound is done by approximate molecular weight determination. Methods for molecular weight determination of non-volatile substances include cryoscopic, ebullioscopic, osmotic pressure and lowering of vapour pressure method. In this unit, we will discuss and study Rast's camphor method, Beckmann's freezing point method and ebullioscopy for determination of molecular weight of different solutes. Rast's camphor method is used to determine the molecular weights of camphor soluble solutes.

6.2 OBJECTIVES

After going through this unit, you will be able to answer the following questions:

- What is molecular weight?
- How can molecular weight of a chemical compound be determined?
- How melting point of a compound can be measured?

6.3 DETERMINATION OF MOLECULAR WEIGHT OF A NON-VOLATILE SOLUTE BY CRYOSCOPY

6.3.1 Rast method

6.3.1.1 Objective

To determine the molecular weight of a non-volatile solute by Rast method.

6.3.1.2 Theory

The method is useful for determination of molecular weight of solutes which are soluble in camphor. The advantage of this method is that molal depression constant of camphor is 40°C (very high) while depression in freezing point is large so that it can be determined by an ordinary thermometer.

6.3.1.3 Procedure

Take a small clean test tube (e.g. 75 x 10 mm) in a hole bored with a cork and place it on the pan of a balance. Take weight of the tube (Empty Tube). Now place about 50 mg of the compound in this test tube of which the molecular weight is to be determined and weigh the tube (Tube+compound) again. Now add 500-600 mg of pure, resublimed camphor (eg the micro-analytical reagent) in the tube and weigh again. Keep the Stopper loose and place the tube in an oil bath previously heated to about 180°C so that the camphor and compounds melt. Now stir the liquid with a platinum wire. Remember not to heat the liquid for more than 1 minute otherwise camphor will sublime from the solutions. Allow the solution to cool. You will get a solid mixture. Transfer this solid to a clean watch glass and crush it to make powder. Now place a small amount of the powder into a thin capillary tube whose one end is closed and is carefully rounded. Now press the solid down into the closed end with the help of a platinum wire. You may use another capillary tube of smaller diameter with closed end.

Remember that the level of the solid should not exceed 2 mm. Now determine the melting point of the mixture using a liquid melting point bath. Use 100-200°C thermometer graduated in 0.1 or 0.2°C, or an electrically- heated apparatus. Remember, good illumination and very careful control of the rate of heating is essential. The melting point is taken as that temperature at which the last fragment of solid disappears. Repeat the melting- point determination with a second sample; if the reading shows much variation then prepare a new mixture as the earlier prepared mixture was not homogeneous. Now determine the melting point of the original camphor. The difference in melting points gives the depression of the melting point of camphor caused by the addition of the compound.

6.3.1.4 Observations

Freezing point of camphor = $T_1°$
Freezing point of mixture of solute and cmphor = $T_2°$
Weight of camphor = W g
Weight of solute dissolved in camphor = w g

6.3.1.5 Calculations

The molecular weight M can then be calculated from the formula:

$$M = \frac{K \times w \times 1000}{\Delta T \times W}$$

Where K is the molecular depression constant of camphor (39.7), w is the weight of the solute dissolved in camphor, W is the weight of the camphor and ΔT (T_1-T_2) is the depression of the melting point.

6.3.1.6 Result

The molecular weight of the given substance is ....

Note: The solute concentration should be above 0.2 M: in dilute solution K increase from 39.7 to about 50.

The Rast camphor method is very simple, but it has some limitations also. One serious problem is the melting point of camphor which is very high Therefore, the possibility of decomposition of the compound whose molecular weight is to be determined is very high. As we know that the solubility of many classes of compound in liquid camphor is very low, so this difficulty restricts its general applicability. The Table 6.1 below contains few useful alternative solvents which have high molar freezing point depression constants:

Table 6.1: Solvents for molecular weight determination by depression of freezing points:

Compound	Melting Point (°C)	Molar depression constant
Cyclohexanol	24.7	42.5
Camphene	49.0	31.0
Cyclopentadecanone	65.6	21.3
Borylamine	164.0	40.6
Borneol	202.0	35.8

6.3.2 Beckmann's freezing point method

6.3.2.1 Objective

To determine the molecular weight of a non-volatile solute (urea, glucose etc.) by Beckmann's freezing point method.

6.3.2.2 Theory

The depression in freezing point of a liquid produced by dissolving a known weight of the solute in a known weight of the solvent is related to the molecular weight of the solute by following equation:

$$m = \frac{1000 \times k_f \times w \times M}{\Delta T \times W}$$

Where k_f = Molal depression constant

W = Weight of sample (solute)

m = Molecular weight of solute

M = Molecular weight of solvent

ΔT = depression in freezing point

6.3.2.3 Procedure

(i). Set the apparatus as shown in Fig. 6.1. Weigh accurately a 50 mL flask filled with distilled water. Transfer about 25 to 40 g of water sufficient to cover the bulb of the Beckmann's thermometer into a cleaned and dried freezing point tube and weigh the flask again. The difference of two readings gives the weight of water taken in the tube.

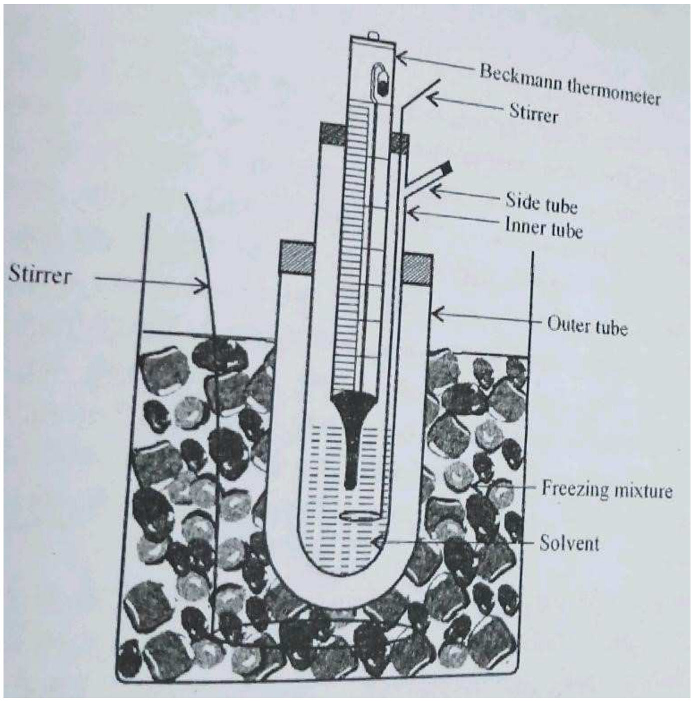


Fig. 6.1. Beckmann's apparatus

(ii). Weigh accurately 0.2-0.3g of the solute whose molecular weight is to be determined.

(iii). Prepare the freezing mixture by mixing crushed ice and common salt and fill in the beaker. Shake it from time to time by stirrer to maintain the temperature of the bath at about -4 to -5°C.

(iv). Now immerse the freezing tube carrying the Beckmann's thermometer and stirrer directly into the freezing mixture. Stir the water slowly. The temperatures fall rapidly and when solid being to separate, note the temperature. This is the freezing point of water. Remove the freezing point tube from the freezing bath and repeat the process two or three times till the concordant reading are obtained.

(v). Now remove the inner tube and melt the ice. Introduce into it the accurately weighed sample through the side tube stir well to dissolve the solute and determine the freezing point of the solution. As above till the concordant reading are obtained. It will be freezing point of the solution. The difference of these two reading gives depression in freezing point (ΔT).

6.3.2.4 Observation

Weight of the empty flask = w_1 g
Weight of the flask + water = w_2 g
Weight of the solute = w g
Freezing point of water = T_1°C
Freezing point of solvent = T_2
Molecular wt. of solvent = M

6.3.2.5 Calculations

Depression in freezing point $\Delta T = (T_1 - T_2)$°C

Weight of water (W) = $(w_1 - w_2)$ g.

Now by substituting the different values in the following formula, the molecular weight of the solute (m) can be calculated.

$$m = \frac{1000 \times k_f \times w \times M}{\Delta T \times W}$$

6.3.2.6 Result

Molecular weight of the given solute is ……...........g.

6.3.2.7 Precautions

(i) The temperature of the freezing bath should not be below more than 3-4^{0}C, the freezing point of the solvent.
(ii) Excessive supper cooling must be avoided.
(iii) The solvent should not form mixed crystal with the solute.
(iv) Stirring should be slow and continuous.
(v) The solution must be dilute.
(vi) The solute must be non-volatile.

6.4 DETERMINATION OF MOLECULAR WEIGHT AND DEGREE OF DISSOCIATION OF A NON-VOLATILE SOLUTE BY EBULLIOSCOPY

6.4.1 Objective

To determine the molecular weight and apparent degree of dissociation of an electrolyte (eg. NaCl) in aqueous solution at different concentrations by Ebullioscopy

6.4.2 Theory

The boiling point of a liquid is that temperature at which it's vapour pressure become equal to atmospheric pressure. Since the vapour pressure of a liquid is lowered by the addition of a non-volatile solute, the boiling point is raised. The elevation in boiling point depends upon the quantity of the substance added. The molecular weight of the solute is calculated by the relation:

$$m = \frac{1000 \; X \; k_v \; X \; w \; X \; M}{\Delta T \; X \; W}$$

Where

k_v = Molal elevation constant

w = weight of solute

W = weight of solvent

M = Molecular weight of solvent

ΔT = Elevation in boiling point

When an electrolyte is dissolved in water, it dissociates into ions. Since the ions behave as molecule, the total number of molecules in solution exceeds than the normal number of molecules. The molecular weight (wt.) of the solute can be expressed as:

$$Molecular\ wt. \propto \frac{1}{Elevation\ boiling\ point}$$

$$Molecular\ wt. \propto \frac{1}{Number\ of\ Particles}$$

Thus,

$$\frac{Observed\ molecular\ wt}{Normal\ molecular\ wt} = \frac{Normal\ No. of\ particles}{No. of\ particles\ after\ dissociation}$$

If one gram mole of solute is taken and X be the degree of dissociation then.

NaCl	→	$Na^+ + Cl^-$		
1		0	0	before dissociation
(1- x)		x	x	after dissociation

Therefore, No. of particles before dissociation = 1+ 0 + 0 = 1

And No. of particles after dissociation = 1- x + x +x = 1 + x

Hence,

$$\frac{Observed\ molecular\ wt}{Normal\ molecular\ wt} = \frac{1}{1+x}$$

If observed and normal molecular weights of the electrolyte are known, its degree of dissociation (x) can be calculated.

The apparatus used is shown in Fig 6.1.which consists of a graduated boiling tube whose middle portion blown into a bulb with a hole in the side. The boiling tube is fitted with a thermometer (reading up to 0.01°C) and a glass tube having a rose head for uniform heating of the solution. The boiling tube is surrounded by an outer tube which receives hot vapours from the inner tube through the hole and prevents the loss of heat by radiation.

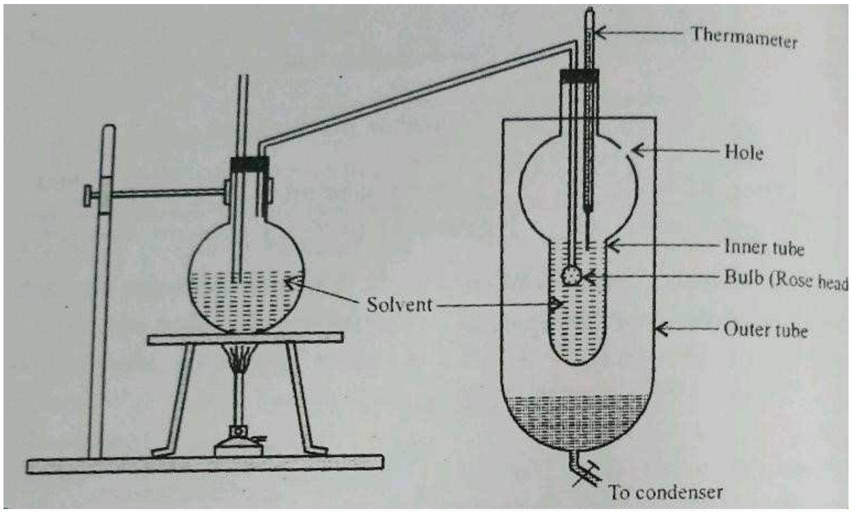


Fig. 6.2 Landsberger's apparatus

6.4.3 Procedure

(i) Set the apparatus as shown in Fig. 6.2. Take about 150 mL of the solvent in a round bottom flask and about 10 mL in the inner tube and fit in it a rose head tube and a Beckmann thermometer.

(ii) Now, heat the flask and pass the solvent vapours through the tube into the inner tube. This will increase the temperature of the solvent which becomes constant at the boiling point of the solvent. Note this temperature. This is the boiling point of the pure solvent.

(iii) Now stop heating and allow the flask to cool. Introduce an accurately weighed amount (1-1.5 g) of the solute (NaCl) into inner tube and shake till it dissolves.

(iv) Fit the inner tube and the thermometer in the apparatus and heat the flask again. Allow the solvent vapours to pass into the inner tube. Note the temperature when it becomes constant. It is the boiling point of the solvent. The difference of two readings (T_1-T_2) will be the elevation in boiling point (ΔT). Similarly, repeat the experiment 2 or 3 times by taking different amounts of the solute.

(v) Note the volume of the solvent on graduated inner tube. Knowing the density of the solvent, the weight of the solvent (W) can be calculated.

6.4.4 Observations

(i) Boiling point of pure solvent = ……..°C

(ii) Density of the solvent at room temperature = …….°C

S.N.	Wt. of the solute added	Wt. of the solvent	Boiling point of solvent (T_1)	Boiling point of solution (T_2)	Elevation boiling point ($\Delta T = T_1 - T_2$)
1		…..	….	….	….
2		…..	….	….	….
3		…..	….	….	….

6.4.5 Calculations

The molecular weight of the solute may be calculated by following formula:

$$m = \frac{1000 \times k_b \times w \times M}{\Delta T \times W}$$

It will be the observed molecular wt. of the solute. Degree of dissociation of NaCl is calculated by the following relation:

$$\frac{Observed\ molecular\ wt}{Normal\ molecular\ wt} = \frac{1}{1+x}$$

Or

$$\frac{Observed\ molecular\ wt}{58.5} = \frac{1}{1+x}$$

From the above relation, the degree of dissociation (x) can be calculated and expressed in percentage.

6.4.6 Result

The degree of dissociation of NaCl is …...........

6.4.7 Precautions

(i) The solvent used must be pure.
(ii) The heating of the solvent in the inner tube must be uniform.
(iii) The solution should be dilute.
(iv) The solute should be non-volatile.

6.5 TERMINAL QUESTIONS

(i) Which solvent you used in the Rast method and why?
(ii) What are the advantages of Rast's method?
(iii) The molar masses of what kind of solute can be determined by Rast's method?
(iv) Which method can be used for finding the molecular weight of a volatile substance?
(v) What are colligative properties?
(vi) Define molal depression constant?
(vii) Rast method is known as micro-method. why?

6.6 SUMMARY

The Rast method for determining molar masses uses camphor as the solvent. Beckmann's freezing point method is based on relationship between depression in freezing point and weight of solute dissolved in weighed solvent. These two methods are based on cryopscopy. On the other hand, enullioscopy is based on elevation of boiling point which intern depends upon quantity of the substance added.

6.7 SUGGESTED READINGS

1. Brain S. Furniss, Antony J. Hannford, P.W.G. Smith and A. R. Tatchell. (1989). Text Book of Practical Organic Chemistry. Pearson Education Press.
2. H. Kaur. (2002). Instrumental Methods of Chemical Analysis. Pragati Prakashan, Meerut.
3. S. C. Tripathi and S. P. S Jadon. (2008). Practical Chemistry. Anusandhan Prakashan.
4. Shashi Chawla. (2002). Essentials of Experimental Engineering Chemistry. Dhanpati Rai & Co (PVT) Ltd.

UNIT 7: ELECTROCHEMISTRY

CONTENTS

7.1 INTRODUCTION

7.1.1 Conductometric methods

Solutions of electrolytes conduct an electric current by the migration of ions under the influence of potential gradient. The movement of ions depend on their charge and size, viscosity of the medium and magnitude of the potential gradient. Like a metallic conductor, the solutions also obey Ohm's law which is I = E / R.

For an applied potential E, the current I, that flows between the electrodes immersed in the electrolyte varies inversely with the resistance of the electrolytic solution. The reciprocal of resistance (I / R) is termed the conductance (L). It is measured in Ohm^{-1} or mhos and in SI, the name Siemen (S) is used. Let us understand some important terminologies being used and their meaning,

7.1.2 Specific resistance

The resistance R of the conductor of uniform cross section is directly proportional to length, and inversely proportional to the cross section a.

Thus,

$$R \propto \frac{1}{a}, \qquad R \propto l$$

$$R = \rho \frac{l}{a}$$

Where ρ is a constant called resistivity or specific resistance. It may be defined as the resistance in Ohm's of a specimen of one cm in length and 1 square cm in cross section. It is the resistance between opposite faces of 1 cm cube of the metal.

$$\rho = R\ \frac{a}{l}\ ohm\ x\ cm^2/cm$$

$$= \text{Ohm cm}$$

7.1.3 Specific conductance

The reciprocal of specific resistance is known as the specific conductance (σ). It is the conductance of one cm cube of the solution of an electrolyte at a specific temperature. Since conductance, σ is directly proportional to length l and inversely proportional to the cross sectional area a of the conductor. Hence,

$$\sigma = 1/\rho = 1/R\ \frac{l}{a}$$

Specific conductance is expressed in $ohm^{-1}cm^{-1}$ or S/ m.

7.2 OBJECTIVES

This unit will be helpful in:

- Understanding conductometric methods
- Determining the strength of the given acid conductometrically using standard alkali solution.

7.3 CONDUCTROMETRIC ANALYSIS

The conductometric analysis is performed by using digital conductivity meter. This instrument is ideal for monitoring salt contents in natural water, treated water, waste water, drinking water, brine solution, sea water and soluble salts in soil. The use of solid state Integarated circuit (I.C.) makes the instrument reliable and versatile. The digital conductivity meter is extremely useful for:

(i) Water quality control in boiler feed water
(ii) Water works departments
(iii) Breweries
(iv) Swimming pools
(v) Agriculture and soil analysis
(vi) Fertilizers to the plants
(vii)Petroleum refineries
(viii)Textile plants, rayon and silk mills etc.

7.3.1 Digital conductivity meter

A conductivity cell dipped in a measuring solution is placed in the inverting input path of an 'operation amplifier' when (e_i) voltage of constant amplitude and suitable frequency is applied to the system, then a given feedback resistance (R_f) the output voltage (e_0) is linearly proportional to the conductance of the solution (G_i). Applying Kirchoff's current law at the inverting input path of an 'operation amplifier' (Figure 7.1).

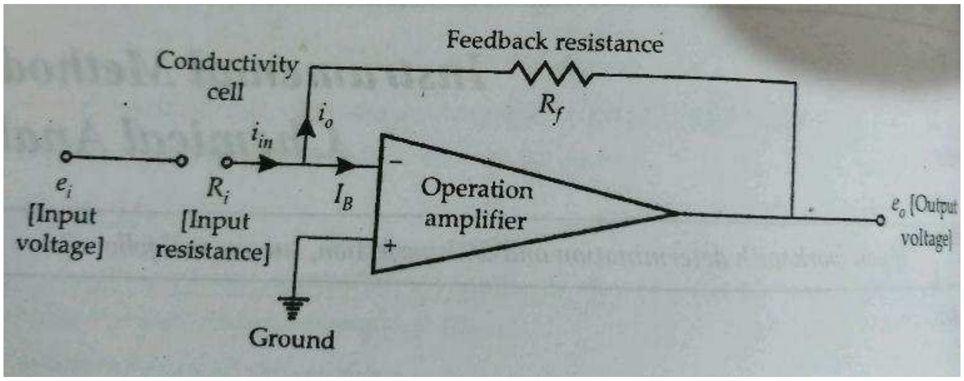


Figure 7.1 Schematic presentation of digital conductivity meter

A virtual ground is presumed to be existing that melting input impedance of the operation amplifier is very high, as a consequence IB = 0

Thus

$$i_m = i_o \quad (1)$$

from ohm's law, voltage (e) = current (I) × Resistance (R)

$$e = IR$$

$$I = \frac{e}{R} (2)$$

Using equation (2) equation (1) becomes:

$$\frac{e_1}{R_i} \neq \frac{e_0}{R_f} \qquad (4)$$

$$\frac{e_i}{R_i} = \frac{e_0}{R_f} \quad (3)$$

$$e_0 = \frac{e_i}{R_i} R_f \ (4)$$

When R_f and e_i are constant

Let R_f $e_i = K =$ constant

Therefore,

$$e_0 = \frac{K}{R_i} \quad (5)$$

or

$$e_0 \, \alpha \frac{1}{R_i} \quad (6)$$

or

$$e_0 \, \alpha \, Coductance \ of \ the \ solution \, (G_i) \quad (7)$$

With the help of cell constant, the conductivity of the solution under test can be dtermined. Thus, the output of the amplifier after conditioning is displayed on a digital display and it indicates directly the conductivity of the solution under test referred at the reference measurement (25°C).

7.3.2 Controls and services of digital conductivity meter

(1) Front panel control (Figure 7.2)

(a) Cell constant: This control is used to compensate for the cell constant variation.

(b) Digital display: It is a LED digital display that displays the conductivity value of any aqueous solution.

(c) Range: The range switch is used for setting one of the five ranges of conductivity. The five ranges are:

200 µs
2 ms
20 ms
200 ms
1000 ms

(d) Temperature: This control is used to compensate for the change in conductivity due to variation in temperature.

(e) Function switch: When at 'cheek' position the conductivity, meter read 1.000. If not, then adjust with 'CAL' control knob provided at rear panel so that the display reads 1.000.

(f) MAN / COND: At this position, the instrument displays the conductivity of the solution under test with manual temperature compensation.

(g) ATC (Available only in selected models): At this position the instrument displays the conductivity of the solution under test with Automatic temperature compensation. In this mode, the temperature probe should be attached to the instrument.

(h) Cell constant: At this position, this instrument displays the cell constant value set by the user.

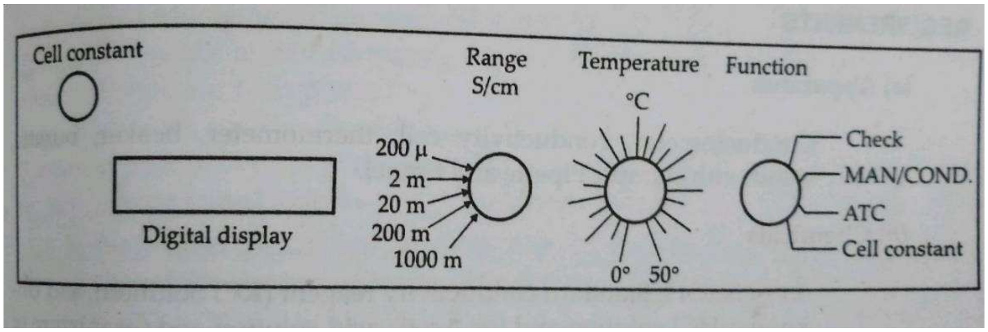


Figure 7.2. Front Panel controls of conductivity meter

(2) Back panel controls (Figure 7.3)

(a) Input: For connecting conductivity cell to the conductivity meter, two input banana sockets are provided at the back panel.

(b) Temperature (available only in selected model): This socket is used for connecting the temperature probe to the conductivity meter for ATC mode.

(c) Cal: When the function switch is at check position this 'CAL' knob is used to adjust 1.000 on the display.

(d) On / Off: This switch is used to switch 'ON' the instrument should be switched 'OFF' when not in use.

(e) Fuse: 100 mA fuse in used to control the current from the supply to the instrument.

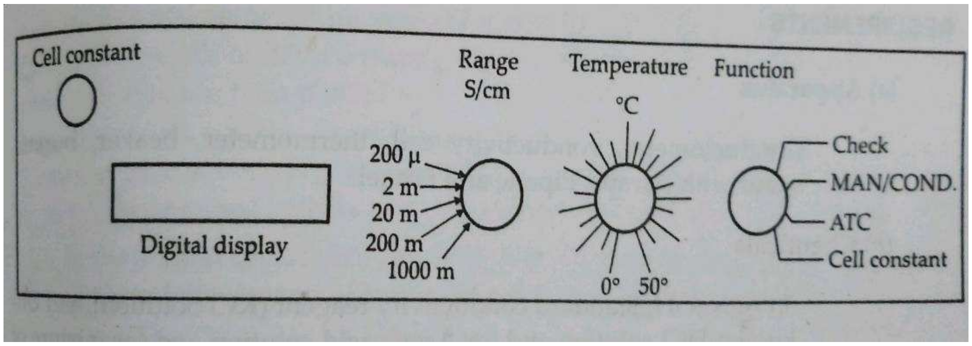


Figure 7.3. Back panel controls of conductivity meter

7.4 DETERMINE THE STRENGTH OF THE GIVEN ACID CONDUCTOMETRICALLY

7.4.1 Objective

To, determine the strength of the given acid (say HCl) conductometrically using standard alkali (say NaOH) solution.

7.4.2 Theory

The conductivity cell is made up of Pyrex glass fitted with Platinum (Pt) electrodes. The electrodes consist of Pt plates sealed into glass tubes which pass through an ebonite cover. The electrodes are connected to the circuit by means of mercury (Hg) placed in the tubes. The electrodes are fixed by cementing the tubes to the ebonite cover. The electrodes are coated with finely divided Pt. the cell is placed in a thermostat. Copper wires re dipped in Hg placed in glass tubes to make concentrations (Figure 7.4).

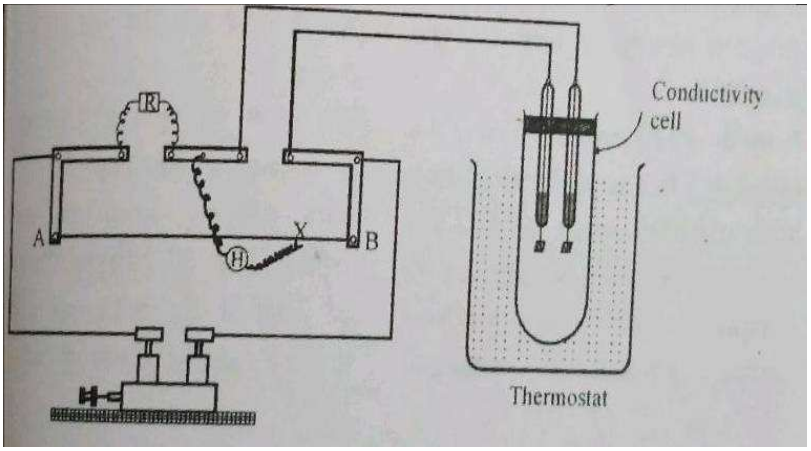


Figure 7.4 Determination of conductivity

$$\frac{Resistance\ of\ solution}{Resistance\ 'R'} = \frac{Length\ BX}{Length\ AX}$$

Thus,

$$Resistance\ of\ solution = \frac{Length\ BX}{Length\ AX} \times Resistance\ R$$

Or

$$Conductivity\ of\ solution = \frac{1}{Resistance\ of\ solution}$$

The titration of strong acid (HCl) with a strong base (NaOH) gives the following ionic reaction:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O \text{ (Freely ionized)}$$

Initially, the conductivity of HCl solution is high due to high concentration of H^+ ions. When NaOH is added, the conductivity of the solution decreases due to the disappearance of H^+ ions which combine with OH^- ions to form feebly ionised H_2O. When all the HCl solution get neutralised and thereby the neutralization is complete, further addition of NaOH increases conductivity of the solution due to presence of OH^- ions.

When conductance is plotted against the volume of NaOH added, a V-shaped curve will obtain. The intersect point thus gives the volume of NaOH required to neutralise the given HCl (Figure 7.5).

7.4.3 Procedure

Pipette out 10 mL of the given HCl solution of N/10 normality in a beaker and dilute it with distilled water so that the electrodes of the conductivity cell are completely dipped in the solution. Fill N/10 NaOH solution in the burette. Connect the cell with Wheatstone bridge and note the conductivity of the HCl solution.

Now add 1 mL of NaOH solution from the burette and note the conductivity. Similarly note down the reading after addition of 1 mL of NaOH solution. Now plot a graph between conductance on Y-axis and volume of NaOH used on X-axis. The intersect of the lines gives volume of NaOH required to neutralize the given HCl.

7.4.3 Observations

(1)Volume of HCl taken = 10 mL.

Observation table

S. No.	Volume of NaOH solution added (in mL)	Conductivity (mhos)
1.	0	….
2.	1	….
3.	2	….
4.	3	….

5.	4	….
6.	5	….
7.	6	….

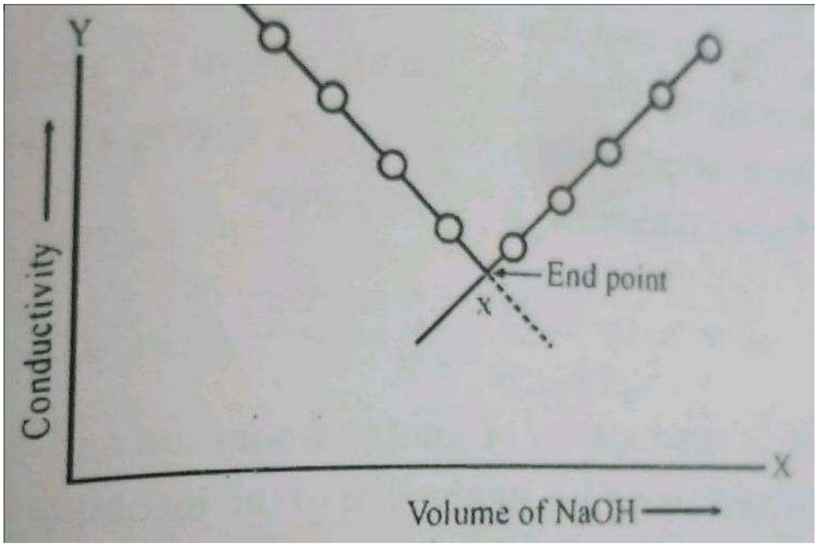


Figure 7.5 Curve showing conductivity changes in acid and base titration

7.4.4 Calculations

Suppose V mL of standard solution of NaOH is consumed at end point.

$$\mathrm{HCl} \equiv \mathrm{NaOH}$$

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 10 = N_2 V_2$$

Therefore,

$$\text{Normality of HCl} = N_1 = N_2 V_2/10$$

$$\text{Hence, the strength of HCl} = \text{Normality of HCl } (N_1) \times 36.5$$

7.4.5 Result

The strength of the supplied HCl is …………… g/ L

7.5 SAPONIFICATION OF ETHYL ACETATE

7.5.1 Objective

To study the saponification of ethyl acetate conductometrically.

7.5.2 Theory

This experiment involves a bimolecular reaction for which a second-order constant may be calculated. A conductometric method is used for this purpose. The rate constant k for chemical reactions is given by the Arrhenius equation:

$$K = Se^{-\Delta Ha/RT}$$

Where e = base of natural logarithms

= energy per mole required for activation

R = gas constant

T = absolute temperature

The expression $e^{-\Delta Ha/RT}$ represents the fraction of molecules having an energy equal to or greater than the energy required for activation.

The rate of a second-order reaction, is proportional to the concentration of each of the two reacting materials, as expressed in the equation.

$$\frac{d_x}{d_t} = k(a - c)(b - x)$$

Where = number of moles reacting in time t

= initial concentration of one reacting material

= initial concentration of the other

= specific reaction rate

The bimolecular reaction studied in this experiment is the saponification of an ester by sodium hydroxide.

$$CH_3COOC_2H_5 + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + C_2H_5OH$$

The hydroxyl ion and ethyl acetate are the reacting materials, the sodium ion being incidental.

A solution containing sodium hydroxide (NaOH) and ethyl acetate ($CH_3COOC_2H_5$) undergoes a marked decrease in conductance with time because the highly conducting hydroxyl ion is replaced by the poorly conducting acetate ion during the reaction.

Accordingly, a conductivity bridge can be used to study the progress of the reaction. An alternative but more tedious procedure is to withdraw sample from the reaction mixture at definite intervals, discharge them into excess standard HCl solution, and back-titrate with standard NaOH.

7.5.3 Procedure

Standard solutions of ethyl acetate and sodium hydroxide having exactly the same normality are to be prepared. Enough pure ethyl acetate is pipetted into a weighed weighing bottle containing about 5 mL of water to prepare 250 mL of 0.02M solution (Flask 1). The bottle is reweighed, the solution transferred quantitatively to a volumetric flask, and distilled water is added to the mark. The exact normality is calculated.

The same volume of NaOH whose normality is exactly equal to that of the ethyl acetate is prepared by quantitative dilution of standardized 0.5N stock reagent (Flask 2).

The flasks (Flask 1 and Flask 2) containing these solutions and a 250 mL flask containing distilled water are clamped in the 25°C thermostat and allowed to come to temperature equilibrium before use. Record the temperature of the water bath.

A compact bridge utilizing an electron ray tube or “magic eye” as an indicator is available on the market and can be highly recommended. The Freas-type conductance cell shown in Figure 7.6.

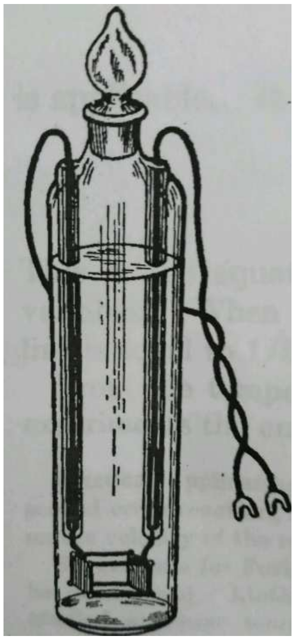


Figure 7.6 Freas-type conductance cell

The conductance bridge is set up by thermostat, and a cell which has been rinsed with distilled water is brought to thermostat temperature. Into another 250 mL flask, exactly 25 mL of ester solution, 25 mL water, and 50 mL NaOH solution should be pipetted. in this order. The flask is swirled rapidly in the thermostat as the NaOH is introduced, and the stop watch started after about half has been added. Measure the first conductance reading after 300 seconds and continuously collect the reading after 300 second intervals for one hour.

For the next run, the proportions of ester and base are reversed, and the experiment is repeated. Next, equal volumes of the base and ester solutions are mixed, and readings are taken for about an hour at 25°C. With solution and apparatus transferred to the 35°C thermostat, the experiment is repeated. It is not necessary to measure a final conductance for these two experiments.

7.5.4 Observations

Temperature of reaction = ________________________________

Time (Sec)	Y (µS)	Y_o-Y (µS)	(Y_o-Y)/t (µS/sec)
300		….	….
600		….	….
900		….	….
1200		….	….
1500		….	….
1800		….	….
2100		….	….
2400		….	….
2700		….	….
3000		….	….
3300		….	….
3600		….	….

7.5.5 Calculations

Appropriate plots should be made, and the rate constants should be determined for each of the experiments performed. The following equation is used where unequal concentrations of ester and base were present.

$$k = \frac{2 \cdot 303}{t(a-b)} log \frac{b}{a} \frac{(a-x)}{(b-x)}$$

To obtain x at time t, the quantity $(y_0 - y_t) / (y_t - y_\infty)$ is multiplied by a or b, whichever was originally present at time t, y_0 is the conductance at time 0, and y_∞ is the conductance at completion of the reaction. The conductance at time 0 is obtained by extrapolation of the first few points on a plot of conductance versus time to zero time. When the concentrations of the two reactants are the same, the equation is applicable.

$$k = \frac{1}{ta}\frac{x}{(a-x)} = \frac{1}{ta}\frac{(y_0 - y_t)}{(y_t - y_\infty)}$$

It may be rearranged to yield

$$y_t = \frac{1}{ka}\frac{y_0 - y_t}{t} + y_\infty$$

This is the equation of straight line with y_t and $\frac{y_0 - y_t}{t}$ as variables. When y_t is plotted against $\frac{y_0 - y_t}{t}$ the slope of the line is equal to $\frac{1}{ka}$.

From the temperature coefficient of k obtained from the last two experiments, the energy of activation is calculated.

7.6 DETERMINATION OF IONIZATION CONSTANT OF WEAK ACID

7.6.1 Objective

To determine the ionisation constant of a weak acid (acetic acid) conductometrically.

7.6.2 Theory

The ionisation of a weak electrolyte (CH_3COOH) may be written as below:

$$CH_3COOH \rightleftharpoons CH_3COO^+ + H^+$$

Applying law mass action:

$$K = \frac{[CH_3COO^-]}{[CH_3COOH]} \text{.......(1)}$$

Where K is the ionisation constant and $[CH_3COO^-]$ $[H^+]$ and $[CH_3COOH]$ are the active masses of CH_3COO^-, H^+ and unionised CH_3COOH respectively.

If 1 mole of the substance is taken and α is the degree of dissociation, v is the total volume in litters then:

$$[H^+] = \frac{\alpha}{v}; [CH_3COO^-] = \frac{\alpha}{v} [CH_3COOH] = \frac{1-\alpha}{v}$$

Substituting these values in equation (1):

$$K = \frac{\alpha^2}{(1-\alpha)v} \ldots\ldots\ldots \quad (2)$$

For weak electrolytes, α is very small hence (1- α) may be taken as unity the equation (2) becomes:

Where C = concentration in gm mole per litre.

To determine the value of ionisation constant K, the value of   is to be determined by conductivity measurements.

$$\alpha = \frac{\lambda v}{\lambda \infty} \quad \ldots\ldots\ldots.(4)$$

Where λv = equivalent conductivity at any dilution v (in litre) and $\lambda\infty$ = equivalent conductivity at infinite dilution. $\lambda\infty$ = is determined by Kohlraush's law i.e.

$$\lambda\infty = \lambda a + \lambda c \ldots\ldots..(5)$$

Where λa and λc are the ionic conductivities of anion and cation respectively.

7.6.3 Procedure

(i) Prepare exact N/2 acetic acid solution.

(ii) Prepare the solution of different strength like N/10, N/20, N/40 and N/50 by diluting with conductivity water and measure conductance directly from conductivity meter.

Determination of cell constant: The cell constant is determined by direct measurement of conductance from conductivity meter.

$$\text{Cell constant} = \frac{\text{Specific conductivity}}{\text{Observed Conductivity}}$$

The specific conductivity of N/10 KCl solution at 25°C is 0.01289.

Thus,

$$\text{Cell constant} = \frac{\text{Specific conductivity}}{\text{Observed Conductivity}}$$

7.6.4 Observation

S. No.	Strength of acetic acid	Observed Conductivity	SP. Conductivity = cell const. × obs. Conductivity	Eq. conductivity $\lambda v =$

7.6.5 Calculation

The value of Ionisation constant can be calculated by the following constant (degree of dissociation) can be calculated by the following relation.

$$K = \frac{\alpha^2}{v} = \alpha^2 C$$

Calculate the value of ionisation constant K for each solution which is constant.

7.6.6 Result

The ionisation constant of acetic acid is ……. .

Note: Standard value of Ionisation constant of acetic acid is 1.75×10^{-5} at 25°C.

7.7 TERMINAL QUESTIONS

Q 1. Explain the following:

(a) Conductivity (b) Specific conductance (c) Cell constant

(d) Equivalent conductivity (e) Molar conductivity.

Q 2. What is the relation between equivalent and molar conductivity?

Q 3. Discuss factors on which conductance of an electrolytic solution depend.

Q 4. Can precipitation titrations be followed by conductance measurements?