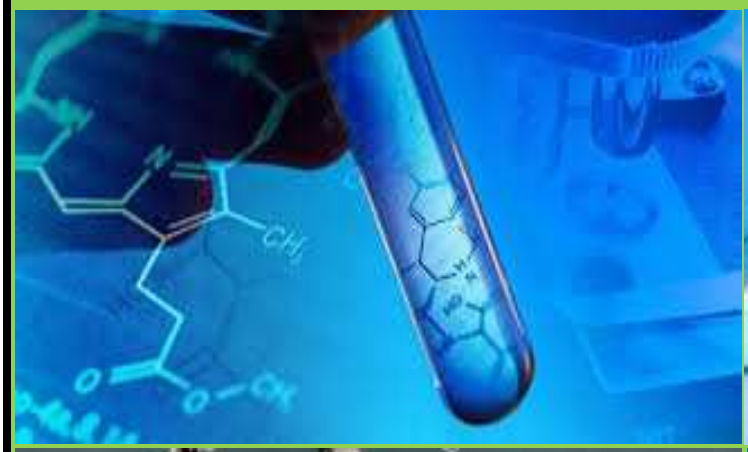
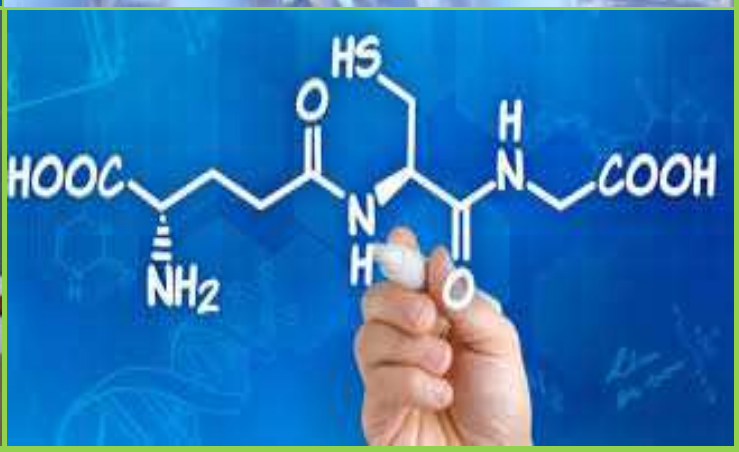
BSCCH- 204

B. Sc. II YEAR

LABORATORY COURSE-II





SCHOOL OF SCIENCES

DEPARTMENT OF CHEMISTRY

UTTARAKHAND OPEN UNIVERSITY

BSCCH-204

LABORATORY COURSE-II

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

Board of Studies

Programme Coordinators

Dr. Charu C. Pant
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Dr. Shalini Singh
(Assistant Professor)
Department of Chemistry
School of Sciences,
Uttarakhand Open University
Haldwani, Nainital

Unit Written By	Unit No.
1. Dr. Dr. Renu Loshali Department of Chemistry, Govt. Degree College, Bazpur	**1, 2, 4 & 6**
2. Dr. Kamal K. Bisht Department of Chemistry R.C.U. Govt. PG College, Uttarkashi	**3 & 5**
3. Dr. Gunjan Rajput Research Scientist Department of Chemistry, R.C.U. Govt. PG College, Uttarkashi	**7, 8 & 9**
4. Dr. Namrata Ghildiyal Department of Chemistry H.N.B. Garhwal University Srinagar-Garhwal, Uttarakhand	**10, 11, 12, 13, 14, 15 & 16**

Course Editor

Prof. Om Prakash
Department of Chemistry
College of Basic Sciences and Humanities
G.B. Pant University of Agriculture & Technology
Pantnager

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UNIT 1: INTRODUCTION TO LAB TECHNIQUES: INORGANIC CHEMISTRY

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1.1 INTRODUCTION

Inorganic chemistry is the branch of chemistry that deals with the properties and behavior of inorganic compounds (non-living compounds). The experiments related to science which include chemistry, biology, physics etc. are carried out in a proper place provided with the facilities for performing the experiments is known as laboratory or colloqially lab. We have studied in lower classes that a chemistry lab consists of different types of chemicals, apparatus, equipment etc. Now moving to higher classes we must have a complete knowledge of laboratory that one have to keep in mind.

The present unit deals with the introduction of lab which includes a general knowledge of how to maintain a laboratory notebook? What are the common apparatus used in the laboratory? How to use analytical balance? How to make standard solution? How many types of standard solutions are there? What are lab reagents? What are the safety measures taken in the laboratory for performing the experiments? The unit is quite interesting provided with suitable figures in order to clear the topic properly.

It is necessary for a science student to have a complete knowledge of laboratories because in laboratory we perform experiments, observe change and obtain result. The whole process can be easily kept in mind as we perform the experiment in spite of reading the same experiment from a book. Working in laboratory makes the topic quite interesting. Now for having a complete knowledge of a laboratory, we move forward.

1.2 OBJECTIVES

After reading this unit you will be able to:

- Maintain a laboratory notebook.
- Have knowledge of commonly used apparatus in the laboratory.
- Know the method of using a pipette, burette, volumetric flask and analytical balance.
- Explain different terms like precipitation, digestion, filtration and ignition, drying, cooling etc.
- Describe the process of titration.
- Classify the titration.

- Classify the indicator.
- Determine the strength of given sodium hydroxide (NaOH) solution.
- Have knowledge of lab reagents.
- Know the safety measures taken in the laboratory.

1.3 LABORATORY

As discussed above, a lab or a laboratory is a place where experiments are performed. To have a complete knowledge of chemistry laboratory, we must go through the following sections which are discussed below:

1.3.1 Laboratory notebook:

A laboratory notebook also known as lab notebook or practical notebook or lab record or lab manual is a record of experiments conducted in the laboratory. The first page of the notebook is of certificate where the name, class, rolls no., institution name is mentioned. The page next to the certificate is index page where the brief idea of the experiment performed are mentioned which includes serial no., name of the experiment, page no., date of experiment, date of submission and remark by teacher. Students are strictly advised to fill the index page. After index page certain chemistry notebook contains basic concept of chemistry like logarithm table, antilogarithm table, pH concept etc. while in other notebooks, after index page the proper pages for writing the experiment are given. Left hand side pages are blank or without lines while the right hand side pages are lined provided with experiment no., date, page no. at the top and teacher's signature at the bottom. On the left hand side tables, calculations, chemical reactions, figure is mentioned with a pencil. On the right hand side, we write with a ball point pen. The notebook should be well covered containing a record of experiments performed in the laboratory.

1.4 PIPETTE

Pipette is a glass apparatus used in laboratories in order to transfer a fixed volume of solution or liquid. It consists of a long narrow tube provided with a bulb in the middle and a single mark towards the upper side indicating the particular volume as shown in Figure

1. Pipettes are used in the preparation of solutions. These are generally available in several ranges like 0.5mL, 1 mL, 5mL, 10 mL, 25 mL.

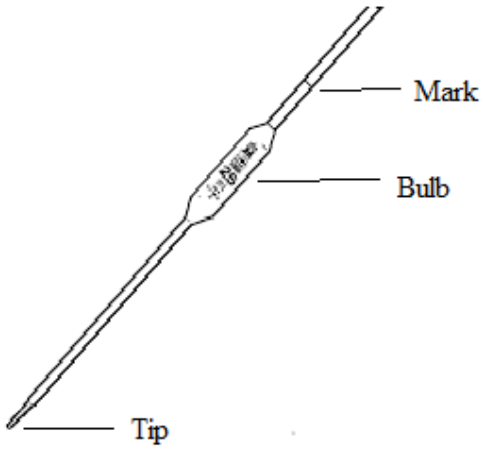

Figure 1. Pipette

A clean pipette is used for transferring a particular volume of a liquid. In order to clean a pipette, fill it with distilled water by sucking with the mouth. Now allow the water to drain. While draining the water, it should be noted that if water drains without leaving drops on the inner surface of the pipette, this shows that pipette is clean. If drops appear on the inner surface of the pipette then clean it with detergent or soap solution and with tap water followed with distilled water at the end. Now a cleaned pipette is ready to use. Suppose we have to transfer 10 mL of liquid 'A' from a beaker to a conical flask using a pipette. We have to follow the steps given below:

- First of all liquid A taken in a beaker. Never pipette the liquid or any solution directly from the stock bottle or container.
- Insert the tip of the 10 mL pipette into the beaker containing liquid A slowly in order to avoid the breakage of the tip. Tip of the pipette should not be pressed against the bottom of the beaker.
- Now hold the pipette in your hand keeping the index finger (finger next to the thumb) free as this finger is used further to cover the pipette.
- Remove the contact of the pipette with the bottom of the beaker and suck liquid A upward above the mark slowly without reaching the mouth. Tilt and roll the pipette so that liquid A runs through the inner wall of the pipette. Now drain liquid A from the pipette. This process is known as rinsing.

- Again liquid A is filled in the pipette above the mark, remove your mouth and quickly put the index finger over it tightly. By removing the index finger slowly, maintain the liquid up to the mark.
- After maintaining the liquid A up to the mark, now take out the pipette from the beaker with index finger at the top of the pipette tightly attached.
- Insert the pipette into a conical flask slowly without breaking the tip almost at an angle of 20^{o}. Remove the index finger in order to release liquid A into the conical flask. When the entire liquid A is released, touch the pipette to the inner wall of the conical flask in order to remove the liquid attached at the tip. It should be noted that no air is to be blown into the pipette for withdrawing the liquid.

1.5 BURETTE

Burette is graduated or calibrated glassware used in laboratories. It consists of a graduated narrow tube provided with the tap at the bottom. The upper part is used for adding the liquid or solution into the burette. Like pipette, burettes are generally used in titration or for delivering known volumes of a liquid. These are available in different volume like 10 mL, 20 mL, and 50 mL. The commonly used burette possesses 50 mL volume. In order to use a burette follow the steps given below:

- Suppose we are using 50 ml burette. It is graduated indicating 0 ml at the top and 50 ml at the bottom of the burette near the tap. First of all hold the burette properly in a burette stand by adjusting it vertically with the tap at the bottom.Place a conical flask below the burette.
- Close the tap of the burette and fill distilled water in it. Now open the tap of the burette and withdraw the water into the conical flask. Let liquid A is to be filled in a burette. Now after withdrawing distilled water, close the tap and add small amount i.e. 5 ml of liquid A into the burette using a funnel so that liquid A run along the walls of the burette. Now open the tap and drain the liquid A. This process is called rinsing of the burette.
- Now fill the burette with liquid A up to 0ml mark keeping the tap of the burette closed. One thing is to be noted that funnel is used only for filling the liquid A and after filling the liquid A, the funnel is to be removed. Now the burette is ready to use.

- If we have to take 10 ml liquid A from the burette, then we open the tap of the burette, withdraw 10 ml of liquid A and close the tap of the burette.The burette will show a reading of 40 ml after withdrawing 10 ml. In this way burette is used for delivering known volume of the liquid A.

As given earlier, burette is used in titration. Therefore in titration one solution is taken in the burette and another solution is taken in a conical flask placed below the burette as shown in Figure 2.Both the solutions are allowed to react by opening the tap of the burette.In this way burette is used in titration.

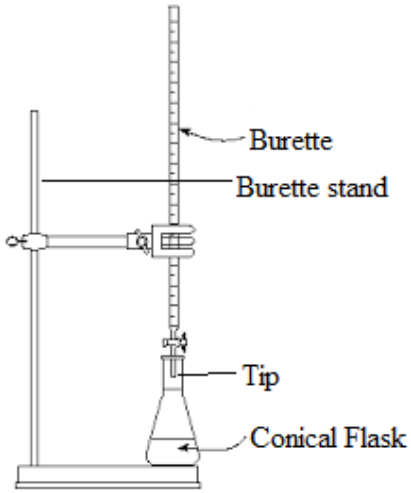

Figure 2. Titration

1.6 VOLUMETRIC FLASK

Volumetric flask is a type of flask used in laboratory for preparing standard solutions. These flasks are also known as measuring flasks or graduated flasks. These flasks are made up of glass and are pear shaped with a long neck and flat bottom as shown in Figure 3.The size of the flask that we generally use in laboratories are 10 mL ,25 mL, 50 mL, 100 mL, 250 mL, 500 mL, 1000 mL and 2000 mL. In each volumetric flask, there is a mark on the neck which indicates the volume. For example if we are using 25 mL volumetric flask, then the mark on the neck of the flask indicates the volume i.e. 25 mL.Let us discuss, how these volumetric flask are used for preparing solutions of desired volume:

- Suppose we have to prepare 1/10 N oxalic acid solution having volume 250 mL. For this first of all the mass of the oxalic acid is calculated using formula w = NEV/1000, Where N is normality of the solution, E is equivalent weight and V is volume of the solution. The mass calculated using the above formula for making 1/10 N oxalic acid solution 250 ml is 1.57 g. Now weigh 1.57 g oxalic acid using an analytical balance. The detail of analytical balance is given in the next section.
- Clean the volumetric flask as required; in this case it is 250 ml with distilled water. Now transfer the above weighted oxalic acid into the volumetric flask using a funnel. During the transfer of the acid, some acid get adhere to the inner wall of the flask.
- Now distilled water is added into the volumetric flask in such a way that the acid attached to the inner walls flow down with the water and volumetric flask is half filled. Now cover the flask using a cap and shake it so that oxalic acid may dissolve.

When the acid gets completely dissolved, again fill the volumetric flask with additional distilled water up to the mark very carefully. If the water crosses the mark then there will be change in the volume of the solution or simply we can say that solution prepared is not correct. Therefore attention is to be taken while adding distilled water. We will observe the formation of meniscus in the neck of the volumetric flask. Meniscus is a curve formed in the container in the upper surface of a liquid. The prepared solution is 1/10 N oxalic acid solution.

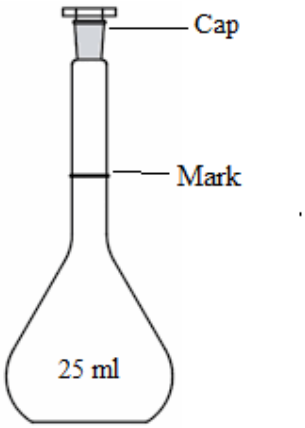

Figure 3. Volumetric flask

1.7 ANALYTICAL BALANCE

Before knowing how to use an analytical balance, let us discuss about these balance. Analytical balances are used in laboratories in order to measure small masses. These balances contain a measuring pan on which a sample is placed. Measuring pans are always placed inside a transparent chamber having doors so that while weighing these doors remains closed and weighing is exact. In laboratories, we use mechanical analytical balance which is also known as chemical balance and digital analytical balance also known as electronic balance as shown in Figure 4. Now a day for quick weighing, electronic balances are preferred over chemical balance. Let us discuss the working of digital analytical balance which is shown in Figure 4. Some digital analytical balance reads mass up to four digit after decimal while some reads two or three digits after decimal in grams. The balance with four digit after decimal gives more accurate results. For weighing aliquid or a powder like substance, we require an appropriate container in which these substances are placed.

Figure 4. *Digital analytical balance*

For the measurement of a solid substance, we can directly measure it as no container is required to place the solid. Follow the given points while weighing a liquid or a powder substance:

- Check the measuring pan of the balance. If it is clean then continue the next step.
- Switch on the digital analytical balance and press on button of the balance.
- Now open the door of the weighing chamber and place a container on the measuring pan. Close the door and observe the reading. The reading will show the mass of the container.

- Now on the balance, there is a tare button. This is used to neglect the mass of the container. Press this tare button and we will observe the zero reading with the container which is placed over the measuring pan. This is done in order to read the mass of a given sample directly from the display.
- Open the door and the substance to be weighed is added into the container with the help of the spatula. Now close the door of the chamber and read the display which indicates the mass of the given sample.

In order to measure a solid substances, switch on the balance, check the reading i.e. zero. Now open the door of the chamber, place a solid substance directly into the measuring pan. Close the door so that weighing errors are minimized and read the display in gram. The display indicates the mass of the solid substance. After using digital analytical balance, check whether the measuring pan is clean or not. If it is not clean, clear it and then cover it.

1.8 HEATING, EVAPORATION, PRECIPITATION, DIGESTION, FILTRATION, DRYING, IGNITION AND COOLING OF PRECIPITATES

In chemistry, we study about gravimetric analysis. In gravimetric analysis, the end product is weighted and has direct relationship with the substance to be quantitatively analyzed or simply we can say that in gravimetric analysis, we convert the soluble form of a substance into a solid which involves heating, evaporation, precipitation, digestion, filtration, drying, ignition and cooling. The solid thus produced is weighted. All these processes are discussed as follows: Precipitation is a formation of a solid (precipitate) in a solution. The chemical substance used to form a precipitate is called as precipitant or precipitating reagent. The precipitate gets collected at the bottom of the solution.The soluble form of a substance whose gravimetric estimation is to be performed, if concentrated is diluted using distilled water and then heated slowly. Now in order to form a precipitate, a precipitating reagent is added into the solution slowly with constant stirring as by this we obtain large crystals. Heating is done in order to have good crystals. Precipitating reagent is added in such an amount that the substance gets completely precipitated because an extra addition of precipitating reagent makes the precipitate partially soluble. In order to check the complete precipitation of the substance, few drops

of precipitating reagent is added in such a way that the solution remains undisturbed. If on adding precipitating reagent, there is formation of a precipitate, then more precipitating reagent is added. If no such precipitation takes place in the solution above the precipitate then it shows that the precipitation is completed. The precipitate thus formed is heated gently or slowly on water bath for half an hour. This process of heating the precipitate slowly for half an hour is known as digestion. The precipitate is said to be digested. After digestion, filtration process is performed. Filtration involves the separation of precipitates from the solution. Filter paper, asbestos mats, porous glass crucibles are used. Porous means with pores. We generally use filter paper and porous crucibles for filtration. Filter papers are available in large amount which differ in the pore size. Whatman number 42 is a commonly used filter paper for the process of filtration. In a funnel, filter paper is wrapped properly and kept over the tripod stand. The solution having precipitate is added slowly over the funnel provided with beaker placed below it. In this way, we obtain precipitate as residue on the filter paper and the solution (liquid) is collected into a beaker.

The precipitate is then washed in order to remove unwanted ions. These ions are attached to the precipitate causing high yield of the precipitate. Washing is done with fast current of the water. Fast current of the water allow the precipitate to agitate due to which ions attached to the precipitate get disturbed. The unwanted ions take time to settle being lighter and as a result they get filtered. After washing, the filtrate is tested in order to detect unwanted ions. If the filtrate contains unwanted ions it is further washed with fast current of water and the process of washing is continued till the filtrate thus obtained is free from unwanted ions. Now after washing of the precipitate, drying of the precipitate is performed. The funnel having filter paper containing precipitate is covered with a paper having small pores is placed on the tripod stand and is heated. This is the common method of drying. It can also be performed in an electric oven also. Dried precipitate is collected on a butter paper in order to avoid the loss of the yield. The precipitate is then covered with a funnel (by inverting it). We will observe that even after removing the dried precipitate from the filter paper, still some precipitate will remain attached to the filter paper. In order to remove some remaining precipitate, the process of ignition is performed. In this process, the filter paper containing some precipitate is folded and is burned completely in a non- sooty flame by holding it with a pair of tongs. A silica crucible taken and is weigh empty. As a result of burning ash is obtained which is then taken in a silica crucible. The ash is then heated till it becomes white. Now the precipitate which gets

reduced is recovered. Different chemicals are required for the recovery of the precipitate. Now the precipitate is transferred from butter paper to the crucible. The crucible is then cooled, weighted by using a digital analytical balance. In this way we can obtain a solid mass from the solution. There are several experiments on the gravimetric analysis which are being discussed in next unit.

1.9 STANDARD SOLUTIONS

We know that a solution is made up of two components, one is solute and other is solvent. The component present in large amount is solvent while component present in small amount constitute solute. Here we will discuss about standard solutions. Solutions having known strength are known as standard solutions. There are different ways of expressing strength of a solution. These are in a form of molarity, molality, normality, percentage by weight or by volume, parts per million and formality. Molarity of a solution is defined as the number of moles of solute dissolved per litre of the solution. It is represented by M. Molality of a solution is defined as a number of moles of solute dissolved in thousand gram of a solvent. It is represented by m. Normality of a solution is defined as number of gram equivalent of the solute dissolved per litre of the solution. It is represented by N. The percentage by weight means mass of solute dissolved in 100 gram of its solution. For example, 20% oxalic acid by weight means that in 100 g of solution of oxalic acid, there is 20 g of the acid. Parts per million can be written as ppm. It is defined as a number of milligrams of solute present in one litre of the solvent. Generally we express hardness in ppm. Therefore we can say that solution with known value of molarity, molality, normality, ppm, percentage by weight or by volume or formality is said to be standard solution. Standard solutions are prepared either by direct weighing of the substance or by standardization. Standardization is a process of making one solution standard by titrating it with another standard solution. On the basis of their preparation, standard solutions are classified as primary standard and secondary standard solutions.

1.9.1 Primary standard solutions:

Those solutions which are prepared by direct weighing of the substance are called primary standard solutions and these substances are said to be primary standard substances or simply primary standards. For example, oxalic acid, ferrous ammonium sulphate, silver

nitrate, potassium dichromate ($K_2Cr_2O_7$), succinic acid. There are certain conditions that a primary standard substance must possess. These are:

- It should be easily soluble in the desired solvent.
- It should not undergo decomposition in the solvent.
- It should be stable in air i.e. it remains unaffected.
- It must have large equivalent weight.
- On standing, there should be no change in its composition.
- Its availability should be in highly pure state.

As mentioned earlier that primary standard substance are obtained by direct weighing therefore in order to calculate the required weight for the preparation of the standard solution, we use a general formula: w = NEV/1000, where N is normality of the solution, E represent its equivalent weight and V represents the desired volume of the solution in mL. Suppose we have to prepare N/10 oxalic acid solution in 500 mL of distilled water. As we know oxalic acid is a primary standard substance hence its standard solution is prepared by direct weighing. Keeping normality = 1/10, E = 63, V = 500 mL, in the above expression for calculating the weight, the weight obtained is 3.15 g. Then 3.15 g of oxalic acid is weighed using digital analytical balance transferred to 500 mL volumetric flask using a funnel. Small amount of distilled water say 50 ml is added into the volumetric flask. Allow the oxalic acid to dissolve. When oxalic acid get dissolve completely, further add distilled water up to the mark indicating that the solution prepared is 500 ml. The prepared solution in the volumetric flask is 500 mL, N/10 oxalic acid solution. In this way, primary standard solutions are prepared.

1.9.2 Secondary standard solutions:

These solutions are not prepared by direct weighing of the substance but are prepared by a process known as standardization. The substance is called secondary standard substance or secondary standards. These substances do not fulfil the conditions that a primary standard substance possesses. For example, sodium hydroxide, potassium hydroxide, hydrochloric acid, sulphuric acid. In the process of standardization, an approximate weight of the secondary standard substance is dissolved in a volumetric flask of required volume and the exact amount of the solution is obtained by titrating it against another standard solution using some indicator. The process of standardization involves

the concept of titration.The preparation of standard solution sodium hydroxide (NaOH) is discussed in section 1.11.

1.10 TITRATION

Titration is a process of mixing of two solutions in order to react in a conical flask. One solution is with known strength or standard while the other solution is unknown solution or solution whose strength is not known. The solution which is to be titrated is taken in a conical flask with the help of a pipette and other solution is taken in a burette. Indicator is added to the conical flask in order to detect the end point or equivalence point. Two solutions are mixed dropwise by opening the tap of the burette. A sharp change in color indicates the end point. At this point, the reaction between two solutions is just completed.

1.10.1 Types of titration:

There are generally four types of titration depending on the reaction taking place between the two solutions. These are as follows:

1. Neutralization titration: These titrations are also known as acid- base titration as it involves two solution, one is of acid while the other is of base. For example, mixing of sodium hydroxide (base) with oxalic acid. This titration is further classified into acidimetry and alkalimetry. In acidimetry, the strength of an acid is determined by titrating it with standard alkali solution. In alkalimetry, the strength of an alkali is determined by titrating it against standard solution of an acid.

2. Redox titration: As the name indicates, redox titration are those titration in which on mixing two solutions, one solution undergoes oxidation while the other solution undergoes reduction or in simple words we can say that redox reaction occurs on mixing. These are also known as reducation- oxidation titration. The substance which undergoes oxidation is known as reducing agent while the substance that undergoes reduction is known as oxidizing agent. In redox reaction, both oxidation and reduction takes place simultaneously. For example, mixing of ferrous ammonium sulphate (FAS) and acidified $KMnO_4$, in which FAS undergoes oxidation and and $KMnO_4$undergoes reduction. Redox titration includes iodine titration where iodine is used as an oxidizing agent. There are two types of iodine titration, one is iodimetric and another is iodometric titration. In iodimetric

titration, standard iodine solution is directly titrated against some reducing agent. The reducing agent used is generally hypo solution, $Na_2S_2O_3$.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

In iodometric titration, iodine is liberated from iodine solution by using some oxidizing agent and then the liberated iodine is titrated with a standard solution of a reducing agent.

3. Precipitation titration: As the name indicates, on mixing two solutions there is a formation of precipitate. Precipitate is a solid mass which get accumulate at the bottom of the solution. For example, on mixing of sodium chloride (NaCl) with silver nitrate solution ($AgNO_3$), there is a formation of precipitate of silver chloride (AgCl). Precipitation titration is also known as Argentometric titration viz; $AgNO_3$ is used as one of the solution during titration for the estimation of chloride content in water using K_2CrO_4

4. Complexometric titration: As the name indicates, on mixing two solutions there is a formation of a complex. Complexes are formed by metals and ligands; in which ligand donate lone pair of electrons to metal mainly transition elements. For example, in the determination of hardness present in given water sample, there is a formation of a complex between Ca^{2+}/ Mg^{2+} with EDTA. EDTA is a hexadentate ligand.One of the solution is of ligand and the other is of a metal containing compound.

1.10.2 Indicators:

Indicators are those chemical substances that indicate the end point during titration by color change. There are three types of indicators:

1. Internal indicators: Indicators which are added in the conical flask containing on of the solutions are known as internal indicators. For example, phenolphthalein, methyl orange etc.

2. External indicators: Indicators which are used outside the conical flask (in a white tile) are known as external indicators. For example, potassium ferricyanide, $K_3[Fe(CN)_6]$.

3. Self-indicators: In titration, two solutions are used. When one of the solutions itself acts as an indicator, it is known as self-indicator viz;, potassium permanganate ($KMnO_4$).

1.11 SAMPLE TITRIMETRIC EXPERIMENTS

There are several experiments based on the type of titrations i.e. acid- base titration, redox titration, precipitation titration and complexometric titration. Let us discuss the determination of strength of given sodium hydroxide solution.

1.11.1 Determination of strength of given sodium hydroxide solution

As we know that NaOH is a secondary standard chemical. Exact weighing of NaOH is not done as it is hygroscopic in nature (it can absorb moisture from the atmosphere). Hence an approximate weight of NaOH is taken in 500 mL volumetric flask. Distilled water is added in a flask. First 50 mL and then allow NaOH to dissolve. After complete dissolution of NaOH, additional distilled water is added up to the mark, thereby making the solution 500 ml. We have simply dissolve NaOH without weighing. Now in order to determine its exact strength, we mix two solutions, one of the solutions is NaOH solution and the other solution is standard solution generally the primary standard solution. NaOH solution is taken in a burette and standard solution of known volume say 10 ml solution of N/10 oxalic acid is taken in a conical flask. The standard solution of oxalic acid is prepared by the method discussed in section 1.9.1. Two or three drops of indicator (phenolphthalein) are added into the conical flask. Now by opening the tap of the burette, both solution one in the burette and another in the conical flask containing the indicator are mixed drop wise in order to react until light pink color appears at the end point indicating completin of reaction. When there is change in color, close the tap of the burette and record the volume of the burette. Repeat the titration for two concordant readings and the repeating volume be V_2 mL. Using law of equivalence ($N_1V_1 = N_2V_2$), the exact normality of NaOH is calculated.

(Oxalic acid) $N_1V_1 = N_2V_2$ (NaOH)

Where N_1 is normality of oxalic acid that is 1/10, V_1 is volume of oxalic acid that is 10 ml and N_2 is normality of NaOH which is to be calculated. The N_2 is the exact normality of NaOH. In this way, the normality of NaOH is determined and is now become standard. The strength of NaOH is calculated by multiplying N_2 with the equivalent weight. For NaOH, equivalent weight is 40.

Strength(S) = Normality × equivalent weight

1.11.2 Instrumental determination of an equivalence point:

There are different instruments used for determining the end point or equivalence point like pH meter, conductivity meter. Using pH meter, we can determine the end point by measuring the pH of the solution while in conductivity meter, we can measure conductance of the solution. Let us discuss the method of determining equivalence point using conductivity meter. It is provided with a conductivity cell which is dipped in a solution for measuring the conductance. There is a display which shows conductance in Siemens or ohm^{-1}. A fixed volume of standard solution is taken in a beaker and its conductance is measured by dipping the conductivity cell. Burette is filled with the solution whose strength is to be determined. The solution is titrated and after every 2 ml addition from the burette, the conductance of the solution is recorded. In this way, we obtain a series of conductance value with similar trend in first half and with different trend in second half. Then these conductance values are plotted against the volume of solution added from the burette. The graph will show two straight lines and their point of intersection represents the equivalence point.

1.12 LAB REAGENTS

Lab reagents are the reagents or chemicals used in laboratory in order to bring about chemical reactions. These reagents may be solid or liquid. Some of commonly used lab reagents are: hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3), acetic acid (CH_3COOH), ammonium hydroxide (NH_4OH), potassium hydroxide (KOH), sodium hydroxide (NaOH), ammonium chloride (NH_4Cl), ammonium oxalate $(NH4)_2C_2O_4.H_2O$, Barium chloride ($BaCl_2.H_2O$), ammonium thiocyanate (NH_4CNS), Lime water $Ca(OH)_2$, potassium ferricyanide $K_3[Fe(CN)_6]$, potassium ferrocyanide $K_4[Fe(CN)_6]$, potassium iodide (KI), potassium permanganate ($KMnO_4$), copper sulphate ($CuSO_4.5H_2O$), lead acetate $(CH_3COO)_2Pb.\ 3H_2O$, Silver nitrate ($AgNO_3$), sodium acetate ($CH_3COONa.3H_2O$), mercuric chloride ($HgCl_2$), bromine water (Br_2/H_2O), chlorine water (Cl_2/H_2O), iodine solution (I_2), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), oxalic acid ($C_2O_4H_2.2H_2O$), Urea (NH_2CONH_2), ferrous sulphate (FeSO4. $7H_2O$), potassium dichromate ($K_2Cr_2O_7$), ethanol (CH_3OH), ethanol (C_2H_5OH), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), formaldehyde (HCHO), formic acid (HCOOH), starch,K_2CrO_4 ,Na_2EDTA, NaEBT etc

1.13 SAFETY MEASURES IN THE LABORATORY

It is not an easy task to work in a laboratory. Everyone should be aware about the safety measures that we have to consider while working in laboratory, any ignorance may lead to an accident. Following points are to be considered:

- Every lab consist of a first- aid box containing cotton, bandages, ointments, thread, needles etc. which should be open to all.
- In case of acid burn, immediately wash with cold water and then with dilute solution of sodium bicarbonate while in case of alkali burn, after washing with water, a dilute solution of acetic acid is used.
- Always wear a lab coat while working in the laboratory.
- Always test tubes and boiling tubes must be taken in a holder.
- Glass apparatus must be made clean by washing with chromic acid and then with distilled water.
- Never throw hot chemicals in a sink. Allow these to cool and then throw in the sink.
- Perform each experiment carefully considering their precautions.
- After performing a practical, students are advised to clean their hands with soap.
- Always use lab reagents in small amount.
- Concentrated acids like HCl, H_2SO_4, and HNO3 are used carefully as their contact may lead to burning of the skin.
- Sometimes while working in the laboratory, vapors enter in the eye. In this case, wash eye with cold water for a long time.
- Always place chemicals properly in the shelf with proper labelling.
- Do not ever taste the chemicals

1.14 SELF-ASSESSMENT QUESTIONS (SAQ)

- Fill in the blanks:

1. Standard solution is a solution of known …….

2. ……. is one of the way of expressing the strength of the solution.

3. Titration of oxalic acid with sodium hydroxide is ……. titration.

4. Acid- base titration is also known as ……. titration.

5. Self- indicator is …….

6. Potassium ferricyanide is an ……. Indicator.

7. ……. standard solution are prepared by direct weighing of the substance.

8. For determining the hardness of water, the titration used is ……..

9. ……. are used for determining the end point during the titration.

10. Sodium hydroxide is ……. standard substance.

11. Least count of burette is……..

1.15 SUMMARY

In this unit, we have discussed the basic introduction of laboratories which include the knowledge of apparatus like pipette, burette, volumetric flask, analytical balance. We have also discussed the concept of gravimetric analysis in which we have studied different processes like precipitation, digestion, filtration, drying, ignition, cooling of the precipitate and about standard solution, its preparation, types including indicators, titration. Further we studied about different reagents used in the laboratories and safety measures that we have to consider while working in the laboratory.

1.16 GLOSSARY

- **Indicators**— Substance that indicates end point by color change.
- **Titration** — Process of mixing of two solution in order to react in a beaker or conical flask.
- **End Point:** Point at which the reaction between two solutions just completes.
- **Standard Solution**: Solution of known strength.

1.17 POSSIBLE ANSWER TO SAQ

1.14 SELF- ASSESSMENT QUESTIONS (SAQ)

- Fill in the blanks:

1. Strength; 2. Molarity/ Normality/ Molality/ ppm/ formality; 3. Neutralization; 4. Neutralization; 5. $KMnO_4$; 6. External; 7. Primary; 8. Complexometric; 9. Indicators; 10. Secondary 11. 0.1mL

1.18 REFERENCES

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1.19 TERMINAL QUESTIONS

1. Explain gravimetric analysis including the various steps involved in it.

2. Discuss the safety measures taken in the laboratory.

3. Classify various types of titrations and indicators

UNIT 2: GRAVIMETRIC ANALYSIS

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2.1 INTRODUCTION

In the previous unit, we have studied the concept of gravimetric analysis in brief. The complete knowledge of the topic is provided in this unit which covers different steps involved during the gravimetric analysis. In the analysis, we convert soluble form of a substance into a solid form which is then weighted using digital analytical balance. This makes the topic more interesting.

As we know that in gravimetric analysis, the end product is weighted (solid) which is directly related with the substance being analyzed quantitatively. The analysis involves different process: heating, evaporation, precipitation, digestion, filtration, washing, drying, ignition, cooling and weighing. In this unit, we will consider several examples like determination of the amount of aluminium as aluminium (III) oxide, copper as copper (I) thiocyanate, iron as iron (III) oxide, sulphate ions as barium sulphate and aluminium as aluminium 8- hydroxyquinolinate.

To understand the topic/ unit more clearly, we must go through each and every step involved during the analysis.

2.2 OBJECTIVES

After reading the unit, you will be able to:

- Define gravimetric analysis.
- Explain different steps involved in the analysis.
- Know the precautions taken during the analysis.
- Know the method of determination of aluminium as aluminium (III) oxide, copper as copper (I) thiocyanate, iron as iron (III) oxide, sulphate ions as barium sulphate and aluminium as aluminium 8- hydroxyquinolinate.

2.3 GRAVIMETRIC ANALYSIS

In gravimetric analysis, the end product is weighted and has direct relationship with the substance to be quantitatively analyzed or simply we can say that in gravimetric analysis, we convert the soluble form of a substance into a solid which involves heating, evaporation, precipitation, digestion, filtration, drying, ignition, cooling and weighing. The solid thus produced should be stable, weighted and possess high molecular weight. All these processes are discussed as follows: Precipitation is a formation of a solid (precipitate) in a solution. The chemical substance used to form a precipitate is called as precipitant or precipitating reagent. The precipitate get collected at the bottom of the solution.The soluble form of a substance whose gravimetric estimation is to be performed, if concentrated is diluted using distilled waterand then heated slowly. Now in order to form a precipitate, a precipitating reagent is added into the solution slowly with constant stirring. Heating is done in order to have good crystals. Precipitating reagent is added in such an amount that the substances get completely precipitated because an extra addition of precipitating reagent makes the precipitate partially soluble. In order to check the complete precipitation, few drops of a precipitating reagent is added in such a way that the solution remains undisturbed. If on adding precipitating reagent, there is formation of a precipitate, then more precipitating reagent is added. If no such precipitation takes place in the solution above the precipitate then it indicates that the precipitation is completed. The precipitate thus formed is heated gently or slowly on water bath for half an hour. This process of heating the precipitate slowly for half an hour is known as digestion. The precipitate is said to be digested. After digestion, filtration process is performed. Filtration involves the separation of precipitates from the solution. Filter paper, asbestos mats, porous glass crucibles are used. Porous means with pores. We generally use filter paper and porous crucibles for filtration. Filter papers are available in large amount which differ in their pore size. Whatman number 42 is a commonly used filter paper for the process of

filtration. In a funnel, filter paper is wrapped properly and kept over the tripod stand. The solution having precipitate is added slowly over the funnel provided with beaker placed below it. In this way, we obtain precipitate as residue on the filter paper and the solution (filtrate) is collected into a beaker which is shown in Figure 1.

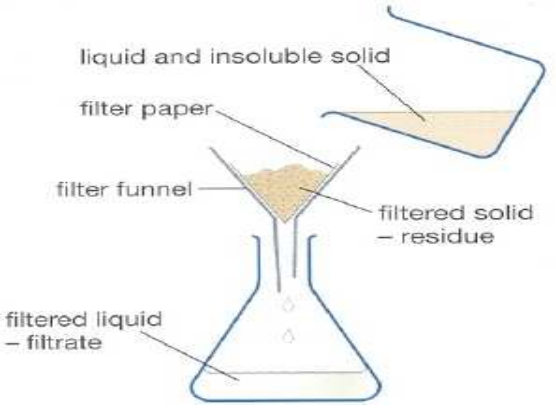


Figure 1. Filtration process

The precipitate is then washed in order to remove unwanted ions. These ions are attached to the precipitate causing high yield of the precipitate. Washing is done with fast current of water. Fast current of the water allow the precipitate to agitate due to which ions attached to the precipitate get disturbed. The unwanted ions take time to settle being lighter and as a result they get filtered. After washing, the filtrate is tested in order to detect unwanted ions. If the filtrate contains unwanted ions, it is further washed with fast current of water and the process of washing is continued till the filtrate thus obtained is free from unwanted ions. Now after washing of the precipitate, drying of the precipitate is performed. The funnel having filter paper containing precipitate is covered with a paper having small pores is placed on the tripod stand and is heated. This is the common method of drying as shown in Figure 2.

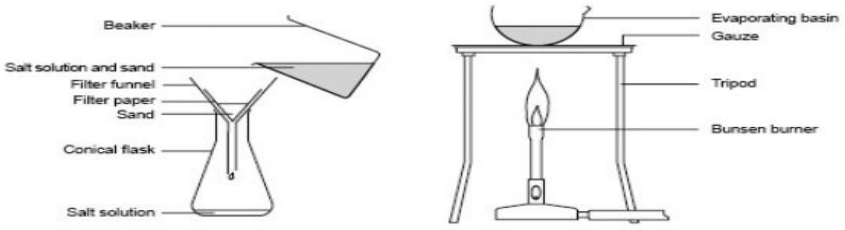


Figure 2. Filtration followed by drying process

It can also be performed in an electric oven also. Dried precipitate is collected on a butter paper in order to avoid the loss of the yield. The precipitate is then covered with a funnel (by inverting it). We will observe that even after removing the dried precipitate from the filter paper still some precipitate remain attached to the filter paper. In order to remove the attaching precipitate, the process of ignition is performed. In this process,a silica crucible is taken, heated to red hot and weigh empty until a constant weight is obtained. The filter paper containing some precipitate is folded and is burned completely in a non- sooty flame by holding it with a pair of tongs. As a result of burning, ash is obtained which is then taken in a silica crucible. The ash is then heated till it becomes white. Now the precipitate which get reduced is recovered. Different chemicals are required for the recovery of the precipitate. Now the precipitate is transferred from butter paper to the crucible. The crucible is then cooled, weigh by using a digital analytical balance. In this way we can obtain a solid mass from the solution in the form of precipitate. There are several experiments on the gravimetric analysis which is discussed below.

2.4 DETERMINATION OF ALUMINIUM AS ALUMINIUM (III) OXIDE

In this section, we will find the weight of aluminium which is precipitated in the form of aluminium (III) oxide (Al_2O_3). For this, a salt of aluminium is taken (potash alum). Let us discuss the complete process below:

2.4.1 Reagents used:

Solution of potash alum (K_2SO_4. $Al_2(SO_4)_3.24H_2O$) which is provided as sample, ammonium nitrate solution (NH_4NO_3), ammonia solution (NH_4OH), ammonium chloride (NH_4Cl) etc.

2.4.2 Apparatus Used:

Volumetric flask, funnel, beaker, dropper, glass rod, tripod stand, burner, filter paper, wire gauge, digital analytical balance, tong, silica crucible, desiccator, butter paper.

2.4.3 Indicator used:

Methyl red is used as an internal indicator. For this, 0.1g of methyl red is dissolved in 50 ml alcohol (ethanol) thereby making an alcoholic solution of methyl red indicator.

2.4.4 Theory:

When ammonia solution is added to the solution of potash alum (sample) under hot condition in the presence of ammonium chloride, then there is precipitation of aluminium as hydroxide. Chemically this can be represented by following reactions:

$$2\,Al_2(SO_4)_3 + 6\,NH_4OH \longrightarrow 2\,Al(OH)_3\downarrow + 3\,(NH_4)_2SO_4$$

From potash alum Precipitate

The precipitate of aluminium hydroxide, Al $(OH)_3$thus formed undergoes filtration, washing, drying, ignition, cooling and weighing. During drying, water is removed from aluminium hydroxide. Thus we obtain the precipitate of aluminium (III) oxide, Al_2O_3as the end product which is weighted.

$$2\,Al(OH)_3 \xrightarrow[\triangle]{} Al_2O_3 + 3\,H_2O$$

2.4.5 Preparation of solutions:

The following solutions are to be prepared: potash alum solution (sample), ammonium nitrate solution and ammonia solution. Let us start with the preparation of sample. The sample will be provided by the teaching staff. A particular amount of potash alum is weighted and transferred to volumetric flask as required. By adding distilled water, the solution is prepared. Now we will discuss the preparation of ammonium nitrate solution. For this, weigh 1.0 g of ammonium nitrate using digital analytical balance and transfer into a beaker. Measure 50ml of distilled water using measuring cylinder and transfer it into the beaker containing 1.0 g ammonium nitrate. In this way 50 ml solution of ammonium nitrate solution is prepared. Moving to the third solution, ammonia solution. Measure 30 ml of liquid ammonia using measuring cylinder and transfer it into a beaker. To the beaker, add 30 ml distilled water. The prepared solution is 1:1 ammonia solution.in this way, we have three solution.

2.4.6 Procedure:

Let us discuss the process involved in the determination of aluminium as aluminium (III) oxide. For this, 500 ml beaker is required. Pipette out 20 ml of sample and

transfer it to 500 ml beaker. Add 130 ml distilled water in it making a total solution of 150 ml in order to avoid co-precipitation. Weigh 2.0- 4.0 g of ammonium chloride (solid) using digital analytical balance and transfer it to the beaker containing sample. Add 3 or 4 drop of alcoholic solution of methyl red indicator into the beaker. In this way, 500 ml beaker contains sample, ammonium chloride and methyl red. Now heat this solution nearly to boiling so that precipitate does not attain colloidal state. Add ammonia solution dropwise slowly into the beaker with constant stirring. Continue the addition of ammonia solution until the solution becomes yellow. The ammonia solution cause precipitation therefore it is a precipitating reagent. On adding ammonia solution, there is formation of precipitate of aluminium hydroxide. In order to accumulate the precipitate, very small amount of tannic acid (solid) is added into the beaker. Now the solution in the beaker is boiled to undergo the process of digestion. After this, the precipitate is allowed to settle (3 to 4 hours) till the supernatant liquid (liquid lying above the precipitate) is clear. Now after setting down of the precipitate, filtration process is to be performed. For this, Whatman filter paper no. 42 is used. The process is explained in section 2.3 with figure. After filtration, the washing of the precipitate is done with ammonium nitrate solution (hot). Precipitate is washed for about 4 to 5 time in order to remove unwanted ions ($SO_4^{2—}$, $Cl^–$). As unwanted ions takes time to settle, they get filtered. For testing SO_4^{2-}, barium chloride is added while for testing $Cl^–$, silver nitrate is used. After washing, drying of the precipitate is done. In drying, the funnel having filter paper containing precipitate of aluminium hydroxide is covered with a paper having small pores. It is then placed over tripod stand having burner below it for drying as shown in section 2.3. Now transfer the precipitate to the butter paper and cover it with inverted funnel. We will observe that after transferring the precipitate, some precipitate still remain attached to the filter paper. Hence in order to increase the yield of the precipitate, the process known as ignition is performed in which the filter paper is placed in a silica crucible which is then burnt strongly using a burner until the formation of white ash. One point to be noted is that before placing filter paper to the silica crucible, the crucible (empty) is heated to red hot, then it undergoes cooling in a desiccators and weighing process using digital analytical balance, till a constant weight of empty crucible is obtained. After the formation of white ash, the precipitate is transferred from butter paper to the crucible. Now allow the crucible containing the precipitate to cool for some time at room temperature and then in a desiccators for 15 minutes. Finally the weighing of the crucible is done. By subtracting the

weight of empty crucible from the weight of crucible containing the precipitate, the weight of precipitate is calculated.

2.4.7 Calculations:

The chemical formula of potash alum is K_2SO_4. $Al_2(SO_4)_3.24H_2O$ which shows that it contains two aluminium. Therefore:

K_2SO_4. Al_2 $(SO_4)_3.24H_2O$ = 2 Al = Al_2O_3

Potash alum

53.94g 101.94 g

Conversion factor = formula weight of 2 Al/ formula weight of Al_2O_3

= 53.94/ 101.94 = 0.5291

Weight of aluminium = conversion factor × weight of the precipitate

= 0.5291 × weight of the precipitate

Weight of the precipitate is calculated as explained above in the procedure by weighing.

2.4.8 Result:

The weight of aluminium which is precipitated as Al_2O_3in the given sample is …….. g.

2.4.9 Precautions:

Several precautions are to be taken while performing the experiment:

1. Weighing should be done carefully.

2. The solution should be hot before adding the precipitating reagent.

3. Precipitating reagent should be added drop-wise with constant stirring using clean glass rod.

4. Remember to add ammonium chloride in order to maintain the pH of the solution as it acts as buffer with ammonia solution.

5. Filter paper having attached precipitate should be burnt completely to ash in the ignition process.

6. Ensure the removal of sulphate and chloride ions

2.4.10 Self- assessment questions (SAQ):

- Fill in the blanks:

1. The chemical formula of potash alum is …….

2. The precipitating reagent in the determination of aluminium as $Al_2O_3$is …….

3. The washing solution used in the determination of aluminium as $Al_2O_3$is …….

4. The precipitating reagent is added to ……. solution.

5. Before drying, the aluminium is precipitated in the form of …….

6. After drying, the aluminium is present in the form of …….

7. The cooling of the precipitate is performed in …….

8. In order to maintain pH of the solution, ……. is added before the addition of ammonia solution.

9…….. and ……. Are used to test sulphate and chloride ions in the solution.

2.5 DETERMINATION OF COPPER AS COPPER (I) THIOCYANATE

In this section, the weight of copper is calculated which is precipitated in the form of copper (I) thiocyanate (CuSCN). For this any salt containing copper is taken, in this case copper sulphate ($CuSO_4.5H_2O$) is used. The whole process is discussed below:

2.5.1 Reagents used:

The following reagents are used: copper sulphate solution (sample), acetic acid, sulphurous acid solution (H_2SO_3), ammonium thiocyanate solution, 20% ethanol, dilute HCl.

2.5.2 Apparatus used:

Volumetric flask, funnel, beaker, dropper, glass rod, tripod stand, burner, filter paper, wire gauge, digital analytical balance, tong, silica crucible, desiccator, butter paper.

2.5.3 Theory:

In the solution of copper sulphate, sulphurous acid is added along with few drops of dil. HCl to make the medium slightly acidic. In the presence of sulphurous acid (reducing agent), there is reduction of Cu^{2+} to Cu^{+}. The copper (I) thiocyanate is precipitated from the solution of copper sulphate. The chemical reactions involved in the process are:

$$2Cu^{2+} + SO_3^{2-} + H_2O \longrightarrow 2Cu^{+} + SO_4^{2-} + 2H^{+}$$

copper sulphate sulphurous acid

Now to the solution, precipitating reagent (ammonium thiocyanate) is added dropwise with constant stirring.

$$2Cu^{+} + 2SCN^{-} \longrightarrow 2CuSCN\downarrow$$

Ammonium thiocyanate Copper thiocyanate (white)

2.5.4 Preparation of solutions:

The following solutions are to be prepared: solution of copper sulphate (sample), ammonium thiocyanate solution, sulphurous acid solution, washing solution. The copper sulphate solution (sample) is provided by the teachers and is prepared in the same manner as discussed in the above experiment. While making the sample, few drops of acetic acid is added in order to check the hydrolysis of the salt. Now moving to another solution i.e. solution of ammonium thiocyanate (NH_4SCN) which acts as precipitating reagent. Weigh 10 g of NH_4SCN using digital analytical balance and transfer it to 100 mL volumetric flask. Add distilled water first in small amount and after dissolution further add distilled water up to the mark. The prepared solution is NH_4SCN solution. For preparing sulphurous acid solution, sulphur dioxide (SO_2) gas is passed in 50 mL of distilled water. SO_2 gas in the laboratory is formed by adding hot concentrated sulphuric acid on copper turnings. For the preparation of washing solution, we require the mixture of distilled water, NH_4SCN and H_2SO_3. To about 100 mL distilled water, 1 mL of above prepared NH_4SCN solution is added along with 3-4 drop of H_2SO_3. The last solution is 20% ethanol. For this 20 ml of ethanol is added in distilled water, making a total volume of 100 mL.

2.5.5 Procedure:

Now in order to estimate copper as copper (I) thiocyanate from copper sulphate solution, the following procedure has to be followed: Pipette out 20 ml of the sample and transfer it to 500 ml beaker. Now to the beaker, dilute solution of HCl is added (few drops) along with 15- 20 mL of sulphurous acid solution. Now add distilled water into the beaker making a total volume of 150 ml so that co- precipitations do not take place. Allow the solution in the beaker to be heated nearly to boiling as it leads to good crystal formation. When solution boils, the precipitating reagent, ammonium thiocyanate solution is added slowly into the beaker dropwise (5 mL) with constant stirring. We will observe the formation of curdy white precipitate of copper (I) thiocyanate. Digest the precipitate and allow it to settle down for 3 to 4 hours. The process of filtration is performed as done in the earlier experiment. Washing is done using washing solution under cold condition to prevent the oxidation of Cu(I) to Cu (II). After washing, drying process is performed at 100^{o}C followed with ignition process (ash treatment). The silica crucible (red hot) is first weigh empty till a constant weight is obtained and then with the precipitate. Now after the formation of white ash as explained in above experiment, the precipitate is transferred from butter paper to the crucible. Now allow the crucible containing the precipitate to cool for 30 minutes in the desiccator and then weighing is done. Finally the weight of precipitate is calculated.

2.5.6 Calculations:

For determining the weight of precipitate (CuSCN), we have taken $CuSO_4.5H_2O$ solution as a sample. Therefore:

$CuSO_4.5H_2O$ contains one copper = Cu = CuSCN

249.68 g 63.5 g 121.63 g

Conversion factor = formula weight of Cu/ formula weight of CuSCN = 63.5/ 121.63 = 0.522

Weight of copper = 0.522 × weight of the precipitate (CuSCN)

2.5.7 Result:

The weight of copper which is precipitated as copper (I) thiocyanate in the given sample is ..... gram.

2.5.8 Precautions:

Several precautions are to be taken while performing the experiment:

1. Weighing should be done carefully.

2. The solution should be hot before adding the precipitating reagent.

3. Precipitating reagent should be added dropwise with constant stirring.

4. Always add sulphurous acid while making washing solution as it prevent the oxidation of Cu(I) to Cu(II).

2.5.9 Self- assessment questions (SAQ):

- Fill in the blanks:

1. In the estimation of Cu as Cu (I) thiocyanate, the precipitating reagent used is …….

2. Sulphurous acid is added into the solution, as it acts as ……. agent.

3. The color of copper (I) thiocyanate precipitate is …….

4. Washing solution is a mixture of ……., ……. and …….

5. The chemical formula of copper sulphate is …….

2.6 DETERMINATION OF IRON AS IRON (III) OXIDE

In this section, we will estimate iron in the form of iron (III) oxide. For this, any salt of iron is taken (in this case, ferrous ammonium sulphate). The complete process is discussed below:

2.6.1 Reagents used:

The following reagents are used in the experiment: solution of ferrous ammonium sulphate (sample), dil. sulphuric acid (H_2SO_4), ammonia solution (NH_4OH), ammonium nitrate solution (NH_4NO_3), conc. nitric acid (HNO_3).

2.6.2 Apparatus used

Volumetric flask, funnel, beaker, dropper, glass rod, tripod stand, burner, filter paper, wire gauge, digital analytical balance, tong, silica crucible, desiccator, butter paper.

2.6.3 Theory:

Ferrous ammonium sulphate solution ($FeSO_4$. $(NH_4)_2SO_4.6H_2O$) is used in order to precipitate iron as iron (III) oxide. In ferrous ammonium sulphate, iron is present as Fe^{2+}. For the oxidation of Fe^{2+} to Fe^{3+}, conc. HNO_3 is added. The reaction involved in the process is as follows:

$$\underset{\text{Mohar's salt}}{2\,Fe^{2+}} + \text{Con. } HNO_3 \longrightarrow 2Fe^{3+}$$

$$2Fe^{3+} + \overline{O}H \longrightarrow Fe(OH)_3\downarrow$$

From NH_4OH

The precipitate of ferric hydroxide Fe $(OH)_3$), is red- brown in color which further undergoes drying to form iron (III) oxide (Fe_2O_3).

$$2\,Fe(OH)_3 \longrightarrow \underset{\text{Red brown}}{Fe_2O_3} + 3H_2O$$

In this way, iron is precipitated as iron (III) oxide gravimetrically.

2.6.4 Preparation of solutions:

The following solutions are to be prepared: solution of ferrous ammonium sulphate (sample), ammonia solution and solution of ammonium nitrate (NH_4NO_3). The sample is prepared by dissolving a particular amount of salt in distilled water in a volumetric flask (fixed volume). The sample is provided by teacher. Another solution to be prepared is of ammonia. For this 30 ml of ammonia is mixed with 30 mL of distilled water making a total of 60 mL. Here ammonia solution is used as a precipitating reagent. Now moving to another solution i.e. ammonium nitrate, 1.0 g of ammonium nitrate is weighted by using digital analytical balance and is transferred to 100 mL volumetric flask using a funnel. Now add distilled water up to the mark. The prepared solution is NH_4NO_3 solution.

2.6.5 Procedure:

In order to estimate iron as iron (III) oxide, we have to follow the given procedure: Pipette out 20 ml of the sample provided and transfer it to 500 ml beaker. In order to avoid co-precipitation, add 30 ml of distilled water into the beaker and the mixture is heated nearly to boiling (as it leads to the formation of good crystals).Allow the solution to cool and then add 5 ml of concentrated HNO_3. HNO_3, nitric acid is a strong acid and acts as an oxidizing agent. Now boil the mixture for 5 minutes so that all Fe^{2+} are oxidized to Fe^{3+}. Now add

200 ml of distilled water into the beaker containing the mixture. Again the mixture is heated to nearly boiling and precipitating reagent i.e. ammonia solution is added dropwise with constant stirring till the medium becomes basic. The presence of the basic medium is detected by the presence of odour of the vapour that appears form the mixture. This leads to the formation of reddish- brown precipitate of $Fe(OH)_3$. Now the precipitate is digested. After digestion, allow the precipitate to settle down. Now filtration is done using Whatman filter paper 42. After filtration, washing of the precipitate is to be done by using the above prepared NH_4NO_3solution (hot) in order to remove unwanted ions like sulphate. After washing, wait for few minutes, dry it and then transfer the precipitate to the butter paper. Then for removing the attached precipitate, ash treatment is done in the same way as done in the earlier experiment. Now transfer the precipitate from butter paper to the silica crucible and allow the crucible to cool in a desiccator. After cooling of the precipitate, weighing process is done and the weight of the precipitate of Fe_2O_3 is calculated as done in earlier experiments. In this way, we determine iron as iron (III) oxide from a solution of ferrous ammonium sulphate.

2.6.6 Calculations:

The chemical formula of is ferrous ammonium sulphate is $FeSO_4.(NH_4)_2SO_4.6H_2O$. Therefore:

$$2\ FeSO_4.(NH_4)_2SO_4.6H_2O = 2\ Fe = Fe_2O_3$$

$$2\ FeSO_4.(NH_4)_2SO_4.6H_2O = 2\ Fe = Fe_2O_3$$

783.92 g 111.68 g 159.68 g

Conversion factor = formula weight of 2 Fe / formula weight of Fe_2O_3

= 111.68/ 159.68 = 0.6994

Weight of iron = 0.6994 × weight of the precipitate (Fe_2O_3)

2.6.7 Result:

The weight of iron which is precipitated as iron (III) oxide in the given sample is …….g.

2.6.8 Precautions:

Several precautions are to be taken while performing the experiment:

1. Before precipitation, all Fe(II) must be oxidized to Fe(III) which can be checked by using potassium ferricyanide. With Fe(II), it gives blue color while with Fe(III), it gives no color.

2. Removal of sulphate ions after washing must be checked.

2.6.9 Self- assessment questions (SAQ):

- Fill in the blanks:

1. The chemical formula of ferrous ammonium sulphate is …….

2. Concentrated nitric acid acts as an ……. agent.

3. The washing solution used in the estimation of iron as iron (III) oxide is …….

4. The precipitating reagent used in the estimation of iron as iron (III) oxide is …….

5. In the given experiment, iron in ……. state is oxidized to ……. state.

2.7 DETERMINATION OF SULPHATE IONS AS BARIUM SULPHATE

In this experiment, we will determine the weight of sulphate ions which are precipitated as barium sulphate. For this, salt containing sulphate is taken in which barium chloride is added to form precipitate of barium sulphate. The complete process is discussed below:

2.7.1 Reagents used

The following reagents are used in the experiment: sample (copper sulphate solution),HCl solution and barium chloride ($BaCl_2$) solution.

2.7.2 Apparatus used

The apparatus used aresame as given in the above experiments.

2.7.3 Theory:

Sulphate ions are precipitated as barium sulphate by adding dilute solution of barium chloride (hot) into the solution containing sulphate ions or sample. The following reaction takes place if the sample provided is of copper sulphate ($CuSO_4$):

$$CuSO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + CuCl_2$$

White precipitate

2.7.4 Preparation of solutions:

The following solutions are to be prepared: Barium chloride solution, solution of copper sulphate sample, HCl solution. Let us start with the preparation of $BaCl_2$ solution. Weigh 5.0 g of barium chloride and transfer it to 100 ml volumetric flask using a funnel, add distilled water up to the mark. The prepared solution is 5% $BaCl_2$ solution. Now moving to the sample, it is prepared by dissolving a particular amount of copper sulphate in the fixed volume of distilled water in a volumetric flask. This solution is provided by the instructor. For HCl solution, 5 mL of conc. HCl is mixed with 5 mL of distilled water.

2.7.5 Procedure:

In order to perform the experiment, first of all pipette out 20 ml of sample ($CuSO_4$) provided and transfer it to 500 ml beaker. Add 100 ml of distilled water into the beaker, making a total of 120 ml solution. Now to the beaker, add 3 ml of dilute HCl solution in order to have high yield of crystals. The solution is then heated to nearly boiling and addition of 5% barium chloride solution is started drop wise with constant stirring. This lead to the formation of white precipitate of barium sulphate ($BaSO_4$). In order to check precipitation, few drops of precipitating reagent is added further. Digest the precipitate and allow it to settle. After setting down of the precipitate, filtration process is carried out followed with washing of the precipitate with hot distilled water. Now the washed precipitate undergoes the process of drying to nearly 100^oC in an oven. After drying, the precipitate is transferred to a butter paper and the remaining precipitate is recovered by the process of ignition. After ignition, the precipitate is transferred from the butter paper to the silica crucible containing the white ash. The crucible is then cooled in a desiccator followed by weighing process. In this way, sulphate ions are precipitated as barium sulphate (white color).

2.7.6 Calculation:

It is clear that sulphate ions taken in the form of $CuSO_4$ is precipitated as barium sulphate, therefore:

$$SO_4^{2-} = BaSO_4$$

96.06 g 233.42 g

Conversion factor = formula weight of SO_4^{2-}/ formula weight of $BaSO_4$

$$= 96.06/ 233.42 = 0.4115$$

Weight of SO_4^{2-}= 0.4115 × weight of the precipitate

2.7.7 Result:

The weight of sulphate ions that are precipitated in the form of barium sulphate in the provided sample is ……. g.

2.7.8 Precautions:

The following precautions are to be undertaken while performing the experiment:

1. Precipitation should be done when the solution is hot.

2. Always remember to add dil. HCl as it leads to the formation of good crystals.

3. For accurate result, drying should be done properly.

2.7.9 Self- assessment questions (SAQ):

- Fill in the blanks

1. The precipitating reagent used in the estimation of sulphate ions as barium sulphate is …….

2. The washing solution used in the above experiment is …….

3. Dilute HCl is added in order to have ……. crystals.

4. The color of barium sulphate crystals is …….

5. Conversion factor is a ratio of …….

2.8 DETERMINATION OF ALUMINIUM AS ALUMINIUM 8-HYDROXYQUINOLINATE

Under this topic, we will determine the weight of aluminium which is precipitated as aluminium 8- hydroxyquinolinate by adding oxine solution (8- hydroxyquinoline). For this, the sample containing unknown salt of aluminium is taken. The detail of the experiment is discussed below:

2.8.1 Reagents used:

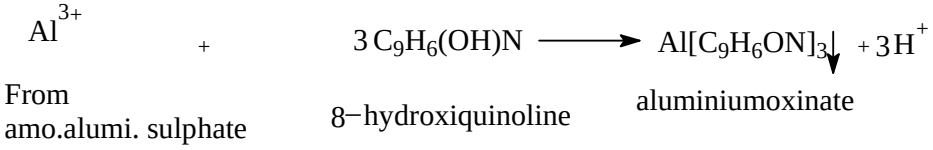
The following reagents are used: ammonium aluminiumsulphate solution (sample), dil. HCl, oxine solution, acetic acid and ammonium acetate solution.

2.8.2 Apparatus used:

The apparatus taken are same as used in earlier experiments.

2.8.3 Theory:

Aluminium is one of the metal that form complex with oxine. The complex is insoluble leading the formation of precipitate of aluminiumoxinate. Oxine is a bidentate ligand which is also known as 8- hydroxyquinoline. When oxine solution is added to the sample containing aluminium (ammonium aluminiumsulphate) in the pH range 4 to 10, Al^{3+} reacts with oxine. The reaction is represented as:



In this way, the precipitate of aluminiumoxinate($Al[C_9H_6ON]_3$) takes place.

2.8.4 Preparation of solutions:

The following solution are to be prepared: ammonium aluminiumsulphate solution, $NH_4Al(SO_4)_2$ which acts as a sample, oxine solution, acetic acid solution and ammonium acetate solution. Let us start with the preparation of the sample which is prepared by dissolving a particular amount of ammonium aluminiumsulphate in distilled water in a

fixed volume (volumetric flask). Now for the preparation of the oxine solution, 1.0 g of oxine is weighted and transferred to 50 mL volumetric flask. About 10% acetic acid solution is prepared and this solution is transferred to the 50 mLvolumetric flask containing the oxine up to the mark. The prepared solution is of oxine. Now for ammonium acetate solution, 15.4 g of ammonium acetate is weighed and transferred to 100 mL volumetric flask. Distilled water is added up to the mark. The solution prepared is of ammonium acetate.

2.8.5 Procedure:

Pipette out 20 mL of the provided sample and transfer it to 500 mL beaker. Add distilled water making a total volume 150 mL. Now add dil. HCl (2 mL) into the beaker. Now the solution is heated nearly to boiling. For precipitation to take place, oxine solution is added dropwise with constant stirring along with addition of ammonium acetate solution slowly. Ammonium acetate acts as a buffer maintaining the pH in the range 4 to 10 that is required for the formation of aluminiumoxinate (precipitate). The precipitate thus formed is digested by heating which is followed by further addition of ammonium acetate solution (nearly 20 mL). In order to check complete precipitation, the supernatant liquid which in the beginning is greenish- yellow in color changes to orange- yellow color at the end of the precipitation. Therefore, the beaker containing the precipitate is covered with watch glass for observing the change in color. Now the precipitate will settle down and the filtration process is followed as done in previous experiments. After this, washing of the precipitate is done by cold distilled water followed by drying of the precipitate at $110^{o}C$ in order to remove moisture. After ash treatment the precipitate is collected in the silica crucible. The precipitate then undergoes cooling process in a desiccator followed by weighing process. In this way, we determine the weight of aluminium which is precipitated as aluminium 8- hydroxyquinolinate or aluminiumoxinate.

2.8.6 Calculations:

In the given experiment, the aluminium is precipitated in the form of aluminium 8-hydroxyquinolinate. Therefore:

Al^{3+}(ammonium aluminiumsulphate) = $Al\,[C_9H_6ON]_3$

26.97 g 459.43 g

Conversion factor = formula weight of Al^{3+}/ formula weight of Al $[C_9H_6ON]_3$

= 26.97 / 459.43 = 0.0587

Weight of aluminium = 0.0587 × weight of the precipitate (Al $[C_9H_6ON]_3$)

2.8.7 Result:

The weight of aluminium which is precipitated as aluminium 8- hydroxyquinolinate in the given sample is …….g.

2.8.8 Precautions:

The following points should be considered while performing the experiment:

1. Dilute HCl should be added in small amount.

2. Precipitating reagent should be added slowly with constant stirring.

2.8.9 Self- assessment questions (SAQ):

- Fill in the blanks:

1. The color of aluminium 8- hydroxyquinolinate is …….

2. The pH range required for the estimation of aluminium is …….

3. The chemical formula of ammonium aluminiumaulphate is …….

4. The chemical formula of aluminium 8- hydroxyquinolinate is …….

5. Oxine is a ……. ligand.

2.9 SUMMARY

In this unit, we have discussed the gravimetric analysis in detail in which we have determined the amount of substance present in a given sample by using the weight of the product formed. In this unit, five different analyses are undertaken. In the first analysis, we have calculated the weight of aluminium which is precipitated as aluminium (III) oxide in the given sample of aluminium salt. In the second analysis, we have calculated the weight of copper which is precipitated as copper (I) thiocyanate in the provided sample of copper salt. In the third analysis, we have calculated the weight of iron which is precipitated as iron (III) oxide in the given sample of salt containing iron. In the fourth analysis, we have

calculated the weight of sulphate ions which are precipitated as barium sulphate in the given sample of salt containing sulphate ions and in the fifth analysis, we have calculated the weight of aluminium which is precipitated as aluminium 8- hydroxyquinolinate in the provided sample.

2.10 GLOSSARY

- **Precipitation –** Process of formation of a solid from a solution.
- **Digestion –** Process of heating of precipitate for about half an hour.
- **Filtration –** Separation of a precipitate from the supernatant liquid.
- **Precipitant –** Chemical substance used to form precipitate (solid insoluble mass).

2.11 POSSIBLE ANSWERS TO SAQ

2.4.10 Self- assessment questions (SAQ)

- Fill in the blanks:

1. K_2SO_4. $Al_2(SO_4)_3.24H_2O$; 2. Ammonia solution; 3. Ammonium nitrate solution; 4. Hot;

5. $Al(OH)_3$; 6. Al_2O_3 ; 7. Desiccator; 8. Ammonium chloride 9. $BaCl_2$ and $AgNO_3$

2.5.9 Self- assessment questions (SAQ)

- Fill in the blanks:

1. Ammonium thiocyanate; 2. Reducing; 3. Curdy white; 4. Ammonium thiocyanate, sulphurous acid, distilled water; 5. $CuSO_4$. $5H_2O$

2.6.9 Self- assessment questions (SAQ)

- Fill in the blanks:

1. $FeSO_4$. $(NH_4)_2SO_4.6H_2O$; 2. Oxidizing; 3. 1% ammonium nitrate; 4. Ammonia solution; 5. Second, Third

2.7.9 Self- assessment questions (SAQ)

- Fill in the blanks

1. Barium chloride solution; 2. Hot distilled water; 3. Good; 4. White; 5. Formula weight of SO_4^{2-}/ Formula weight of $BaSO_4$

2.8.9 Self- assessment questions (SAQ)

- Fill in the blanks:

1. Yellow; 2. 4 to 10; 3. $NH_4Al(SO_4)_2$; 4. Al $[C_9H_6ON]_3$; 5. Bidentate

2.12 REFERENCES

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2.13 TERMINAL QUESTIONS

1. Explain the process of determination of aluminium as aluminium (III) oxide and aluminium 8- hydroxyquinolinate respectively.
2. Taking two example, explain how the amount of substance is determined by gravimetric analysis.

UNIT 3: VOLUMETRIC ANALYSIS

CONTENTS:

3.1 Objective

3.2 Introduction

3.3 Determination of sodium carbonate and sodium hydroxide in a mixture by indicator method

3.3.1 Chemicals and equipments required:

3.3.2 Theory

3.3.3 Procedure

3.3.4 Observation table

3.3.5 Calculations

3.3.6 Results

3.3.7 Precautions

3.4 Determination of the strength given farrous ammonium sulphate solution by permanganatometry

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3.4.4 Observations and calculations

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3.5 Determination of the percentage of iron in given farrous ammonium sulphate solution by chromatometry

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3.6 Determination of the percentage of available chlorine in given water sample containing bleaching powder

3.6.1 Chemicals and equipments required

3.6.2 Theory

3.6.3 Procedure

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3.6.5 Calculations

3.6.6 Result

3.6.7 Precautions

3.7 Determination hardness (total, permanent and temporary) of water by complexometry

3.7.1 Introduction

3.7.2 Chemicals and equipments required

3.7.3 Theory

3.7.4 Procedure

3.7.5 Observations

3.7.6 Calculations

3.7.7 Results

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3.8 Summary

3.9 Terminal questions

3.10 Answers

3.1 OBJECTIVE

Laboratory exercises discussed here are designed to give you knowledge and skills to design, understand and perform volumetric analyses. You should be able to implement this knowledge to various analysis scenarios. Volumetric analysis refers to titrations, a quantitative analysis technique widely used to determine quantity of a constituent present

in analyte of interest. Titrations are of several types, for instance, acid-base titrations, complexometric titrations, redox titrations and precipitation titrations.

First experiment, *i.e.*, determination of sodium carbonate and sodium hydroxide in a mixture by indicator method is an acid-base titration. You will learn that different indicators can be used depending on the pH range of indicator and the pH of reaction mixture at end point. Second and third experiments are the redox titrations utilizing oxidizing agents $K_2Cr_2O_7$ and $KMnO_4$ respectively. These experiments essentially involve oxidation reduction reactions between the analyte and titrant. Exercises 3.4 and 3.5 also put across that a suitable indicator can be used if the colour change of analyte or titrant at the end point of redox titrations is not remarkable. Iodometric titration discussed in fourth exercise is essentially a redox titration. It should be kept in mind that in iodometric titration, the either appearance or disappearance of elementary iodine can be utilized to indicate the end point. Exercise 3.6 uses disappearance of iodine as indicator event. Exercise 3.7 portrays a complexometric titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. This experiment teaches how the formation of a complex can be used to indicate the end point of a titration.

Experiments in a chemistry laboratory almost always involve reagents those have several hazardous associated with them. Some reagents that we use are strong oxidizing agents; others are flammable or form toxic vapours. Learning safe laboratory practices is always one of the prime objectives of laboratory exercises. Hence, you will learn to deal with titration assemblies, delicate glassware and liquid reagents etc.

3.2 INTRODUCTION

Chemical analyses are of two types; qualitative and quantitative. Qualitative analysis involves identification of the constituents, *e.g.*, elements, ions or functional groups, present in a substance whereas quantitative analysis involves determination of the quantities of particular constituents present in a substance. Volumetric analysis is the term used for quantitative chemical analyses which involve measurement of volumes of substances or their solutions in order to determine the particular constituents of the substance of interest. A term, titrimetric analysis is also often used to describe such experiments. Thus, titrimetric analysis or titrimetry is a common laboratory method of

quantitative chemical analysis. It is used to determine the unknown concentration of a known analyte by treating a certain volume of it with known concentration and volume of a reagent called titrant. You must bear in mind that volume measurement play most vital role in titrimetric or volumetric analysis, hence such measurements should be performed with utmost care.

3.3 DETERMINATION OF SODIUM CARBONATE AND SODIUM HYDROXIDE IN A MIXTURE BY INDICATOR METHOD

3.3.1 Chemicals and equipments required:

An aqueous solution of NaOH and Na_2CO_3 (mixture solution), phenolphthalein indicator, methyl orange indicator, standard hydrochloric acid (0.1 N), burette, pipette, conical flasks etc.

3.3.2 Theory:

Determination of sodium carbonate and sodium hydroxide in a solution containing mixture of these alkalies by indicator method involves acid base titration. Thus, the solution containing both alkalies is titrated against a strong acid such as hydrochloric acid. Reaction of hydrochloric acid with sodium hydroxide is a single step neutralization reaction as presented by equation (i). At the equivalence point of reaction (i) solution turns neutral due to complete neutralization of strong alkali sodium hydroxide by the strong acid hydrochloric acid. This equivalence can be determined by indicator phenolphthalein.

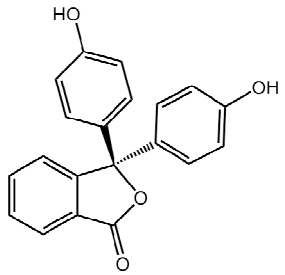


Figure 1. Molecular structure of phenolphthalein indicato

On the other hand neutralization of sodium carbonate with hydrochloric acid involves two steps presented by equations (ii) and (iii). At equivalence points of reactions (ii) and (iii)

the reaction solutions are alkaline and acidic due to the formation of sodium bicarbonate and carbon dioxide respectively. Thus, suitable indicators for determining the equivalence points of reactions (ii) and (iii) are phenolphthalein and methyl orange respectively.

$$HCl + NaOH \longrightarrow NaCl + H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots \text{(i)}$$

$$HCl + Na_2CO_3 \longrightarrow NaHCO_3 + NaCl \quad \cdots\cdots\cdots\cdots\cdots\cdots \text{(ii)}$$

$$NaHCO_3 + HCl \longrightarrow H_2O + CO_2 + NaCl \quad \cdots\cdots\cdots\cdots\cdots\cdots \text{(iii)}$$

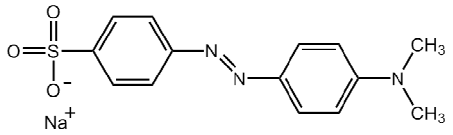


Figure 2. Molecular structure of methyl orange indicator

3.3.3 Procedure:

Set the glassware assembly for the titration experiment. Fill the burette with supplied standard (0.1 N) hydrochloric acid. Take 10 mL mixture solution in a conical flask and add 2-3 drops of phenolphthalein. Phenolphthalein indicator gives pink colour in the alkaline mixture solution. Perform titration by incremental addition of hydrochloric acid from burette in to the conical flask very carefully and stop when the colour of phenolphthalein disappears. At this moment sodium hydroxide is neutralized completely and sodium carbonate is converted to sodium bicarbonate. Now add few drops of methyl orange indicator to the same conical flask. The solution turns yellow in colour. Again perform titration by adding hydrochloric acid from burette. At equivalence point a sharp colour change from yellowish orange to red is observed. At this moment all of the sodium bicarbonate neutralizes as presented in equation (iii). Repeat the experiment three times and tabulate your results in observation table. 1

3.3.4 Observation table:

Table 1 Titration of mixture of NaOH and Na_2CO_3 against acid

S. N.	Volume of mixture in conical flask (mL)	Burette reading for titration with phenolphthalein (mL)			Burette reading for titration continued with methyl orange (mL)			(V_1-V_2)
		Initial	Final	Volume (V_1)	Initial	Final	Volume (V_2)	
1	10 mL							
2	10 mL							
3	10 mL							

3.3.5 Calculations:

For calculations reactions (i), (ii) and (iii) can be interpreted as if the volume of acid consumed for titration in presence of phenolphthalein neutralizes all the sodium hydroxide and half of the sodium carbonate while the titration in presence of methyl orange neutralizes remaining amount of sodium carbonate. Therefore,

$N_{HCl} \times 2V_2 = N_{Sod.carbonate} \times 10$

$N_{Sod.carbonate} = N_{HCl} \times 2V_2/10$

Strength of sod. carbonate = $N_{Sod.carbonate}$ × equivalent weight (g/L)

Strength of sod. carbonate = $N_{Sod.carbonate}$ × 53 (g/L)---------**(iv)**

On the other hand,

$N_{HCl} \times (V_1 - V_2) = N_{NaOH} \times 10$

$N_{NaOH} = N_{HCl} \times (V_1 - V_2)/10$

Strength of NaOH = N_{NaOH} × equivalent weight (g/L)

Strength of NaOH = N_{NaOH} × 40 (g/L)---------**(v)**

Strength of sodium hydroxide and sodium bicarbonate present in the mixture can be calculated using equation (iv) and (v).

3.3.6 Results:

Supplied mixture solution contains _____ g/L sodium hydroxide and _____ g/L sodium bicarbonate.

3.3.7 Precautions:

1. Burette and other glassware must be cleaned and dried before performing experiment.
2. Lower meniscus should be read for taking observations.
3. Acid should be added carefully and dropwise in to the conical flask.
4. Least count of common laboratory burettes is 0.1 mL, hence all readings should be recorded up to first place of decimal in observation table.

3.4 DETERMINATION OF THE STRENGTH OF GIVEN FAROUS AMMONIUM SOLUTION SOLUTION BY PERMANGANATOMETRY

3.4.1 Chemicals and equipments required:

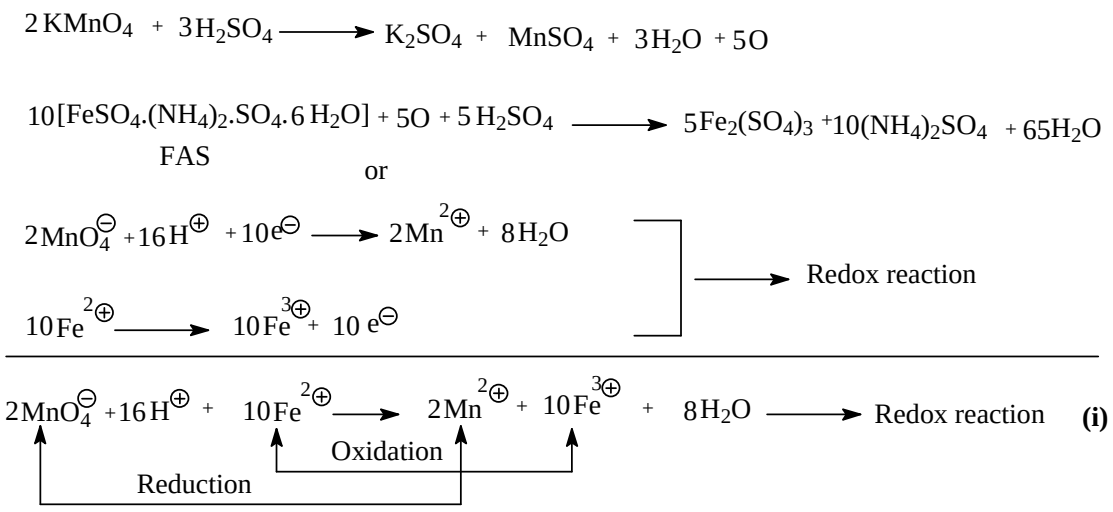
FAS solution, standard ferrous ammonium sulfate solution, KMnO4 solution, sulphuric acid, distilled water, beakers, water bath, glass rod, digital balance, burette and pipette etc.

3.4.2 Theory:

In this experiment you will use an oxidation-reduction (redox) reaction to determine the percentage of iron in a given FAS solution. This experiment consists of three parts.

1. Preparation of standard FAS solution.
2. Standardization of $KMnO_4$ solution by titrating it against standard ferrous ammonium sulfate (FAS) solution
3. Titration of unknown FAS solution against standard $KMnO_4$ solution

   The $KMnO_4$ solution in presence of H_2SO_4 converts the Fe^{2+} to Fe^{3+} as per the following reaction:-



The reaction is carried out at room temperature as on heating $FeSO_4$present is FAS gets oxidised to $Fe_2(SO_4)_3$ by air or elevated temperature.

3.4.3 Procedure:

(i) Preparation of standard ferrous ammonium sulphate solution.

FAS is a primary standard chemical its standard solution can easely be prepared in present experiment this solution will be used to standardise $KMnO_4$ solution. To prepare standard FAS solution prepares N/10 solution in 100 or 250 mL volumetric flask as per your convenience. To prepare N/10 FAS solution in 100 or 250 mL weigh desired weight of FAS by using following equation:

$$w = \frac{ENV}{1000}$$

w = weight needed, E = equivalent weight, N = normality, V= desired volume

The equivalent weight of FAS is 392.

Transfer the weight quantitiy of FAS to a volumetric flask of 100 or 250 mL capacity and add half test tube of dil. H_2SO_4 in order to avoid hydrolysis of FAS. Shake the flask well till all the particls of FAS are dissolved. Add additional distilled water to make-up the volume of 100 or 250mL which represent N/10 FAS solution.

(ii) Standardization of $KMnO_4$ solution:

Rinse a clean burette with distilled water followed by supplied $KMnO_4$ solution. Mount the burette on a stand and fill up to the zero mark with supplied $KMnO_4$. Record the burette reading in observation table. Pipette out 10.0 mL of standard Mohr's salt solution into a conical flask and add 10 mL dilute sulphuric acid. Titrate the two solutions until a permanent light pink colour is obtained which indicates the endpoint of the titration. Record the final burette reading in observation table. Repeat the titrations to get at least two concordant readings and record all readings in observation table 2 (do not heat the titration mixture during the process of titration).

(iii) Determination of the strength of unknown FAS solution:

Refill the burette with same standardized $KMnO_4$ solution and take 10mL unknown FAS solution in conical flask and follow the same procedure as above in step (ii). Repeat the titrations to get two concordant readings. Record all readings in the observation table 3.

3.4.4 Observations and calculations:

Table: 2 Standard FAS solution vs potassium permanganate solution

S.N.	Volume of standard FAS taken in the conical flask (mL)	Burette readings		Volume of $KMnO_4$ used (mL)
		Initial	Final	
1	10.0			
2	10.0			
3	10.0			

Table:3 Titration of unknown FAS solution vs stanandardised $KMnO_4$

S.N.	Volume of FAS solution taken in the conical flask (mL)	Burette readings		Volume of $KMnO_4$ used, (mL)
		Initial	Final	
1	10.0			
2	10.0			
3	10.0			

3.4.5 Calculations

Standardisation of $KMnO_4$

$N_1 \times V_1 = N_2 \times V_1$

$KMnO_4$ = FAS $\quad N_{KMnO_4} = \frac{N_{FAS} \times V_{FAS}}{V_{KMnO_4}}$

Normality of unknown FAS solution

FAS = $KMnO_4$

$N_1 \times V_1 = N_2 \times V_1$

$$N_{FAS} = \frac{N_{KMnO_4} \times V_{KMnO_4}}{V_{FAS}}$$

Strength of unknown FAS solution = N_{FAS} × equivalent weight

N_{FAS} × 392 = ----------g/L

3.4.6 Result:

The strength of given FAS solution is----------g/L

3.4.7 Precautions:

1. Use clean and dry glassware for titration.
2. Take $KMnO_4$ solution in burette. Since $KMnO_4$ is dark violet coloured solution, read upper meniscus.
3. Add sufficient sulphuric acid in conical flask before titration.

3.5 DETERMINATION OF THE STRENGTH OF GIVEN FERROUS AMMONIUM SULPHATE SOLUTION BY CHROMATOMETRY

3.5.1 Chemicals and equipments required:

FAS solution, standard ferrous ammonium sulfate solution, $K_2Cr_2O_7$ solution, 1% solution of diphenylamine indicator, sulphuric acid (1M), phosphoric acid (85%) distilled water, beakers, glass rod, digital balance, burette and pipette etc.

3.5.2 Theory:

In this experiment you will use redox reaction between ferrous and dichromate ions to determine the strength of given FAS solution. This experiment consists of three parts. First being preparation of standard FAS solution. Second, standardization of $K_2Cr_2O_7$ solution by titrating it against standard ferrous ammonium sulfate (FAS) solution in presence of diphenyl amine indicator and the third part of experiment involves titration of unknown FAS solution against standardized $K_2Cr_2O_7$ solution in presence of diphenyl amine indicator. Diphenyl amine, a colourless compound in its benzenoid form gets oxidized to bluish-violet coloured quinonoid form in the presence of strong oxidizing agent, $K_2Cr_2O_7$. However, Fe^{2+} are more susceptible towards oxidizing agent that the indicator. Hence, as long as $Fe^{2+}$are present in titration flask, the solution remains colourless. As soon as the Fe^{2+} are completely consumed/converted to Fe^{3+}, $K_2Cr_2O_7$ reacts with indicator diphenyl amine producing blue-violet colour marking the end point of the reaction.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$6[FeSO_4.(NH_4)_2.SO_4.6H_2O] + 3O + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 39H_2O$$

FAS

or

$$Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6e^{\ominus} \longrightarrow 2Cr^{3\oplus} + 7H_2O$$

$$6Fe^{2\oplus} \longrightarrow 6Fe^{3\oplus} + 6e^{\ominus}$$

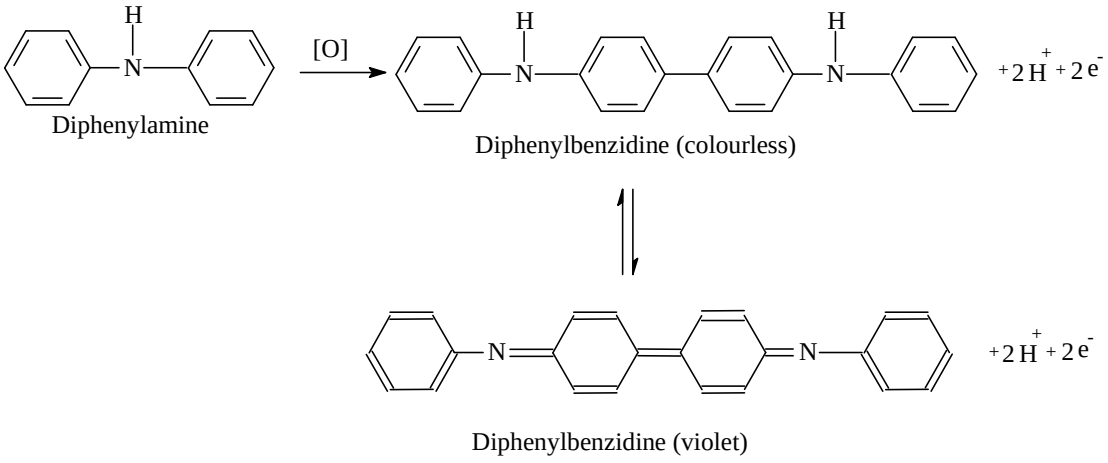
$\longrightarrow$ Redox reaction

$$Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6Fe^{2\oplus} \longrightarrow 2Cr^{3\oplus} + 6Fe^{3\oplus} + 7H_2O \longrightarrow \text{Redox reaction} \quad \textbf{(i)}$$

Oxidation

Reduction

Reaction of $K_2Cr_2O_7$ with diphenylamine



3.5.3 Procedure:

(i) **Preparation of standard ferrous ammonium sulphate solution**.

Transfer a known weight of Mohar's salt (say1.0g) in to a 100 mL volumetric flask. Add a test tube of dil.H_2SO_4 solution to the volumetric flask to prevent hydrolysis of the Fe^{2+} ions. Dissolve Mohar's salt in distilled water and make up the volume up to the mark with additional distilled water. Make the solution homogeneous; invert the flsk, six to ten times, to mix thoroughly.

(ii) **Standardization of $K_2Cr_2O_7$ solution:** Rinse a clean burette with distilled water followed by supplied $K_2Cr_2O_7$ solution. Mount the burette on a stand and fill up to the zero mark with supplied $K_2Cr_2O_7$. Record the burette reading in observation table. Pipette out 10.0 mL of standard Mohr's salt solution into a conical flask and add 10 mL dilute sulphuric acid and half test tube syrupy phosphoric acid (or one test tube of 1:1 mixture of dil. H_2SO_4 – phosphoric acid). Now add 2-3 drops of indicator and titrate until the blue violet colour is obtained which indicates the endpoint of the titration. Record the final burette reading in observation table. Repeat the titrations to get at least two concordant readings and record all readings in observation table1

(iii) Determination of the Molarity of unknown FAS solution: Refill the burette with same standardized $K_2Cr_2O_7$ solution and take unknown FAS solution in conical flask.

Repeat the titrations by following above method to get two concordant readings. Record all readings in the observation table. 2

3.5.4 Observations and calculations:

a. Preparation of standard FAS solution

Mass of FAS transferred into 100 mL of volumetric flask

$$\text{Molarity of ferrous ammonium sulphate solution } (M_1) = \left[\frac{\text{mass}}{\text{molar mass}} \times \frac{1000}{V \text{ (in cm}^3\text{)}}\right] \text{mol dm}$$

$$= \left[\frac{m}{392{\cdot}15} \times \frac{1000}{100\,\text{cm}^3}\right] \text{mol dm}^{-3}$$

$$= \text{..... mol dm}^{-3}$$

Table 1: Standardisation of $K_2Cr_2O_7$ solution

S.N.	Volume of standard FAS taken in the conical flask (mL) V_1	Burette readings		Volume of $K_2Cr_2O_7$ used (mL) V_2
		Initial	Final	
1	10.0			
2	10.0			
3	10.0			

b) Standardization of $K_2Cr_2O_7$ solution.

Molarity of standard Mohar's salt (FAS solution) $= M_1$

$=$.....mol dm^3

Volume of standard Mohar's salt (FAS solution) pipetted $= V_1 = 10{\cdot}0$ cm^3

Volume of $K_2Cr_2O_7$ solution used (table 1) $= V_2 =$ .....cm^3

Molarity of $K_2Cr_2O_7$ $= M_2 = ?$ Table 2: Unknown FAS solution v_s standard $K_2Cr_2O_7$ solution

Using molarity equation, $M_1V_1 = 6M_2V_2$

Molarity of dichromate solution, $M_2 = \frac{M_1V_1}{6V_2}$ = ...mol dm^{-3}

S.No.	Volume of givin FAS solution taken in the conical flask, (mL) V_4	Burette readings		Volume of $K_2Cr_2O_7$ used, (mL) V_3
		Initial	Final	
1	10.0			
2	10.0			
3	10.0			

a. Molarity and strength of unknown FAS solution

Molarity of $K_2Cr_2O_7$ $= M_3 = M_2 =$ .....mol dm^{-3}

Volume of $K_2Cr_2O_7$ solution used (table 2) $= V_3 =$ ..... cm^3

Volume of given Mohar's salt(FAS solution) pipetted $= V_4 = 10{\cdot}0\ cm^3$

Molarity of given Mohar's salt (FAS solution) $= M_4 = ?$

Using molarity equation, $M_4V_4 = 6M_3V_3$

Molarity of dichromate solution, $M_4 = \dfrac{6M_3V_3}{V_4}$ = ...mol dm^{-3}

Strength of given Mohar's salt(FAS solution) = Molarity x molar mass

$= M_4 \times 392{\cdot}15\ g\ dm^{-1}$

= .....g dm^{-3}

3.5.5 Result:

The strength of given Mohar's salt (FAS solution) is _____ g/ dm^3

3.5.6 Precautions:

1. Use clean and dry glassware for titration.
2. Take $K_2Cr_2O_7$ solution in burette and handle carefully as it is corrosive and carcinogenic and also cxause chromium dermatitis.also handle phosphoric acid carefully it cause severe irritation and burns to the area of contact

3. Handle diphenylamine carefully as it has been dissolved in con. H_2SO_4

3. The endpoint of this experiment involves greenish to blue-violet colour change which requires special care for identification.

4. Add sufficient sulphuric acid in conical flask before titration.

3.6 DETERMINATION OF THE PERCENTAGE OF AVAILABLE CHLORINE IN GIVEN GIVEN WATER SAMPLE CONTAINING BLEACHING POWDER

3.6.1 Chemicals and equipments required:

Hypo solution, copper sulphate solution, starch indicator, bleaching powder, distilled water, flasks, glass rod, bath, beaker, burrete, pipette etc.

3.6.2 Theory:

Chlorine sets free from bleaching powder after the reaction with mineral acids is known as available chlorine. Bleaching powder is added to municipal water used for drinking purpose in order ti disinfecting the water from bacteria. Available chlorine repture the cell wall of bacteria by oxidation. In this experiment available chlorine is determined iodometrically in which iodine is first liberated from KI in presence of oxidising agent then the liberated iodine is titrated against standardised hypo solution as per the following chemical reactions:-

$$Ca(OCl) + 2HCl \longrightarrow \underset{\text{Available chlorine}}{CaCl_2 + H_2O + Cl_2}$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2Na_2S_4O_6 + NaI$$

Hence $2Na_2S_2O_2 \equiv I_2 \equiv Cl_2$

$Na_2S_2O_2 \equiv \frac{1}{2} I_2 \equiv \frac{1}{2} Cl_2$

Since eqivalent weight of $Na_2S_2O_2$ = M.W.; equivalent wt. of iodine = AT.wt. and equivalent weight of chlorine = At. wt

Therefore 1 gm. equiovalent of hypo $\equiv$ 1gm. equivalent of chlorine

3.6.3 Procedure:

(i) Preparation of solution of bleaching powder

Weigh about 5g of bleaching powder. Transfer it to a porcelain dish, make paste and transfer without loss it to 500 mL measuring flask. Make up the volume with distilled water. Shake well. A turdid solution of bleaching is in this way obtained.

(ii) Preparation of primary standard ($CuSO_4$) solution

In order to standardise hypo solution because of its secondary ature prepare N/20 $CuSO_4$ Solution in 100 mL of volumetric flask. To prpare N/20 solution for 100mL weigh 1.25 g of $CuSO_4.5H_2O$ as per the equation 'A' and transfer it to 100 mL volumetric flask with the help of flask.Add half test tube of CH_3COOH in order to check the hydrolysis of the salt, dissolve the particles by proper shaking and finally add distilled water to make uo the volume of 100 mL

$$w = \frac{ENV}{1000} \quad \text{.....'A'}$$

Where w = weight, E = equivalent weight, V = desired volume i.e. 100 mL or 200 mL

(iii) Standardization of hypo solution

Rinse the the cleane burrete with hypo solution and fill it with same solution not the initial reading. Pipette out 10 mL of $CuSO_4$ solution in a conical flask add about half t.t acetic acid and about 2 mL of KI solution. Mix the reaction mixture well, cover the mouth of conical flask and and allow the mixture to stand for 3-5 min in dark.The solution becomes brown in colour due to liberated iodine.Titrate the liberated iodine against hypo solution taken in burrete till the colour of reaction mixture turns faint yellow colour. At this stage add 2 mL of starch solution. This immediately forms adeep blue iodo- starch complex. Add firther hypo solution drop by drop till the blue colour just disappears and does not return within 10 seconds Note the final reading and and repeat the titration until two concordant readings are obtained. Record the observations in table 1 The following reactions takes place during the course of titration:-

$$2CuSO_4 + 4KI \longrightarrow \underset{\text{white ppt.}}{2CuI} + 2K_2SO_4 + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow \underset{\text{sod. tetrathionate}}{Na_2S_4O_6} + 2NaI$$

$$2CuSO_4.5H_2O \equiv I_2 \equiv Na_2S_2O_3$$

(iv) Titration of unknown sample against standardized hypo solution

Same procedure as for step (iii) is followed. Take unknown water sample in place of $CuSO_4$ solution in a conical flask. Record the observations in table 2. The reaction in titration flask takes place as under:-

$$Cl_2 + 2\ KI \longrightarrow 2\,KCl + I_2$$

Available chlorine

$$I_2 + \text{starch solution} \longrightarrow \text{iodo starch complex (blue colour)}$$

$$\text{iodo starch complex (blue colour)} + 2\ Na_2S_2O_3 \longrightarrow 2Na_2S_4O_6 + NaI + \text{starch solution}$$

Blue colour diappear (end point)

Hence $2Na_2S_2O_2 \equiv I_2 \equiv Cl_2$

$$Na_2S_2O_2 \equiv \frac{1}{2} I_2 \equiv \frac{1}{2} Cl_2$$

3.6.4 Observations

Table 1. Data for standardization of hypo solution

S.N.	Volume of $CuSO_4$ solution, (mL)	Burette Reading (mL)		Volume of $Na_2S_2O_3$, used up (mL)
		Initial	Final	
1	10.0			
2	10.0			
3	10.0			

Table 2. Data for titration of unknown water sample against standard hypo solution

S.N.	Volume of water sample taken (mL)	Burette Reading (mL)		Volume of $Na_2S_2O_3$ solution, (mL)
		Initial	Final	
1	10.0			
2	10.0			
3	10.0			

3.6.5 Calculations

A standardization of hyposolution

$N_1V_1 = N_2V_2$
$CuSO_4$ = hypo.

$$N_{hypo} = \frac{N_{CuSO_4} \times V_{CuSO_4}}{10{\cdot}0} = \text{Say x N}$$

B Determination of percentage of available chlorine in given water sample

Say w = weight of bleaching powder dissolved in 500 mL distilled water
V = volume of standardized (xN) hypo solution used with10 mL of bleaching powder solution(water sample)
x = Normality of hypo solution

Now 1 g equivalent of available chlorine (Cl_2) = 1g equivalent of hypo solution
i.e Vol. x Normality of Cl_2 = Vol. x Normality of hypo.solution

Therefore normality of $Cl_2 = \frac{V \cdot xN}{10}$, Since equivalent weight of chlorine = 35·46

Strength of available chlorine in g/L = Normality of Cl_2 x Equivalent wt. = $\frac{V \cdot 35{\cdot}46 \cdot x}{10}$

Or amount of available chlorine in mL of prepared bleaching powder solution = $\frac{V \cdot 35{\cdot}46 \cdot xN}{2 \times 10}$ g

Percentage of available chlorine in bleaching powder (i.e. in 100 g)

$$= \frac{V \cdot 35{\cdot}46 \cdot xN \cdot 100}{2 \times 10 \times w}$$

3.6.6 Result:

The strength and percentage of available chlorine found was -------g/L and .....% respectively

3.6.7 Precautions:

1. All glassware must be cleaned and dried before performing experiment.
2. Standard solutions should be prepared with extreme care.
3. Sufficient amount of KI solution should be added.
5. Starch solution should be added just before the end point (when the solution turns light yellow).
6. Use starch solution does not use its powder form directly.
7. Prepare starch solution in warm water

3.7 DETERMINATION OF TOTAL, PERMANANT AND TEMPORARY HARDNESS OF WATER BY COMPLEXOMETRY

3.7.1 Introduction:

Water containing high amounts of dissolved minerals is called hard water. Hardness of water is generally due to the presence of bicarbonate, chloride and sulfate salts of calcium and magnesium ions. Presence of these cations in water significantly decreases the cleaning action of soaps. Water hardness is of two types, temporary and permanent. Temporary hardness is due to the presence of bicarbonate salts of calcium and magnesium. It can be removed by boiling. On the other hand, permanent hardness is due to the presence of chloride and sulfate salts of calcium and magnesium, which can not be removed by boiling.

3.7.2 Chemicals and equipments required

Water samples, standard Na_2EDTA solution, standard hard water (SHW), ammonia buffer solution (pH 10±1), Eriochrome black- T(EBT sod. salt) indicator, burette, pipette, conical flask etc.

3.7.3 Theory

Water hardness is, in general, expressed as the measure of total concentration (ppm) of calcium and magnesium ions expressed as calcium carbonate. It is determined by performing complexometric titration using a standard sodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) solution. Eriochrome black T indicator, which is an azo dye is used as indicator to determine the endpoint of this complexometric titration.

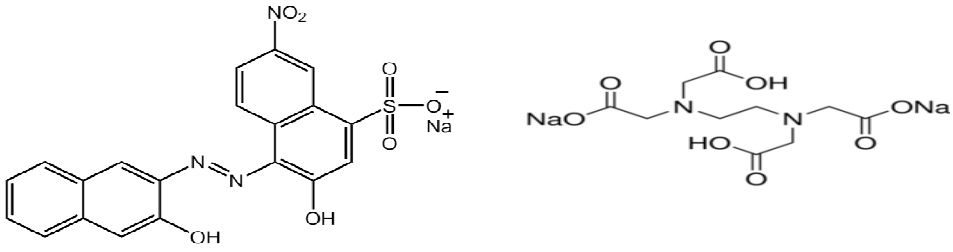
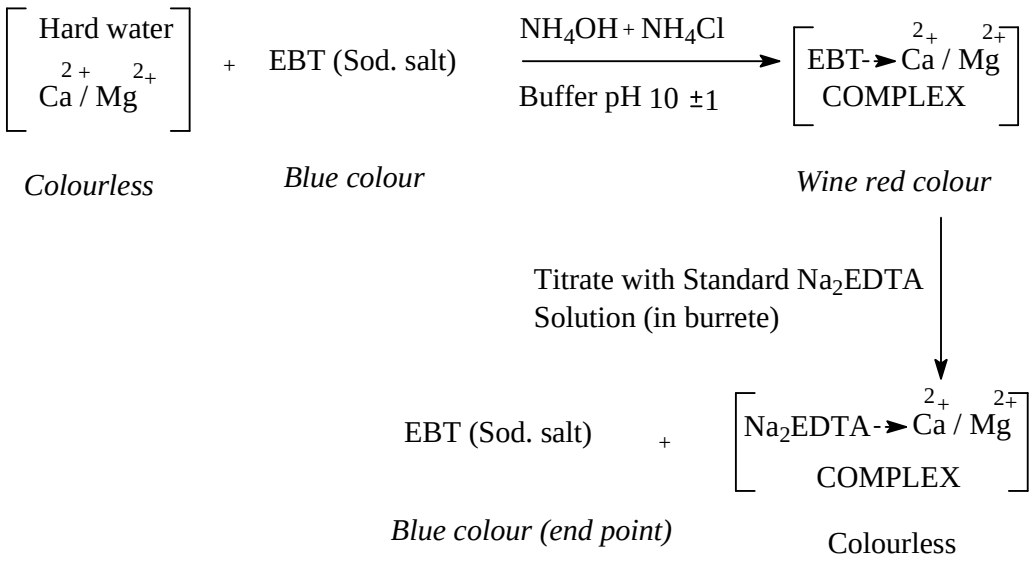


Figure 3. Molecular structure of EBT indicator and Na_2EDTA

Eriochrome black T forms a wine red coloured weak complex with calcium ions present in hard water. During the course of titration, Na_2EDTA solution is added to the hard water. Na_2EDTA abstracts all the calcium ions from wine red coloured complex. That means at end point of this titration calcium-indicator complex breaks down completely and all the calcium ions form chelate with Na_2EDTA and solution turns blue in colour (**Scheme 1**). The blue colour is due to the presence of Eriochrome black T in ammonia buffer solution.



Scheme 1 Reaction of hard water with EBT and Na_2EDTA solution during titration

(I) Preparation of Na_2EDTA Solution: 0.01N aqueous solution of Na_2EDTA is prepared by in distilled water and making the volume up to one liter (This solution can be standardized by titration against standard solution of magnesium sulfate).

(II) Preparation of ammonia buffer (pH = 10±1): Weigh 17 gm of NH_4Cl and dissolve in 142.5 m1 of concentrated aqueous ammonia solution and subsequently dilute to 250 mL with distilled water.

(III) Preparation of standard hard water (SHW): Prepare 1000 ppm standard hard water as follow:-

Weigh 0.1g $CaCO_3$ and transfer it in 100 mL (1.0mg/L = 1.0ppm) volumetric flask add about half test tuble of HCl to dissolve $CaCO_3$ and make up the volume dy adding

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

distilled water up to the mark of 100 mL. $CaCO_3$ is insoluble hence is first converted to water soluble $CaCl_2$ by treating it with HCl

3.7.4 Procedure:

Rinse and fill the burette with 0.01N Na_2EDTA solution. Pipette out 10 mL of SHW in aconical flask, add 2mL of buffer solution abd two-three drops of EBT indicator. Wine red colour is obtained. Titrate the reaction mixture with Na_2EDTA solution taken in burette till blue colour appears at the end point.Note the reading of burette and repeat the same process till three concordant readings are obtained (V_1). Similarly follow the same process for unknown hard water. The volume of Na_2EDTA solution used corresponds total hardness (V_2). Tabulate your results in observation table.

For permanent hardness, take 250 mL of hard water in a 500mL beaker and boil till it reduces half. Filter the solution in 250mL flask and add distilled water to make the final volume of 250mL. Titrate 10 mL of this solution using buffer and EBT as indicator. The volume of Na_2EDTA solution used in this step corresponds permanent hrdness (V_3). Tabulate your results in observation table.

3.7.5 Observations:

(i) Reading with SHW

S.N.	Vol. of SHW taken (mL)	Reading of burette		Vol of Na_2EDTA solution used up(mL)
1.	10.0	Initial	Final	Rough reading
2.	10.0	-	-	V_1
3.	10.0	-	-	V_1
4.	10.0	-	-	V_1

$V_{1=}$ concordant reading

(ii) Reading with unknown hard water

S.N.	Vol. of unknown hard water taken (mL)	Reading of burette	Vol of Na_2EDTA solution used up(mL)

1.	10.0	Initial	Final	Rough reading
2.	10.0	-	-	V_2
3.	10.0	-	-	V_2
4.	10.0	-	-	V_2

$V_{2=}$ concordant reading

(iii) Reading after boiling the solution (Permanent hardness)

S.N.	Vol. of boiled hard water taken (mL)	Reading of burette		Vol of Na_2EDTA solution used up(mL)
1.	10.0	Initial	Final	Rough reading
2.	10.0	-	-	V_3
3.	10.0	-	-	V_3
4.	10.0	-	-	V_3

$V_{2=}$ concordant reading

3.7.6 Calculations:

The hardness of the water sample is calculated in parts of $CaCO_3$ per million of water (ppm).

(i) 1 mL of SHW =1 mg $CaCO_3$

V_1 mL Na_2EDTA =10 mL SHW solution

= 10 mg $CaCO_3$

1 mL Na_2EDTA = $10/V_1$mg $CaCO_3$

(ii) Total hardness

10 mL unknown hard water =V_2mL Na_2EDTA solution

= $V_2 \times 10/V_1$ mg $CaCO_3$

1mL unknown solution =$V_2/V_1 \times 10/10$ mg $CaCO_3$

1000 mL unknown solution = $V_2/V_1 \times 1000$ mg $CaCO_3$

Total hardness = $V_2/V_1 \times 1000$ mg $CaCO_3$

= $V_2/V_1 \times 1000$ ppm

(iii) Permanent hardness

10 mL boiled hard water =V_3mL Na_2EDTA solution

Permanent hardness = $V_3/V_1 \times 1000$ ppm

(iv) Temporary hardness

Total hardness – Permanent hardness

3.7.8 Results:

(i) Total hardness of given water sample is _____ ppm.

(ii) Permanent hardness of water sample is_____ppm

(iii) Temporary hardness of water sample is_____ppm

3.7.9 Precautions:

1. Burette and other glassware must be cleaned and dried before performing experiment.
2. Lower meniscus should be read for taking observations.
3. Standard solutions should be prepared with extreme care.
4. Least count of common laboratory burettes is 0.1 mL, hence readings should be recorded up to first place of decimal.

3.8 SUMMARY

First experiment reveals the titration of hydroxyl and carbonate ions by titFrating the mixture solution against HCl. This experiment gives us an idea about alkalinity of water and its types.basically hydroxyl and carbonate alkalinity. Experiment two and three rducate us how amount of iron in its ore and compound can be determined volumetrically basically through permagnatometry and chromatometry (redox titrations). Bleaching powder is generally used in municipal drinking water for disinfection it liberates chlorine in water known as available chlorine, which kills the bacteria by oxidising their cells. This experiment has thus been incorporated to get aware about how water is disinfected by

bleaching powder. This experiment educate us how the amount and percentage of available chlorine is determined by volumetiric methods generally iodometrically? The last experiment (fifth) is about the determination of various types of hardnesses in water, the one of the most important water quality parameter for health and industrial point of view.

3.9 TERMINAL QUESTION

Short Answer type questions

Q.1 Discuss the procedure of titrations, in general.

Q.2 What are endpoint and equivalence point?

Q. 3 What is an indicator?

Q.4 What is equivalent weight of sodium carbonate?

Q.5 How does *pH* of the solution changes for titration of NaOH-Na_2CO_3 mixture solution with hydrochloric acid in presence of phenolphthalein and methyl orange?

Q.6 Justify your choice of phenolphthalein and methyl orange indicators for the titration of NaOH-Na_2CO_3 mixture solution with hydrochloric acid.

Q.7 Why preparation of standard solutions must be done with extreme care?

Q.8 How do you identify the endpoint of titration of FAS solution with $KMnO_4$?

Q.9 Why cleaning effectiveness of soap decreases in hard water.

Q.10 What are features of a good indicator used for the visual detection of end points in the experiment, determination of hardness of water?

Q.11 What is available chlorine?

Q.12 What indicator you have used in iodometric titration?

Q.13. While bleaching powder is added to water?

3.10 ANSWERS

A.1 Titration is chemical analysis by which the quantity of some constituent of a sample is determined by reacting exactly known quantities of sample and a titrant. The process usually involves gradual addition of a standard solution of titrant, from a glass burette to

an Erlenmeyer flask (a conical flask with narrow neck) containing analyte solution and internal indicator, if required. The addition of titrant is stopped when the endpoint is reached as indicated by colour change of contents of Erlenmeyer flask.

A.2 At the equivalence point of a titration, an exactly equivalent amount of titrant has been added to the sample. The experimental point at which the completion of the reaction is marked by some signal is called the end point.

A.3 Indicator is a substance that changes colour in response to a chemical change. Colour change of indicator suggests that endpoint of titration has arrived. Endpoint is an approximation of equivalence point. Acid-base indicators such as phenolphthalein and methyl orange; redox indicators such as iodine and diphenyl amine and complexometric indictors such as EBT are commonly used in laboratory.

A.4 Sodium carbonate is a diacidic alkali, hence its equivalent weight is half of its molecular weight, *i.e.*, 106/2 = 53 g/mol.

A.5 First part of titration involves neutralization of NaOH and conversion of Na_2CO_3 in to $NaHCO_3$. pH of the solution at this stage is just below 8.3. Since the pH range of phenolphthalein is 10 to 8.3, hence disappearance of colour of phenolphthalein indicates that the neutralization of NaOH and conversion of Na_2CO_3 in to $NaHCO_3$ is completed. Further titration in presence of indicator methyl orange involves neutralization of sodium bicarbonate to result in acidic solution with pH value close to 4. This is well within the range (3.1-4.4) of methyl orange indicator.

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A.7 Any mistake (such as incorrect weight or volume) done during the preparation of standard solutions, causes deviation from standard values. Such mistakes carry through the entire experiment and significantly affect the accuracy of the results.

A.8 Potassium permanganate is purple in aqueous solution, whereas the final products of the reaction between ferrous ion and KMnO4 are colourless. Hence the completion of reaction is indicated by the appearance of slight pink colour in the conical flask containing sample being titrated.

A.9 Because soap precipitates as insoluble salts of calcium and magnesium ions present in hard water. Hence, presence of bivalent cations in water decreases the cleaning action of soaps.

A.10 The color change on completion of metal ions chelation process must be sharp. The indicator must be sensitive towards minute amounts of metal ion. The metal–indicator complex must be less stable than the metal–EDTA complex to ensure that all metal ions are bound to EDTA when end point of the titration reaches.

A.11 The chlorine liberated from bleaching powder when dissolved in water is known as available chlorine

A.12. Starch

A.13 Bleaching powder is added to water as disinfectant

3.11 REFERENCES

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UNIT 4: INORGANIC PREPARATION

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4.5.2 Apparatus required

4.5.3 Procedure

4.5.4 Chemical reaction involved

4.5.5 Result

4.5.6 Precautions

4.5.7 Self- assessment questions (SAQ)

4.6 Preparation of potassium trioxalatoferrate (III) trihydrate

4.6.1 Chemicals required

4.6.2 Apparatus required

4.6.3 Procedure

4.6.4 Chemical reaction involved

4.6.5 Result

4.6.6 Precautions

4.6.7 Self- assessment questions (SAQ)

4.7 Summary

4.8 Glossary

4.9 Possible answer to SAQ

4.10 References

4.11 Terminal questions

4.1 INTRODUCTION

As we know that inorganic chemistry is a branch of chemistry that deals with the properties and behavior of inorganic compounds. In order to understand the unit more clearly, one have to understand the concept of inorganic compounds. Inorganic compounds are those compounds which are obtained from non-living things either by natural process or by preparing them in laboratories. These compounds comprises of double salts and coordination compounds.

In the present unit we deal with the methods of preparation of these inorganic compounds in the laboratories which is quite interesting. We will discuss the preparation of potash alum, tetraamminecopper (II) sulphate monohydrate and potassium trioxalatoferrate (III) trihydrate.

To understand the unit more clearly we must have a knowledge of inorganic compounds which includes the way of preparing these compounds, different conditions for the formation of a particular inorganic compounds and the yield of inorganic compounds prepared.

4.2 OBJECTIVES

After going through the unit thoroughly we will be able to:

- Define inorganic compounds.

- Explain coordination compounds.
- Explain double salts.
- Prepare potash alum, tetraamminecopper (II) sulphate monohydrate and potassium trioxalatoferrate (III) trihydrate.
- Know the apparatus required for the formation of these inorganic compounds.
- Know the precautions that must be taken into consideration during the preparation of inorganic compounds.

4.3 INORGANIC COMPOUNDS

As discussed above those inorganic compounds consists of double salts and coordination compounds. It is important to have knowledge of these inorganic compounds before going to perform their preparation. Let us start with double salts. Double salts are the compounds that contain more than one cation or anion. These are obtained by combination of two different salts. These two different salt crystallize together and form a single substance. It is important to note that when these double slats are dissolved in water, there is ionization of two different salts. The examples of double salts are ferrous ammonium sulphate, potash alum. Ferrous ammonium sulphate also known as FAS or Mohr's salt is a double salt of ferrous sulphate, $FeSO_4$ and ammonium sulphate, $(NH_4)_2SO_4$. Mohr's salt is $FeSO_4.(NH_4)_2SO_4.6H_2O$. There are two different cations in Mohr's salt, Fe^{2+} and NH_4^+. It is light green in color. Potash alum on the other hand is a double salt of potassium sulphate, K_2SO_4 and aluminum sulphate, $Al_2(SO_4)_3$ having a chemical composition $K_2SO_4.Al_2(SO_4)_3.24H_2O$.vernacularly, potash alum is known as fitkari which is used in the purification of water. This contains two cations, K^+ and Al^{3+}.

Now coming to coordination compounds. These compounds are formed by almost all transition metals. In these compounds a coordinate bond is formed between metal and ligands. The ligands must have lone pair of electrons and may be neutral or negatively charged. The ligands donate electrons to metal atom and metal atom accept these electrons to form a type of covalent bond known as coordinate bond. The numbers of ligands surrounding the central metal atom constitute the coordination number of a coordination compounds. The brackets enclosing the coordination compound is a coordination sphere. For example: $[Ni(CO)_4]$, $K_2[PdCl_4]$, tetraamminecopper (II) sulphate monohydrate, potassium trioxalatoferrate (III) trihydrate. In $[Ni(CO)_4]$, the ligand is CO (carbonyl) each

of which donate one electron pair to Ni (metal atom). In $K_2[PdCl_4]$, potassium acts as counter ion and the compound when ionizes to form K^+ and $[PdCl_4]^{2-}$ ions. Tetraamminecopper (II) sulphate monohydrate and potassium trioxalatoferrate (III) trihydrate are discussed later in the unit.

4.4 PREPARATION OF POTASH ALUM

As discussed in above section, potash alum is a double salt of potassium sulphate, K_2SO_4 and aluminum sulphate, $Al_2(SO_4)_3$ having a chemical composition K_2SO_4. $Al_2(SO_4)_3$. $24H_2O$; here $24H_2O$ is a water of crystallization. This water of crystallization is defined as a water which is present in a metal complex or salt not directly bond to the metal in the crystalline framework. It is also known as water of hydration or crystallization water.

4.4.1 Chemicals required

The following chemicals required for the preparation of potash alum are potassium sulphate, aluminum sulphate, sulphuric acid (H_2SO_4).

4.4.2 Apparatus required

The apparatus required for the preparation of potash alum are beaker, porcelain dish, and burner. Beaker is like a wide cylinder provided with a beak at the top. Porcelain dish is glassware used in laboratory for evaporating the liquids or solutions so that a concentrated solution or a solid of the dissolved substance may obtain.

4.4.3 Procedure

Let us discuss the procedure involved during the preparation of potash alum:

- Weigh 2.5g of potassium sulphate and 10g of aluminum sulphate with the help of a chemical balance or an electronic balance.
- Take 40ml of distilled water (water free from impurities) into a clean beaker.
- Add above weighted amount of potassium sulphate and aluminum sulphateinto a beaker containing 40ml distilled water. We will observe that the solution turns milky.
- In order to make clear solution, few drops of concentrated sulphuric acid is added into the beaker. After adding sulphuric acid if still some milkiness exist, then the solution is to be filtered using a filter paper. For filtration, the filter paper is putted

over the inner wall of the funnel and the funnel is kept over the tripod stand. Take another beaker and put it below the funnel. Pour the solution over the funnel having filter paper. The solution obtained in the beaker is filtrate and the substance which remains on the filter paper is residue.

- Now take the filtrate into a porcelain dish and put it over the tripod stand for evaporating using the burner. Evaporate the filtrate to reduce its volume to half.
- Now allow the filtrate to cool and stand without disturbing for about 5 to 7 hours. We will observe the transparent crystals of potash alum. Dry the crystals by pressing it in between the filter paper and weigh the amount of crystals prepared for obtaining the yield. In this way we obtain the fine crystals of potash alum.

4.4.4 Chemical reaction involved

As clear from the above section that potassium sulphate, aluminum sulphate and water are mixed during the preparation of potash alum. The reaction that takes place is as follows:

$$K_2SO_4 + Al_2(SO_4)_3 + 24\,H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24\,H_2O$$

Crystals of potash alum

4.4.5 Result

The yield of potash alum prepared is…….g

4.4.6 Precautions

- Use concentrated sulphuric acid carefully.
- Use burner with proper handling.
- Weighing should be done accurately in order to have an exact yield.
- While drying with filter paper, use only one filter paper in order to avoid the loss of crystals.

4.4.7 Self- assessment questions (SAQ)

- Fill in the blanks:

1. The chemical composition of potash alum is.....

2. Potash alum is used in…… of water.

3. Potash alum ionizes into …… cation.

4. In potash alum, there are 24 molecules of water of……

5. The chemical added to make clear solution during preparation of potash alum is……

6. The square bracket in the coordination compounds represents its ……

- True and False

1. The color of potash alum is orange.

2. Potash alum consists of the combination of two salts.

3. Water of crystallization is also known as water of hydration.

4. Porcelain dish is used for evaporating the liquid.

5. In beaker, beak is present at the bottom.

6. Electronic balance is used for measuring the weight of the sample.

7. [Ni $(CO)_4$] is coordination compound.

- Short Answer Questions

1. Give the chemical reactions involved in the preparation of potash alum.

2. Give the name of chemicals that are required for the preparation of potash alum.

4.5 PREPARATION OF TETRAAMMINE-COPPER (II) SULPHTE MONOHYDRATE

As the name indicates tetraamminecopper (II) sulphate monohydrate, its chemical formula is $[Cu(NH_3)_4]\ SO_4.\ H_2O$ where Cu represents copper which is a transition metal, NH_3 represents ammine which is a ligand, SO_4 represents counter ion and H_2O represents water of crystallization or hydration. As there are four ammine ligand therefore the coordination number is four and geometry is square planar with dsp^2 hybridization. It is a deep blue colored coordination compound with odour of ammonia. The blue color is due to the presence of an unpaired electron in the complex i.e. Cu^{2+}. Let us discuss the method for the preparation of tetraamminecopper (II) sulphate monohydrate.

4.5.1 Chemicals required

The chemicals required for the preparation of tetraamminecopper (II) sulphate monohydrate are copper sulphate ($CuSO_4$. $5H_2O$), ammonia solution taken in a form of concentrated NH_4OH and ethanol (C_2H_5OH). Copper sulphate which is also known as blue vitriol is a blue crystalline odourless solid. Dilute solution as we know contain more solvent (generally water) than the solute while the concentrated solution contain more solute than the solvent.

4.5.2 Apparatus required

The apparatus required for the preparation of tetraamminecopper (II) sulphate monohydrate are beaker, glass rod, dropper, watch glass, Buchner funnel, measuring cylinder. Watch glass is a plate like made up of glass. Buchner funnel which is made up of porcelain or glass is a type of funnel used for rapid filtration. Measuring cylinder is used for the required measurement of the solution or a liquid.

4.5.3 Procedure

Let us discuss the procedure involved in the preparation of tetraamminecopper (II) sulphate monohydrate:

- Weigh 2.5g of finely powdered copper sulphate with the help of electronic balance or chemical balance.
- Transfer above weighted amount of copper sulphate into a beaker. Now add very small amount of water approximately 10ml in it.
- Measure 5ml of ammonia solution (NH_4OH) with the help of measuring cylinder and transfer it into a beaker drop by drop with constant stirring using glass rod. On adding ammonia solution, the formation of blue precipitate takes place initially which is due to copper sulphate. The further addition of ammonia dissolves the blue precipitate thereby giving a deep blue color solution having odour of ammonia.
- Now measure 20ml of ethanol with the help of measuring cylinder and transfer it drop by drop to a beaker containing deep blue color solution with constant stirring.
- After adding ethanol, allow the solution to stand for four to five hours by covering it with the help of watch glass so that the crystals of tetraamminecopper (II) sulphate monohydrate may form. Covering is done in order to avoid the release of ammonia.

- After 4 to 5 hours, crystals thus formed are filtered using a Buchner funnel and are washed with ethanol. Dry the crystals by using filter paper and the amount of crystals formed is measured. In this way deep blue color crystals of tetraamminecopper (II) sulphate monohydrate are obtained.

4.5.4 Chemical reaction involved

As discussed above, when concentrated ammonia solution is added into a beaker containing copper sulphate, there is a formation of deep blue color precipitate which get dissolve on further addition of ammonia solution. This blue color is due to the presence of $[Cu(NH_3)_4]^{2+}$ ion which can be explained by the given chemical reaction:

Initially:

$$2Cu^{2+}(aq) + SO_4^{2-}(aq) + 2NH_3(aq) + 2H_2O \longrightarrow Cu(OH)_2.CuSO_4(s) + 2NH_4^{+}(aq)$$

Blue color precipitate

On further addition of ammonia:

$$Cu(OH)_2.CuSO_4(s) + 8NH_3(aq) \rightarrow 2[Cu(NH_3)_4]^{2+}(aq) + 2OH^{-}(aq) + SO_4^{2-}(aq)$$

Blue color solution

4.5.5 Result

The yield of tetraamminecopper (II) sulphate monohydrate prepared is …… g.

4.5.6 Precautions

Several precautions are to be taken during the experiment.

- Avoid the use of several filter papers for drying as it affects the yield.
- Stir the solution properly while adding ammonia solution.
- Ammonia solution should be added dropwise.
- Weighing of the crystals should be done carefully.

4.5.7 Self- assessment questions (SAQ)

- Fill in the blanks:

1. The blue color of tetraamminecopper (II) sulphate monohydrate crystal is due to the presence of……

2. The geometry of [Cu $(NH_3)_4$] SO_4. H_2O is……

3. The number of unpaired electrons in Cu^{2+} is……

4. Buchner funnel is used for……

5. $CuSO_4$. $5H_2O$ is also known as…… vitriol.

- True and False

1. In Cu (II), the oxidation state of copper is +2.

2. In tetraamminecopper (II) sulphate monohydrate, there are four ligands.

3. The sulphate group in tetraamminecopper (II) sulphate monohydrate is a ligand.

4.The crystals of tetraamminecopper (II) sulphate monohydrate possess sp^3hybridization.

5. The electronic configuration of Cu(II) is $3d^9 4s^0$.

6. During the preparation of tetraamminecopper (II) sulphate monohydrate, watch glass is used for covering the beaker.

- Short Answer Questions

1. Discuss the chemicals reactions involved in the preparation of tetraamminecopper (II) sulphate monohydrate crystals.

2. Discuss the precautions involved in the preparation of the crystals of tetraamminecopper (II) sulphate monohydrate.

4.6 PREPARATION OF POTASSIUM TRIOXALATOFERRATE (III) TRIHYDRATE

As the name indicates potassium trioxalatoferrate (III) trihydrate, it is clear that the crystals contain potassium (K), trioxalato, ferrate and trihydrate or three molecules of water of crystallization. Its composition is $K_3[Fe(C_2O_4)_3]$. $3H_2O$. We all known about oxalic acid, its chemical composition is $C_2O_4H_2$. As it is an acid, it can donate proton (H^+). It has a capacity to donate two protons therefore it is diprotic and form $C_2O_4^{2-}$which is oxalate.This crystal contains three oxalate group i.e. trioxalate. An oxalate is a bidentate ligand as two oxygen donates electron pair to iron atom. Here the central metal atom that is iron is present in +3 oxidation state and potassium (K^+) is a counter ion. The crystals of

potassium trioxalatoferrate (III) trihydrate possess octahedral structure with coordination number six. This shows that central metal atom i.e. Fe is coordinated to six oxygen atom. The crystals are fluorescent green in color. In solution the crystals dissociates to form [Fe $(C_2O_4)_3]^{3-}$(ferrioxalate anion) and $3K^+$. Let us now consider the preparation of potassium trioxalatoferrate (III) trihydrate crystals.

4.6.1 Chemicals required

Following chemicals are required for the preparation of potassium trioxalatoferrate (III) trihydrate: Ferrous ammonium sulphate, oxalic acid, dilute sulphuric acid (H_2SO_4), potassium oxalate ($K_2C_2O_4$), ethanol, hydrogen peroxide (H_2O_2). Ferrous ammonium sulphate is also known as Mohr's salt. Its chemical composition is $FeSO_4$. $(NH_4)_2SO_4.6H_2O$ and is a double salt that contains two cations Fe^{2+} and NH_4^+.

4.6.2 Apparatus required

The apparatus required for the preparation of potassium trioxalatoferrate (III) trihydrate are beaker, burner, stirrer, conical flask, pipette, burette, Buchner funnel, chemical balance, filter paper.

4.6.3 Procedure

Let us discuss the procedure involved in the preparation of potassium trioxalatoferrate (III) trihydrate:

- Weigh 2g of ferrous ammonium sulphate with the help of weighing balance or electronic balance and transfer it to a beaker containing 25ml distilled water having few drops of dilute sulphuric acid in it. The addition of dilute sulphuric acid prevents the hydrolysis of the ferrous ammonium sulphate.
- Weigh 3g of oxalic acid with the help of chemical or electronic balance and transfer it to another beaker containing 15ml of distilled water.
- Now add the above prepared oxalic acid solution into a beaker containing ferrous ammonium sulphate solution. Heat this mixture using the burner with constant stirring up to boiling. We will observe that there is a formation of yellow colored precipitate which is due to ferrous oxalate. The reaction that takes place is explained in the next section under heading chemical reactions involved. Allow this ferrous oxalate precipitate to settle down.

- Now remove the liquid below which the precipitate settles down. After the removal of precipitate, it is washed with distilled water.
- Now potassium oxalate is taken and a saturated solution is prepared by dissolving it in distilled water. For making saturated solution, add potassium oxalate into distilled water until it stops dissolving. Filter the solution and the filtrate thus obtained is the saturated solution of potassium oxalate. Measure 10mL of this saturated solution of potassium oxalate with the help of the measuring cylinder and transfer it to a beaker containing precipitate of ferrous oxalate. Heat this mixture to about 40^{o}C with the help of the burner.
- Now we have to prepare 3% hydrogen peroxide solution. Add 40 mL of this hydrogen peroxide solution into the beaker containing the mixture. Out of 40mL hydrogen peroxide solution, add half of it (20mL) slowly with constant stirring and remaining half (20mL) in one time into the beaker containing the mixture. The solution is then heated up to boiling. Now we have to add oxalic acid of molarity 1M into the beaker. Using the formula (w =MMV/1000), where M is molarity, M is molar mass, V is required volume, the weight for the preparation of 1M oxalic acid solution is calculated.
- Now measure 10mL of oxalic acid solution with the help of measuring cylinder or with the pipette and transfer it to a beaker containing the boiled mixture of ferrous oxalate, potassium oxalate, hydrogen peroxide following the first 5ml addition at once and then remaining 5ml addition drop wise with the help of the dropper. Again heating is done till the solution in the beaker becomes bright green in color.
- Now with the help of filter paper, the above prepared green color solution is filtered in a clean conical flask.
- Measure 20 mL ethanol with the help of measuring cylinder or with the pipette and transfer it to a conical flask containing green color solution. Heat the solution to about 70^{o}C. Further extra ethanol is added until the solution just becomes cloudy. It means there is a formation of precipitate or crystals.
- The conical flask is then allowed to stand in a dark cupboard for some time so that the crystals thus formed may settle down. Filter the crystals using Buchner funnel for rapid filtration. The crystals are then washed with ethanol and are dried by pressing them in between the filter paper. Using a chemical or electronic balance,

the crystals are weighed and the yield is recorded. In this way, the green color crystals of potassium trioxalatoferrate (III) trihydrate are prepared.

4.6.4 Chemical reaction involved

As discussed in the procedure, initially oxalic acid is added into a solution of ferrous ammonium sulphate which leads to the formation of yellow colored ferrous oxalate. Then potassium oxalate, hydrogen peroxide and oxalic acid is added for oxidation of ferrous oxalate which leads to the formation of green crystals of potassium trioxalatoferrate (III) trihydrate. The reactions that involved in the above process are as follows:

$FeSO_4.(NH_4)_2SO_4.6H_2O\,(aq) + C_2O_4H_2\,(aq) \longrightarrow FeC_2O_4.2H_2O\,(s) + (NH_4)_2SO_4\,(aq) + H_2SO_4$

Ferrous ammonium sulphate + Oxalic acid → Ferrous oxalate

$2FeC_2O_4.2H_2O\,(s) + H_2O_2\,(aq) + C_2O_4H_2(aq) + 3K_2C_2O_4\,(aq) \rightarrow 2K_3[Fe(C_2O_4)_3].3H_2O$

Green crystals

In this way, yellow colored ferrous oxalate precipitate and then green crystals of potassium trioxalatoferrate (III) trihydrate are formed.

4.6.5 Result

The yield of potassium trioxalatoferrate (III) trihydrate crystals obtained is ……g.

4.6.6 Precautions

Following precautions are to be taken during the experiment:

- Weighing should be done accurately.
- Neat and clean apparatus should be used in the experiment.
- Before starting the experiment, go through the procedure and requirements thoroughly.
- Handle the burner with care.

4.6.7 Self- assessment questions (SAQ)

- Fill in the blanks:

1. The color of potassium trioxalatoferrate (III) trihydrate crystals is……

2. Ferrous oxalate thus formed in the experiment are…… in color.

3. Ferrous ammonium sulphate is a……standard substance.

4. Oxalic acid contains…… oxalate group.

5. Hydrogen peroxide is added for…… of ferrous oxalate.

- True and False

1. In ferrate, iron is in +3 oxidation state.

2. The coordination number of iron in potassium trioxalatoferrate (III) trihydrate is six.

3. $C_2O_4^{2-}$is an oxalic acid.

4. In solution, the crystals dissociates to form ferrioxalate anion and potassium ion.

5. The structure of potassium trioxalatoferrate (III) trihydrate is octahedral.

6. Mohr's salt is ferrous ammonium sulphate.

7. Mohr's salt is a coordinated compound

8. Oxalic acid is a secondary standard substance.

- Multiple choice questions

1. The chemical formula of ferrous ammonium sulphate is

a. $FeSO_4$

b. $(NH_4)_2SO_4$

c. $FeSO_4.\ (NH_4)_2SO_4.\ 6H_2O$

d. None of the above

2. In potash alum, the number of molecules of water of crystallization is

a. Six

b. Twenty four

c. Eight

d. Twelve

3**.**The chemical formula of potash alum is

a. K_2SO_4

b. K_2SO_4. $Al_2(SO_4)_3$. $24H_2O$

c. $Al_2(SO_4)_3$

d. All the above

4. The element potassium belongs to

a. Transition metal

b. Inner- transition metal

c. Halogen

d. Representative element

5. The chemical formula of tetraamminecopper (II) sulphate monohydrate is

a. $[Cu\ (NH_3)_4]\ SO_4$. $2H_2O$

b. $[Cu\ (NH_3)_6]\ SO_4$. H_2O

c. $[Cu\ (NH_3)_4]\ SO_4$. H_2O

d. $[Cu\ (NH_3)_4]\ SO_4$. $6H_2O$

6. The chemical species ethanol is an

a. Aldehyde

b. Ketone

c. Alcohol

d. Aldol

7. Potassium trioxalatoferrate (III) trihydrate is represented as

a. $K_3\ [Fe\ (C_2O_4)_3]$. $3H_2O$

b. $K_2\ [Fe\ (C_2O_4)_3]$. $3H_2O$

c. $K_4\ [Fe\ (C_2O_4)_3]$. $3H_2O$

d. $K_3\ [Fe\ (C_2O_4)_3]$. $2H_2O$

8. $C_2O_4^{2-}$ is a ligand which is

a. Monodentate

b. Bidentate

c. Tetradentate

d. Hexadentate

9. $[Fe\ (C_2O_4)_3]^{3-}$ is

a. Ferroxalate anion

b. Ferrioxalte anion

c. Ferroferrioxalate anion

d. Ferrioxaltecation

10. The color of tetraamminecopper (II) sulphate monohydrate crystals is

a. Orange

b. Blue

c. Green

d. Colorless

11. In coordination compounds, ligands possess

a. Primary valency

b. Secondary valency

c. Counter ion

d. None of the above

12. In ferrous ammonium sulphate, the number of molecules of water of crystallization is

a. Six

b. Twenty four

c. Eight

d. Twelve

- Short Answer Questions

1. Write the chemical reactions involved in the preparation of potassium trioxalatoferrate (III) trihydrate.

2. Write the chemicals that are required for the preparation of potassium trioxalatoferrate (III) trihydrate.

4.7 SUMMARY

The present unit deals with the preparation of inorganic compounds which has been undertaken with respect to the preparation of potash alum, tetraamminecopper (II) sulphate monohydrateand potassiumtrioxalatoferrate (III) trihydrate. The preparation of these compounds are discussed under three sections that includes procedure, chemical reactions involved, results and precautions. In the preparation of potash alum, potassium sulphate, aluminum sulphate, sulphuric acid are required. In the preparation of tetraamminecopper (II) sulphate monohydrate, copper sulphate, ammonia solution and ethanol are required while in the preparation of potassium trioxalatoferrate (III) trihydrate, ferrous ammonium sulphate, oxalic acid, dilute sulphuric acid, potassium oxalate, ethanol, hydrogen peroxide are required.

4.8 GLOSSARY

- **Double salts** – Inorganic compounds that contain more than one cation or anion.
- **Coordination compounds** - Inorganic compounds formed by a large number of transition metals in which metal atom is bound to a ligand by a coordinate bond.
- **Buchner funnel** – Funnel used for fast filtration.
- **Water of crystallization** – Water present within the crystal.
- **Mohr**,**s salt**– Ferrous ammonium sulphate
- **Coordination compounds –** It include double slats and coordination compounds.
- **Potash alum -** K_2SO_4. $Al_2(SO_4)_3$. $24H_2O$
- **Tetraamminecopper (II) sulphate monohydrate -** $[Cu\ (NH_3)_4]\ SO_4$. H_2O
- **Potassium trioxalatoferrate (III) trihydrate -** $K_3\ [Fe\ (C_2O_4)_3]$. $3H_2O$

4.9 POSSIBLE ANSWER TO SAQ

4.4.7 Self- assessment questions (SAQ)

- Fill in the blanks

1. K_2SO_4. $Al_2(SO_4)_3$. $24H_2O$; 2. Purification; 3. Two; 4. Crystallization; 5. Sulphuric acid; 6. Coordination sphere

- True and False

  1. False; 2. True; 3. True; 4. True; 5. False; 6. True; 7. True

4.5.7 Self- assessment questions (SAQ)

- Fill in the blanks

  1. $[Cu\ (NH_3)_4]^{2+}$; 2. Square planar; 3. One; 4. Filtration; 5. Blue

- True and False

  1. True; 2. True; 3. False; 4. False; 5. True; 6. True

4.6.7 Self- assessment questions (SAQ)

- Fill in the blanks

  1. Green; 2. Yellow; 3. Primary; 4. Two; 5. Oxidation

- True and False

  1. True; 2. True; 3. False; 4. True; 5. True; 6. True; 7. False; 8. False

- Multiple Choice Questions

  1. c. $FeSO_4$. $(NH_4)_2SO_4$. $6H_2O$; **2.**b.Twenty four; **3.**b. K_2SO_4. $Al_2(SO_4)_3$. $24H_2O$

  4.d. Representative element; **5**. c. $[Cu\ (NH_3)_4]\ SO_4$. H_2O; **6**. c. Alcohol; **7.**a. $K_3\ [Fe\ (C_2O_4)_3]$. $3H_2O$; **8.**b. Bidentate; **9.**b. Ferrioxalate anion; **10.**b. Blue; **11**. b. Secondary valency; **12**. a. Six

4.10 REFERENCES

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4.11 TERMINAL QUESTIONS

1. Explain the method of preparation of potash alum along with the chemical reactions involved, apparatus required, precautions and chemical required.
2. Explain the method of preparation of potassium trioxalatoferrate (III) trihydrate along with the chemical reactions involved, apparatus required, precautions and chemical required.
3. Explain the method of preparation of tetraamminecopper (II) sulphate monohydrate along with the chemical reactions involved, apparatus required, precautions and chemical required.

UNIT 5: SEPARATION METHODS

CONTENTS:

5.1 Objective

5.2 Introduction

5.3 Demonstrate ion exchange method to remove calcium ions from hard water.

5.3.1 Chemicals and equipments required

5.3.2 Theory

5.3.3 Procedure

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5.4 To separation of acetanilide from a mixture with salicylic acid by solvent extraction technique

5.4.1 Chemicals and equipments required

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5.4.5 Calculations

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5.5 Summary

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5.7 Answers

5.8 References

5.1 OBJECTIVE

Separation methods are an integral part of synthesizing pure compounds in the laboratory or industry. Industrial processes make use of some or the other separation method for production of a given chemical. Separation processes are even very common in

laboratories and in household routines. For example, boiling of water is a separation technique which removes temporary hardness from the water. Removing seeds from fruit juices by filtering raw juice through a strainer is another household separation method. Separation of a precipitate from a liquid by means of filter papers is most frequent separation technique used in laboratories.

These routine examples indicate that the principle behind separation techniques is sorting out of molecules of a kind from a mixture. In order to achieve separation of desired molecules, the separation techniques make use of a certain property of the molecules that contrasts with those of the remaining mixture. For example, filtration makes use of different particle sizes of particles for sorting the desired component. This chapter deals with two separation techniques, *viz*., ion exchange and solvent extraction. Ion exchange relies on the exchange of similar ions using a stationary polymeric matrix whereas the solvent extraction process is based on the unlike solubility of solute in different solvents. Thus, objective of this chapter is to understand the principles of and to acquire practical skills of two very important separation methods used in laboratories and industry.

5.2 INTRODUCTION

A separation method is technique to sort out a desired component (or molecule) from a mixture of components (or different molecules). Separation methods are closely related to the purification techniques. The difference between the two is, when using separation methods the ratio of desired and undesired molecules present in the mixture do not differ much. However, purification methods are used when the impurities in the bulk mixture are present in low quantity.

As mentioned, the target of a separation process is sorting out of different molecules. Since we cannot pick individual molecules to separate them thus we try to provide some kind of force under the influence of which different molecules are segregated over a period of time. The sorting out of molecules under a given set of condition is called partition or distribution processes. Some of the commonly employed separation techniques can be classified as crystallization, distillation, solvent partition and adsorption processes.

(i) Crystallization: In crystallization the partition occurs between a solid and solution(Figure 1). Here we want molecules of type A only to crystallize and separate out.

For this purpose we must use a solvent in which A is highly soluble while molecules of B will tend to crystallize. After dissolving all of the mixture the temperature is lowered so that B starts to crystallize first whereas the solution is not saturated enough for A to crystallize. This is followed by mechanical separation (filtration).

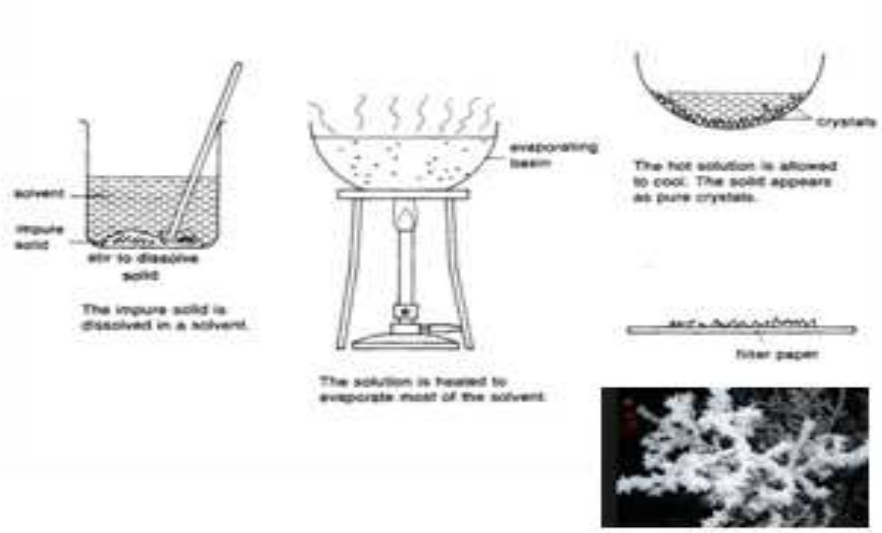

Figure 1 Process of crystallization

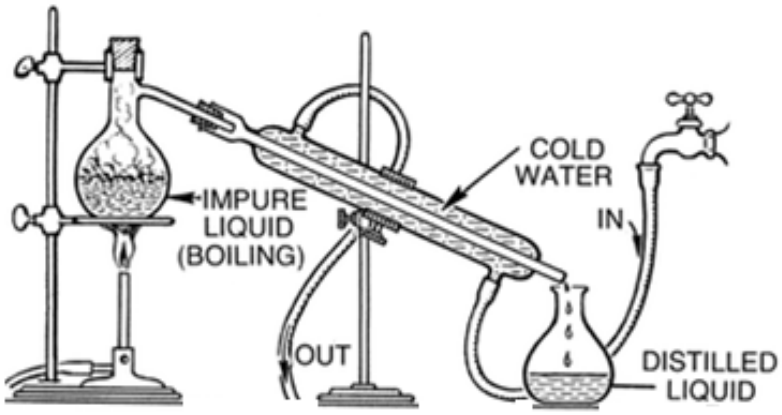

Figure 2 Process of distillation

(ii) Distillation: In a distillation flask containing a solution of two types of liquid, one having boiling point higher than the other by almost 25 °C. The flask also contains the vapor of liquids which are in equilibrium with the solution phase. If solvent A is more volatile than B then there is higher tendency of A to enter into vapor phase. Thus by heating this solution relatively more number of molecules of A will enter into vapor phase than B. These vapors can be condensed and collected giving a solution richer in A than B. Repeating the process will lead to much purer sample of A. The process of simple distillation has been depicted in figure 2

(iii) Liquid-liquid Partition: In this separation method the distribution is done between two liquid phases. Suppose A and B molecules are present in a given solvent say any organic solvent such as dichloromethane. Although A and B are present in dichloromethane but a prior knowledge of the molecular structure can help in deciding the solubility preferences of A and B. We can suppose here that A is such an organic molecule that will preferably dissolve significantly in non polar or polar organic solvent and B is such a compound that is ionic and would dissolve in polar protic solvents. This information helps us in deciding that if the mixture is added to another solvent that is immiscible with dichloromethane such as water, A and B can be separated. Now these two immiscible liquids are shaken together and allowed to separate into layers using mechanical tools such as a separatory funnel. Thus with the judicious choice of solvents we can separate the molecules of A and B into two different layers of solvent depending upon their higher solubility in any a given solvent. The substances A and B can be recovered by evaporating the solvents.Peruase figure 3 for the separation of two immiscible liquids

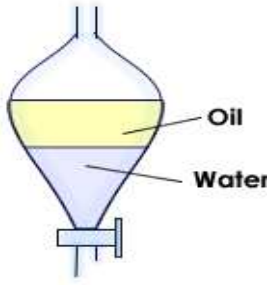

Figure 3 Process of distillation

(iv) Adsorption separations: In this method the partition is achieved between a solution (or gas phase) and a surface phase (may be interfacial). The phenomena by which molecules become concentrated at the surface of a material or substrate by virtue of their physical and chemical behavior is called adsorption. In this process the choice of solvent and a surface plays a crucial role. The surface should provide maximum area per unit mass hence fine powdered adsorbents are used which provide enough surface area. We know that fine particles can provide maximum surface area for a given mass. Porous materials such as clays and charcoal are also being used as an adsorbent. Here also the choice of surface is important. The surface should be such that the solvent in which the mixture of A and B will be dissolved should form an interface phase and should selectively adsorb only one type of molecules, let us assume A is adsorbed more selectively than other molecules. Now when the adsorbent is shaken with the mixture partition occurs adsorbing molecules of a more than other molecules because A has greater tendency to form interface with the adsorbent. Thus A along with the adsorbent can be separated by filtration.

5.3 DEMONSTRATE ION EXCHANGE METHOD TO REMOVE CALCIUM IONS FROM HARD WATER

5.3.1 Chemicals and equipments required

Deionized water, experimental hard water, Eriochrome black T indicator, a glass column, cationic exchange resin (for example, wet amberlite resin, and hydrogen form), pipette, conical flasks etc.

5.3.2 Theory

Ion exchange is a separation method often used in water-softening and other laboratory processes. Most frequent ion exchange processes involve exchange of ions between an electrolyte solution and a solid polymeric ion-exchanger. Derivatives of cellulose, agar-agar or synthetic organic polymers are used as ion-exchangers. Ion exchangers usually have either cationic or anionic functionalities hooked to their polymer matrix. Counter ions of the hooked ions electrostatically adhere to the system but easily can be exchanged with another ion of same type. Thus, Cl^- ions from an electrolyte solution can be exchanged with free OH^- ions of an anionic exchanger resin. Similarly, Ca^{2+} from hard water can be changed with H^+ ions using a cationic exchanger resin.

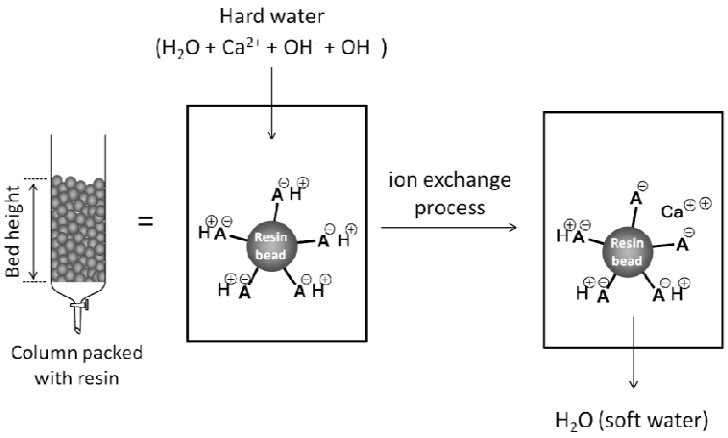

Figure 1. Schematic depiction of resin bed in a packed column and ion exchange process.

5.3.3 Procedure

1. Clamp a clean and dry column (100 mL) equipped with stopcock on a stand.

2. Take 25 mL wet cation exchange resin in a beaker. Stir with glass rod and allow settling down of resin. Decant the additional brown coloured liquid and discard. Remember the resin should never be dried hence liquid level just sufficient to keep resin wet must be maintained.

3. Add 10 mL of deionized water swirl carefully and fill it in the column already clamped vertically on a stand. Dab on the walls of column for close packing of resin and to avoid trapping of air bubbles.

4. Open the stopcock of column and drain out the excess liquid above the bed height of the resin. Bed height is the length of the column up to which resin is filled. Let us assume the resin makes up to the 10 mL mark (if it is graduated) on the column.

5. Rinse the resin with buffer solution supplied by your laboratory or by deionized water. Do not drain the liquid completely. Maintain the level of liquid level as high as the bed height of the resin.

6. Take the supplied sample of hard water in a clean beaker or alternatively prepare it. Hard water can be prepared by dissolving few mg of calcium hydroxide in deionized water.

7. Carefully add 10 mL of water sample in the column with the help of a pipette. Care must be taken that the resin bed should not be disturbed.

8. Open the stopcock of the column and drain out *ca* 10 mL of the liquid. Now all the previous liquid must have been eluted and the resin must be charged with the sample.

9. Carefully add another 10 mL of water sample in the column with the help of a pipette. Drain out 10 mL of the liquid and collect it in a conical flask labeled as **A**.

10. Repeat the step 9 thrice and hence now you will have three conical flasks, **A**, **B** and **C** each with 10 mL water sample drained out of the column.

11. Take 10 mL of hard water sample in a fourth conical flask labeled as **D**. Remember the flask **D** contains untreated water or water sample not passed through the ion exchange column.

12. Add two drops of Eriochrome black T indicator in each of the four flasks.

5.3.4 Observation

Eriochrome black T gives greenish blue colour in pure water and forms a wine red coloured complex with calcium ions present in hard water. Hence you must carefully observe the colours of the conical **A**-**D** after addition of indicator Eriochrome black T. Wine red colour of conical flask **D** indicates the presence of hardening ion in the untreated sample whereas appearance of blue colour in beakers **A**-**C** indicates that the water sample run down the ion exchange column is free of calcium ions.

5.3.5 Results

Exchange of calcium ions present in hard water with the H^+ ions present on cationic exchange resin has been demonstrated.

5.3.6 Precautions

1. The resin bed should not be disturbed while charging column with different liquids.

2. Any liquid should be charged only when the level of liquid present in column is just up to the height of resin bed.

3. Mixing of two liquids above the resin bed affects the results.

4. Drying the resin will deteriorate its performance. Hence care must be taken to keep it wet throughout the experiment.

5.4 TO SEPARATION OF ACETANILIDE FROM A MIXTURE WITH SALICYLIC ACID BY SOLVENT EXTRACTION TECHNIQUE

5.4.1 Chemicals and equipments required

Mixture of salicylic acid and acetanilide, separatory funnel, ring stand for separatory ethyl acetate, distilled water, brine (aq. NaCl solution), conical flasks, beakers, funnel, water bath, glass rod, burner or spirit lamp, digital balance etc.

5.4.2 Theory

Extraction is a separation technique used in the laboratory to isolate desired components from a mixture. In the process of solvent extraction the solute mixture is dissolved in a solvent (say water) followed by addition of an immiscible volatile organic solvent (such as ethyl acetate, ether, chloroform or methylene chloride). This biphasic system is then taken in a separatory funnel and vigorously shaken for distribution of desired component in one of the phases (usually organic). Solvents are chosen judiciously so that the maximum amount of desired component extracts to organic phase leaving all the impurities in aqueous phase.

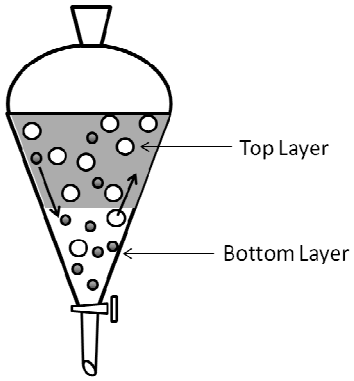

Figure 2. Schematic depiction of solvent extraction using a separatory funnel

When a solute is shaken with two immiscible solvents, it distributes between the two solvents in a ratio proportional to its solubility in those solvents. At equilibrium, the ratio of concentration of solute in two solvents is called partition coefficient (K_d).

$$K_d = \frac{[solute]_{org}}{[solute]_{aq}} = \frac{W_{org}/V_{org}}{W_{aq}/V_{aq}}$$

Where [solute] represents concentration, W represents weight of solute and V represents volume of solvent. Suffix, *org* and *aq* represent organic and aqueous phases respectively. The larger the value of K_d in above equation indicates that more solute will be distributed in organic layer. Repeated extractions can thus result in transfer of almost all solute to the organic components, which can be recovered by evaporating the volatile organic solvent.

5.4.3 Procedure

(i) Preparing the experimental solute mixture: Solute mixture will be provided by your laboratory instructor. If instructor asks you to prepare the mixture by yourself, take 0.5 g of each of acetanilide and salicylic acid and mix them to obtain experimental solute mixture.

(ii) Choice of solvents: Acetanilide is slightly soluble in water but fairly soluble in diethyl ether. Salicylic acid is soluble in water. Its deprotonated form (salicylate) is insoluble in ether. Hence, water and diethyl ether make a suitable solvent pair for extraction of acetanilide and salicylic acid.

(iii) Steps for solvent extraction:

a. Take 1.0 g mixture of salicylic acid and acetanilide in the separatory funnel.

b. Add 25 mL of diethyl ether in the separatory funnel and swirl until the solid mixture is dissolved.

c. Add 15 mL of 5% $NaHCO_3$ solution in the separatory funnel. Put on the stopper and carefully shake the funnel for few seconds so that the solute can distribute between phases. Frequently release the pressure developed inside the separatory funnel during the extraction process.

d. Keep the separatory funnel on ring stand for two minutes to allow settling of two layers.

e. Water is denser than the diethyl ether, therefore aqueous layer settles as bottom layer in separatory funnel, over which diethyl ether layer settles.

f. Carefully drain the aqueous layer into a beaker.

g. Repeat the similar process again (steps c-f) by adding 10 mL of 5% $NaHCO_3$ solution in the separatory funnel. Combine both the aqueous layer components in the same beaker.

h. Cool the beaker containing aqueous layer by placing in refrigerator or ice bath. Acidify the cold aqueous layer by carefully adding concentrated hydrochloric acid which results in formation of white precipitate. Continue adding HCl until no more precipitate is produced.

i. Filter the precipitate and place on a dish for drying in air. Collect the diethyl ether layer in another beaker, dry over anhydrous sodium sulfate, filter and evaporate the solvent to recover the dissolved component.

j. Weigh both components once dried. Take the melting points of both solids. Also calculate the percentage of the recovered solids.

5.4.4 Observations

S.N..	Amount of 1:1 solute mixture taken	Total volume of ether used	Total volume of $NaHCO_3$ used	Weight of acetanilide	Weight of salicylic acid recovered
1	1.0 g	25 mL	25 mL	X g	Y g
2					
3					

5.4.5 Calculations

Calculate the partition coefficient (K_d) of acetanilide as follows:

$$K_d = \frac{[solute]_{org}}{[solute]_{aq}} = \frac{W_{org}/V_{org}}{W_{aq}/V_{aq}}$$

$$or, \quad K_d = \frac{X/25}{(0.5 - X)/25}$$

Similarly, partition coefficient (K_d) of salicylic acid can also be calculated. If you are instructed to repeat the experiments several times, do so and enter the details in the observation table.

5.4.6 Result

Acetanilide is separated from a mixture of it with salicylic acid by solvent extraction technique. Partition coefficient of acetanilide was found to be _____ for diethyl ether and water.

5.4.7 Precautions

1. Use clean and dry glassware for experiment.
2. Avoid contact of chemicals with skin. In instance of contact, wash immediately with plenty of water.
3. Wear safety goggles while handling the concentrated acid and using the separatory funnel.
4. Label the dishes used to evaporate different solutions carefully.

5.5 SUMMARY

In this chapter we have learnt about two important experiments. First one is based on the ion exchange separation technique. In the experiment we have understood how the hard ion calcium can be exchanged with the H^+ ion to remove the permanent hardness of water. Usually more than one kind of ions may be present in solutions to be purified. For instance, Mg^{2+} also remains present in natural hard water samples. Ion exchange technique is very useful for such situations. Remember the cationic exchange resins can simultaneously remove all cations from the feed solution. Similarly, anionic exchange resins can simultaneously remove all anionic impurities from a given sample. Thus, for obtaining a water sample completely free of foreign ions it is necessary to run it through a pair of anionic and cationic exchange columns. We must also remember that this methods is not limited to the water purification only but also widely used in laboratories for separation of molecules for example amino acids.

Another experiment, the solvent extraction is a commonly practiced laboratory separation technique. It is often used to separate an organic compound from the reaction mixture after completion of a reaction. As we have seen solvent extraction makes use to differnt solubility of a solute in two immiscible solvents. As there are a number of polar and non polar organic solvents which are immiscible with water, a basic knowledge of 'like dissolves like' can help us to choose suitable solvent pairs for extraction of a compound from rest of the components. Understanding the principles behind these two experiments and acquiring skill to perform these experiments will help the students during their research endeavours.

5.6 TERMINAL QUESTION

Short answer type questions

Q.1 What is a separation technique?

Q.2 Give example of two separation techniques used at houses?

Q. 3 What are ion exchange resins?

Q.4 Why the drying of a wet resin is not recommended?

Q.5 How do you make experimental hard water for the experiment? Is it similar to the naturally occurring hard water?

Q.6 What indicator did you use to show that ion exchange process has taken place?

Q.7 What is partition coefficient?

Q.8 Why the aqueous solution of sodium bicarbonate is added instead of water?

5.7 ANSWERS

A.1 Separation technique is a method to sorting out of molecules of a kind from a mixture.

A.2 Removing temporary hardness of water by boiling and filtration of tea or juice are two household separation methods.

A. 3 Ion exchange resins are insoluble polymeric matrices having cationic or anionic organic functionalities on their surfaces. Counter ions of surface charges of these materials can be exchanged for ions of same charge present in an experimental solution.

A.4 Because drying of the resin may alter the functionality on the surface of resin which can affect the end result of the experiment.

A.5 We dissolved few milligrams of calcium hydroxide to prepare hard water sample. This is not similar to natural hard water as naturally occurring hard water often contains more foreign cations and anions such as Mg^{2+}, Cl^- and SO_4^{2-} etc.

A.6 We have used Eriochrome black T indicator which gives greenish blue colour in pure water and forms a wine red coloured complex with calcium ions present in hard water. Ion exchange process occurring in the column exchanges all calcium ions present in the sample with H^+ ions, which is indicated by blue colour of indicator.

A.7 At equilibrium in the solvent extraction process, the ratio of concentration of solute in two solvents is called its partition coefficient (K_d) and is given by following expression:

$$K_d = \frac{[solute]_{org}}{[solute]_{aq}} = \frac{W_{org}/V_{org}}{W_{aq}/V_{aq}}$$

Where [solute] represents concentration, W represents weight of solute and V represents volume of solvent. Suffix, *org* and *aq* represent organic and aqueous phases respectively.

A.8 Because sodium bicarbonate is a weak base which deprotonates the salicylic acid to yield salicylate. Being ionic species salicylate has great affinity to go in aqueous solution and practically no affinity for ether. Hence, for achieving better separation of mixture, we used sodium bicarbonate solution rather than water.

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UNIT 6: INTRODUCTION TO LAB TECHNIQUES: ORGANIC CHEMISTRY

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6.1 INTRODUCTION

In the previous unit 1 of inorganic chemistry i.e. introduction to lab techniques, we have discussed the topics like how to make laboratory notebook? What are the commonly used apparatus in inorganic laboratory and different process related to inorganic chemistry? The present unit deals with the introduction to lab techniques of organic chemistry.

In this unit, we will discuss about the apparatus and the techniques commonly used in organic laboratory and the knowledge of which is compulsory for a chemistry students.

To make the topic more interesting, we will discuss the commonly used apparatus in detail along with the figure. Different techniques are undertaken which are discussed below to have a complete knowledge of laboratory.

6.2 OBJECTIVES

After reading this unit you will be able to:

- Know the commonly used apparatus in organic chemistry.
- Describe different techniques involved in organic chemistry.
- Determine the melting point of an organic compound.
- Determine the boiling point of a liquid.
- Prepare sodium extract.
- Know how to perform the distillation process.
- Know the safety measures that must be taken in the laboratory.

6.3 LABORATORY NOTEBOOK

A laboratory notebook or lab manual is a record of experiments conducted in the laboratory. The first page of the notebook is of certificate where the names, class, roll no., institution name is mentioned. The next page is index page where the brief idea of the experiment performed are mentioned which includes serial no., name of the experiment, page no., date of experiment, date of submission and remark by teacher. After index page the proper pages for writing the experiment are given. Left hand side pages are blank or without lines while the right hand side pages are lined provided with experiment no., date, page no. at the top and teacher's signature at the bottom. On the left hand side tables, calculations, chemical reactions, figure is mentioned with a pencil. On the right hand side, we write with a ball point pen. The notebook should be well covered containing a record of experiments performed in the laboratory.

6.4 COMMONLY USED APPARATUS

In order to perform practical in organic chemistry laboratory, one should have knowledge of apparatus that are commonly used. These apparatus includes flasks, test tubes, petri

dish, reagents bottles, boiling tubes, pipette, burette, funnel, beakers, centrifuge tubes, ignition tubes, porcelain dish, water bath, heating mantle, magnetic stirrer, condenser and desiccator. Let us discuss these apparatus in detail.

6.4.1 Flask

Different types of flasks are used in the laboratory. This includes round- bottom flasks, flat- bottom flasks, volumetric flasks, filtration flasks.

6.4.1.1 Round – bottom flasks

These flasks as the name indicates possess bottom which is spherical in shape as shown in Figure 1. These flasks are also known as round – bottomed flasks or simply RB flasks. Chemical reactions are performed in these flasks and are made up of glass (borosilicate). These are available in several range that 5 ml to 20 l. These flasks are used for boiling the liquid, in distillation and for storing the reaction mixture. Due to the presence of round bottom, these flasks are kept on a cork ring or are clamped on a stand.

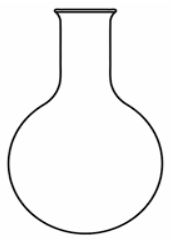


Figure 1. Round- Bottom Flask

Round bottom flasks are further classified into one necked round bottom flasks, two necked round bottom flasks and three necked round bottom flasks. In one necked round bottom flasks, there is one neck with one opening at the tip as shown in Figure 1 above. In two necked round bottom flasks, there are two neck with two opening at the tip as shown in Figure 2.

Figure 2. Two necked- round bottom flask

In three necked round bottom flasks, there are three neck with three opening at the tip as shown in Figure 3. The necks allow the flask to join with other glass system.

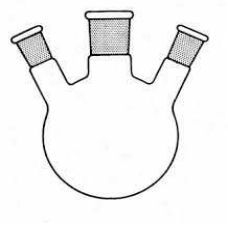


Figure 3. Three necked- round bottom flask

6.4.1.2 Flat – bottom flask

These flask are also known as flat –bottomed flasks as their bottom are flat. This makes the flask to stand by their own on a level surface. The uses are same as round- bottom flask. These flask possess one neck as shown in Figure 4. These flasks are preferred over round- bottom flasks as former stands by its own.

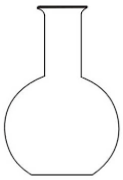


Figure 4. Flat- bottom flask

6.4.1.3 Volumetric flask

These flasks possess long neck with the stopper at the top and are like pear in shape as shown in Figure 5. These flasks are made up of plastic or glass which is used for preparation of the solution of desired volume. These flasks are not used for heating. The size of these flasks generally used in laboratories varies from 25 ml to 2000 ml.

Figure 5. Volumetric flask

6.4.1.4 Filtration flask

Filtration flasks are flat- bottom flasks provided with a spout through which it get attach to other system as shown in Figure 6. These flasks are Erlenmeyer flasks.

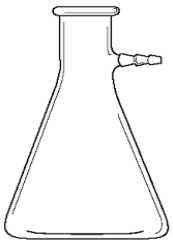


Figure 6. Filtration flask

6.4.1.5 Distilling flask

These flasks are used for separating the liquid mixture on the basis of their boiling points. During distillation, this flaks is heated and the liquid mixture get converted into vapour. The liquid with low boiling point changes to vapour firstly than the liquid with more boiling points. In this way, these funnels are used to separate liquid mixture.

6.4.2 Test tubes

This is one of the commonly used apparatus in the laboratory. These are long glass tube provided with bottom which is round in shape. These are available in many size as shown in Figure 7. Test tubes are used to carry a chemical reaction even those that requires heat. One of the advantage of using test tube is that these are of low cost and acquire small amount of chemical for carrying a particular reaction.While performing the experiments, test tubes are fitted in a test tube holder.

Figure 7. Test- tube

6.4.3 Petri dish

Petri Dish is also known as Petri plate or cell- culture dish. These dishes are named after the name of the scientist J. R. Petri. These are flat bottom apparatus commonly used in biology for fungal growth as shown in Figure 8.

Figure 8. Petri Dish

6.4.4 Reagents bottles

These bottles as the name indicates are used for storing chemicals (liquid or solid). These bottles are either made up of glass or plastics as shown in Figure 9. Each bottle is provided with an air tight cap so that the chemical placed in them remains as such in a purified form. Every laboratory contains wooden shelves in which these reagents bottles are arranged properly. Some chemicals are stored in a brown bottles as these are light sensitive. Commonly used reagent bottles possess volume 100 ml, 250 ml, 500 ml, higher volumes are also known.

Figure 9. Reagent bottle

6.4.5 Boiling Tubes

These tubes are like test tubes but are wider and larger in size as shown in Figure 10. As the name indicates, these tubes are used for boiling the chemical. Glasses having high heat resistant capacity are used for the preparation of boiling tubes.

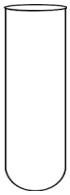


Figure 10. Boiling tube

6.4.6 Pipette

Pipette is a glass apparatus used in laboratories in order to transfer a fixed volume of solution or liquid. It consists of a long narrow tube provided with a bulb in the middle and a single mark towards the upper side indicating the particular volume as shown in Figure 11. These are generally available in several range like 0.5ml, 1 ml, 5ml, 10 ml, 25 ml.

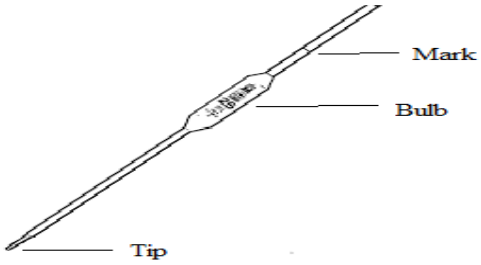


Figure 11. Pipette

A clean pipette is used for transferring a particular volume of a liquid. In order to clean a pipette, fill it with distilled water by sucking with the mouth. Now allow the water to drain. While draining the water, it should be noted that if water drains without leaving drops on the inner surface of the pipette, this shows that pipette is clean. If drops appears on the inner surface of the pipette then clean it with detergent or soap solution and with tap water followed with distilled water at the end. Now a cleaned pipette is ready to use.

6.4.7 Burette

Burette is graduated glassware used in laboratories. It consists of a graduated narrow tube provided with the tap at the bottom as shown in Figure 12. The upper part is used for adding the liquid or solution into the burette. Like pipette, burettes are generally used in titration or for delivering known volumes of a liquid. These are available in different volume like 10 ml, 20 ml, 50 ml. The commonly used burette possesses 50 ml volume.

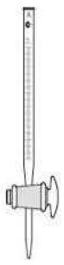


Figure 12. Burette

6.4.8 Funnel

This apparatus used in chemistry laboratory is narrow towards the bottom and wider towards the tip. These are made up of glass or plastic. Funnels are used for transferring the liquid into the container that are provided with small opening as shown in Figure 13. We also use funnels in home for transferring the liquid.

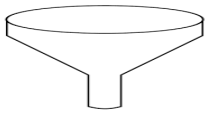


Figure 13. Funnel

There are different types of funnel used in chemistry laboratory. These are as follows:

6.4.8.1 Filter funnel

These funnels as the name indicates are used for filtration which separates solid from a liquid. These funnels are provided with filter paper for carrying the process of filtration. This funnel includes Hirsch funnel, Buchner funnel.

6.4.8.2 Thistle funnel

These funnels are provided with a reservoir at the top which extends to a long narrow tube.

6.4.8.3 Separating funnel

These funnels are also known as dropping funnels or separatory funnels. As the name indicates, separating funnels are used to separate the component of a mixture in between the two immiscible liquids. Some of these funnels are cylindrical in shape; some are pear in shape while some are conical in shape. A stopper is provided at the top of the funnel which is shown in Figure 14.

Figure 14. Separating funnel

6.4.9 Beakers

Beakers are commonly used apparatus in chemistry laboratory. This are made up of glass (borosilicate) and is provided with a beak at the top as shown in Figure 15. These are used for storing solution. These are available in several volumes like 5 mL, 10 mL, 25 mL, 50 mL, 100 mL, 250 mL, 500 mL and even more than this.

Figure 15. Beaker

6.4.10 Centrifuge Tubes

These tubes as the name indicates are used in centrifuge. Centrifuge is a device which rotate the object around a fix axis causing the denser particle to settle down at the bottom of the tube.These tubes are smaller in size like 1 ml as shown in Figure 16. Centrifuge tubes are made up of plastic and are used for storing the chemicals.

Figure 16. Centrifuge tube

6.4.11 Ignition tubes

Ignition tubes are small in size but possess thick wall which is shown in Figure 17. These tubes are commonly used in laboratory in the formation of sodium extract. Sodium extract is a solution used for the detection of elements like nitrogen, halogens and sulphur. These tubes have a capacity to hold small amount of the substance that undergoes strong heating. One of the main disadvantage of using ignition tubes is that they can be used only once as we have to break the tube while making the sodium extract. In organic analysis, ignition tubes play an important role.

Figure 17. Ignition tube

6.4.12 Porcelain dish

Porcelain dish is also known as evaporating dish. These dishes as the name indicates are used for the process of evaporation so that we can convert liquid form of a substance into a solid mass or to more concentrated form. These dishes are made up of porcelain (ceramic material), hence the name porcelain. As shown in Figure 18, these dishes possess a beak and are white in color. During evaporation, these dishes are placed on the tripod stand. Upto 10 ml of a liquid is taken in the porcelain dish.

Figure 18. Porcelain dish

6.4.13 Water bath

Water bath as the name indicates as an apparatus used in chemistry laboratory that contains water. This water is heated up to desired temperature for conducting the experiments. We can maintain a constant temperature in a water bath. An advantage of using water bath is that it is used for heating those substances that catches fire easily in an open flame. As we know that the boiling point of water is 100 ^{o}C, therefore the maximum temperature that can be attained in a water bath is 100 ^{o}C approximately. As we know that the water bath is filled with water as shown in Figure 19, so it should always be covered in order to prevent the process of evaporation and to avoid the growth of micro-organisms. The apparatus is provided with a plate having holes in order to insert the sample into the water for carrying a reaction at constant temperature.

Figure 19. Water bath

6.4.14 Heating mantle

The apparatus as the name indicates is used for heating the reaction mixture enclosed in a container. For example, if a reaction is conducted in a round- bottom flask at high temperature then the flask is placed over the heating mantle directly. Heating mantle consist of strips of fabrics in which electric wires are embedded giving the shape of basket as shown on Figure 20.

Figure 20. Heating mantle

6.4.15 Magnetic stirrer

With the help of magnetic stirrer, we can stir the solution by spinning a magnet. The spinning of the magnet results in the formation of magnetic field.

6.4.16 Condenser

Condenser is an apparatus that convert a substance from a gaseous or vapours state to a liquid state. Condenser cools the gases or vapours and converts it into a liquid form. These are used in refrigerators, air conditioners and in the process of distillation which is discussed later on in this unit. The structure of condenser is given in Figure 21

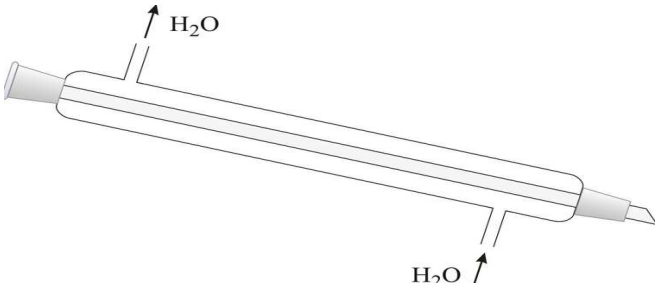


Figure 21. Condensor

6.4.17 Desiccator

Desiccator is a thick- walled glass apparatus used for protecting the chemicals that reacts with moisture present in the atmosphere. It consists of a big jar having a cap as shown in Figure 2.2.

Figure 22. Desiccator

6.5 DISTILLATION

In the chemistry laboratory, we have heard about the distilled water. The distilled water which is used for making the solution is prepared by the process of distillation. Distillation is defined as the process that involves evaporation followed with condensation resulting in the separation and purification of the liquids on the basis of their boiling points as every liquid possess a definite boiling point. In order to separate two or more liquids by the process of distillation, firstly we heat the flask (round bottom flask or distilling flask). On heating, formation of vapours takes place. More volatile liquid separate first than the other having low volatility. The vapours thus produced passes through the

condenser so that is gets converted into the liquid form which is collected in a container. The liquid having low volatility will evaporate after heating the flask in excess. In this way liquid mixture are separated by distillation on the basis of their boiling point. The whole process is represented below in Figure 2.3.

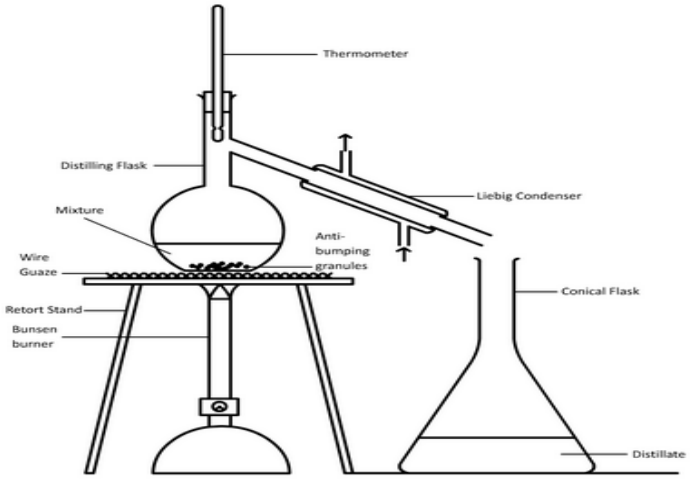


Figure 23. Distillation

Distillation is classified into two types: one is simple distillation and the other is fractional distillation. The apparatus of simple distillation is shown above in Figure 22. It consist of a round – bottom flask with an adapter at the top through which thermometer is inserted. To the other adapter, a condenser is connected. Using heating mantle, the flask is heated which leads to the formation of vapours. Cold water runs through the condenser leading to the conversion of vapour into the liquid which is then collected. Fractional distillation on the other hand is same like a simple distillation but possess a fractionating column in between the condenser and the round – bottom flask. The column provides the better separation between the liquid. Generally we use simple distillation process in the laboratory.

6.6 SODIUM EXTRACT

Sodium extract is a solution used in organic analysis for the detection of elements like nitrogen, halogen and sulphur present in a given organic compound. For the preparation of sodium extract, the following procedure is to be followed: First of all, small pieces of metallic sodium is taken and are dried by pressing it in a filter paper. Now ignition tube is taken into which sodium piece is placed. Then above the piece of sodium, a very small amount of given organic sample is placed. In this way two or three layers of sodium and sample is prepared. Now ignition tube is holded using a pair of tong and is heating slowly by a burner. Heat the tube till it becomes red hot. When the tube becomes

red hot, transfer it to the porcelain dish containing 10 ml of distilled water. The ignition tube will break in water. Allow two more ignition tubes to break in the same porcelain dish using the same organic sample. Now we stir the solution in the porcelain dish with the help of a stirrer so that the unreacted sodium reacts with water. Allow the solution to boil for five minute. After boiling, filtration is done by using a filter paper and the filtrate thus obtained is sodium extract. The filtrate should be clear and transparent as the dark color indicates the incomplete fusion. If the filtrate is not clear then repeat the process again. By preparing the sodium extract, the elements like nitrogen, sulphur, and halogen are converted into water soluble sodium compounds like to ionisable sodium cyanide, sodium sulphide and sodium halides respectively. This process is known as Lessaigne's test that's why sodium extract is also known as Lessaigne's solution.

6.7 DETERMINATION OF BOILING POINT

The boiling point of a liquid is defined as the temperature at which a liquid form of a substance changes into a vapour form. At this temperature, the vapour pressure of the liquid becomes equal to the atmospheric pressure. Different liquids boils at different temperature which shows that boiling point is the characteristic property of a particular liquid. For measuring the boiling point, very small amount of a liquid is required about 1 ml to 2 ml. An apparatus used for measuring the boiling point of a liquid is shown in Figure 24.

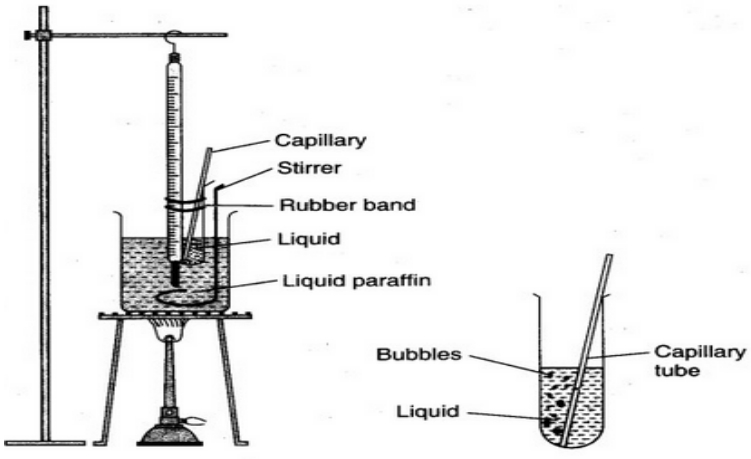
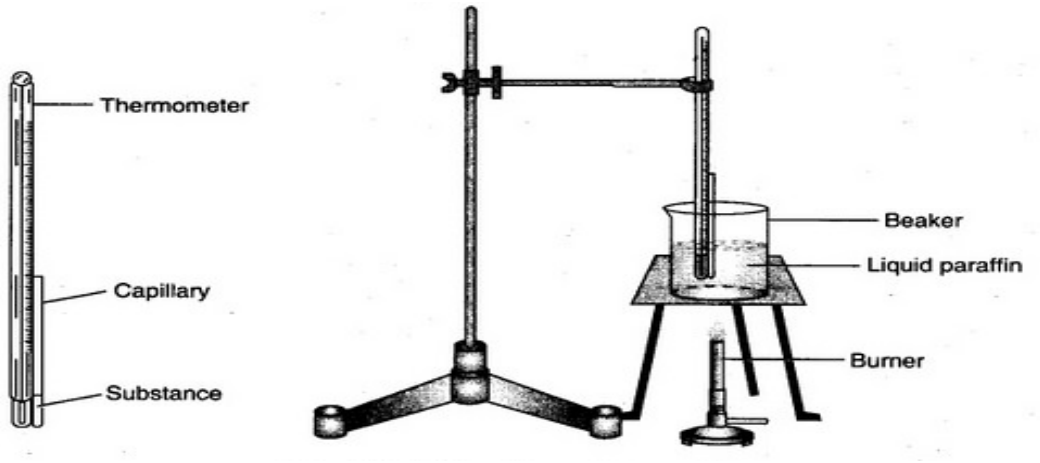


Figure 24. Determination of boiling point

It is clear from Figure 23 that there is a boiling tube fitted with a cork in which a thermometer and a bent tube is inserted. The vapour escapes through the bent tube. The liquid whose boiling point is to be determined is taken in the boiling tube. Small pieces of porcelain is added into the liquid in order to avoid bumping.The tube is then allowed to stand. The thermometer is adjusted in such a way that the surface of the liquid is about 1 cm below. Now a burner is placed below the boiling tube in order to heat the liquid. Now open the burner and heat the liquid slowly so that the boiling takes place. An increase in temperature will observe which become constant after some time. This constant temperature is noted which is the boiling point of the liquid. In this way, the boiling point of a given liquid is determined.

6.8 DETERMINATION OF MELTING POINT

Like boiling point of a liquid, melting point of a solid is one of the characteristic property of a solid. The melting point of a solid is defined as the temperature at which the solid melts. In order to determine the melting point, the following set up is used which is shown in



Figure

Figure 25. Determination of melting point

The figure consist of a round- bottom flask which is holded by using a stand. The flask is filled with concentrated sulphuric acid (nearly to half). A tube is taken into which a small amount of concentrated sulphuric acid is added. Allow the tube to stand and insert it into the round –bottom flask containingsulphuric acid.In order to measure the melting point, a thermometer is placed into the tube. Now a capillary is taken and is heated from one end

in order to close it. Now a solid whose melting point is to be determined is taken in a powdered and dry form into the capillary tube. The capillary is then placed into the tube at the side of the thermometer with closed end towards the bottom. The open end of the capillary should remain inside the tube. Now heat the flask slowly using a burner placed below it. We will observe an increase in temperature and at a particular temperature, the solid inside the capillary will melt and become transparent. This temperature is recorded which is the melting point of the given liquid. The presence of moisture in the solid may lower the melting point therefore the solid should be dry and in pure state.

6.9 LAB REAGENTS

These are the substances or compounds that undergoes a chemical reaction. There are several lab reagents used in the organic chemistry laboratory. Some of which are discussed in unite 1 of inorganic chemistry while some are as follows that are commonly used in organic analysis: sodium bicarbonate solution, ceric ammonium nitrate solution, sodium hydroxide, ferric chloride solution, bromine water, 2,4-dinitrophenyl hydrazine, silver nitrate, nitrous acid (HCl + $NaNO_2$), Schiff 's reagent (p-rosaline hydrochloride + SO_2), Tollen 's reagents ($AgNO_3$ + NaOH), Fehling 's solution A ($CuSO_4$ + H_2O), Fehling 's solution B (H_2O + sodium potassium tartrate + sodium hydroxide), Benedict's solution (water + copper sulphate + sodium nitrate + anhydrous sodium carbonate), Molisch's reagent (alpha napthol + rectified spirit), Lucas reagent (Anhydrous $ZnCl_2$ + HCl), Barfoed's reagent (copper acetate + glacial acetic acid + water).

6.10 SAFTEY MAESURES IN LABORATORY

While working in the laboratory, everyone should be aware of the safety measures that we have to consider while working in laboratory, any ignorance may lead to an accident. In every laboratory, there is a first- aid box. In case of acid burn, immediately wash with cold water and then with dilute solution of sodium bicarbonate while in case of alkali burn, after washing with water, a dilute solution of acetic acid is used. In order to have good experimental results, clean the apparatus properly with chromic acid and then with distilled water. While performing the experiments, always wear lab coat in order to protect your clothes. Special attention should be taken while working with acids as they cause burning.

6.11 SELF ASSESSMENT QUESTIONS (SAQ)

- Fill in the blanks

1. Distillation process involves ……. followed with …….
2. A tube used for preparing sodium extract is called ……. tube.
3. ……. is used to convert a substance from vapour state to a liquid state.
4. The two immiscible liquids are separated by using ……. funnel.
5. In ……., magnet is used for stirring the solution.
6. At the boiling point, ……. form of a substance changes to ……. form.
7. An apparatus used for protecting the chemicals that are hygroscopic in nature is …….
8. Sodium extract is also known as ……. solution.

- True and False.

1. Sodium extract is a solution used for the detection of elements like nitrogen, halogens and Sulphur.
2. Round- bottom flasks are preferred over flat bottom flasks.
3. The flask provided with long neck with a mark is called volumetric flask.
4. Filtration flasks are round- bottom flasks.
5. Porcelain dish is also known as evaporation dish.

6.12 SUMMARY

In this unit we have discussed the general idea of apparatus and techniques used in the organic laboratory. We have discussed about the commonly used apparatus like desiccator, condenser, heating mantle, magnetic stirrer etc. and also about different techniques like distillation, methods of determining the boiling point and melting point. Further we discussed about the reagents and the safety measures taken in the laboratory.

6.13 GLOSSARY

- **Distillation –** Process of separating liquids on the basis of their boiling points.
- **Evaporation –**Process of conversion of a substance from a liquid state to a vapour state.

- **Condensation -**Process of conversion of a substance from a vapour state to a liquid state.
- **Boiling point –**Temperature at which vapour pressure of a liquid becomes equal to the atmospheric pressure.
- **Melting point –**Temperature at which the liquid melts.

6.14 POSSIBLE ANSWERS TO SAQ

6.11 Self- Assessment Questions (SAQ)

- Fill in the blanks:

  1. Evaporation, condensation; 2. Ignition; 3. Condenser; 4. Separating; 5. Magnetic stirrer; 6. Liquid, vapour; 6. Liquid, vapour; 7. Desiccator; 8. Lessaigne's

- True and False

  1. True; 2. False; 3. True; 4. False; 5. True

6.15 TERMINAL QUESTIONS

- Discuss different types of apparatus used in organic chemistry and explain it.
- Discuss the safety measures taken in the laboratory.

6.16 REFERENCES

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UNIT 7: ORGANIC PREPARATION

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7.1 OBJECTIVE

Objective of the laboratory exercises in this unit is to provide you with basic skills of organic synthesis that essentially covers fundamental understanding of laboratory equipments used to carry out organic transformations, knowledge to handle numerous chemicals in laboratory and ability to assemble laboratory equipments for experiments such as hydrolysis and condensation.

First five exercises of this unit will assist us to synthesize few molecules and break down few others those are very important in chemical industry and are also used in household products such as medicines. Thus you will learn to prepare acetanilide, nitroacetanilide and naphthyl benzoate. On the other hand fourth exercise will give you insight about the hydrolysis process which is not only very important chemical process for industry but also for the biological systems. Reverse process to hydrolysis is called condensation and the fifth experiment will teach you to perform condensation reaction.

Many organic compounds are available in plenty in natural sources and it is often viable to isolate them from naturally available sources rather than synthesizing in laboratory. Last two experiments of this unit will teach you how to extract useful compounds from plants.

Almost all of these laboratory experiments involve hazardous chemicals, for example, Claisen condensation is performed in the presence of a strong base, hence you will also be learning about the important precautions to handle chemicals and to perform each of the experiments.

7.2 ACETANILIDE

Acetanilide is an important medicinal compound which helps in relieving pain. Its chemical formula is C_8H_9NO and molar mass is 135.17 $g \cdot mol^{-1}$. Acetanilide is also known as N-phenylacetamide. It is an odourless solid at room temperature and possesses flake-like appearance. Its melting point is 114.3 °C. Acetanilide is soluble in organic solvents such as ethanol, diethyl ether, acetone and benzene. Acetanilde is used as additives in varnishes and used for preparation of dyes. It is also used for production of sulfa drugs,

penicillin and other pharmaceuticals. Structural formula of acetanilide is given in **Figure 1**.

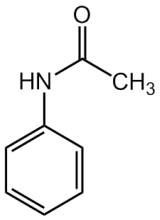


Figure 1. Structural formula of acetanilide (C_8H_9NO).

In laboratory acetanilide is synthesized by condensation of aniline with acetic anhydride. This reaction is also called *acetylation* reaction because acetyl group is introduced to the amino functionality of aniline molecules. Acetic anhydride is an irritant and combustible liquid compound which smells like acetic acid (***smelling chemicals in laboratory is not recommended)***. Acetic anhydride is not procured by many laboratories due to some legal regulations by government; therefore acetyl chloride is also used for acetylation reactions. Hence, you can synthesize acetanilide by condensation of aniline and acetyl chloride also. Both of these experiments are discussed in following section.

7.2.1 Preparation of acetanilide from aniline and acetic anhydride

7.2.2 Chemicals and equipments required

Aniline, acetic anhydride, distilled water, beakers, water bath, boiling tube, glass rod, dropper, burner or spirit lamp, ice bath, buchner funnel, chemical or digital balance, and melting point apparatus etc.

7.2.3 Theory

Acetylation of aniline using acetic anhydride is a typical condensation reaction as depicted in **Figure 2**. In laboratory acetanilide is synthesized by condensation of aniline with acetic anhydride. This reaction is also called *acetylation* reaction because acetyl group is introduced to the amino functionality of aniline molecules.

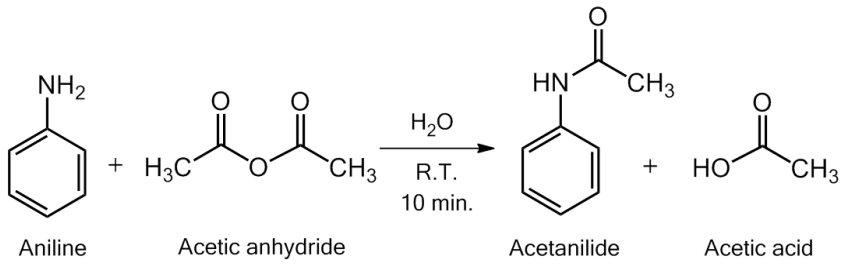


Figure 2. Synthesis of acetanilide from aniline and acetic anhydride.

7.2.4 Procedure

Procedure of this experiment can be subdivided in two parts. The first part covers the synthesis of acetanilide yielding crude product and the second part is recrystallization of the crude product to obtain pure crystalline form of the acetanilide. Both parts are discussed in the following section.

7.2.5 Synthesis

Using a dropper place 0.20 g of aniline (approx 10 drops) in a boiling tube. Add 5mL of distilled water followed by addition of 20 drops of acetic anhydride with the help of a dry dropper. Stir the mixture with a glass rod for 10-15 minutes until white solid forms.

7.2.6 Recrystallization

In order to get the pure product we must recrystallize the solid. For this purpose add 5 mL of water in the same reaction test tube and heat the test tube in hot water bath (for hot water bath take some water in a 100 mL beaker and heat it on a burner). Keep stirring the reaction mixture at short intervals till the solid dissolves. Now remove the test tube from hot water bath and keep aside for cooling for 5 minutes and then chill it in ice bath. Within few minutes you would observe formation of crystals of the product. Filter the crystals on a Buchner funnel. Allow the product to dry completely and collect the product as white crystalline powder.

7.2.7 Characterization

The obtained white solid crystalline flakes are characterized by determining the melting point. Melting point obtained in the temperature range 113-115°C indicates the formation of desired compound.

7.2.8 Result

Acetanilide was synthesized by condensation of aniline and acetic anhydride.

Appearance = White crystalline flakes

Yield = _____ g

Melting point (before recrystallization) = _____ °C

Melting point (after recrystallization) = _____ °C

7.3 PREPARATION OF ACETANILIDE FROM ANILINE AND ACETYL CHLORIDE

7.3.1 Chemicals and equipments required

Aniline, acetyl chloride, distilled water, beakers, water bath, boiling tube, glass rod, dropper, burner or spirit lamp, ice bath, buchner funnel, chemical or digital balance, and melting point apparatus etc.

7.3.2 Theory

Acetylation of aniline using acetyl chloride is a typical condensation reaction as depicted in **Figure 3**. This reaction is also called *acetylation* reaction because acetyl group is introduced to the amino functionality of aniline molecules. Acetylation using acetyl chloride is usually done in presence of pyridine. If pyridine is not available the reaction can be performed by using glacial acetic acid.

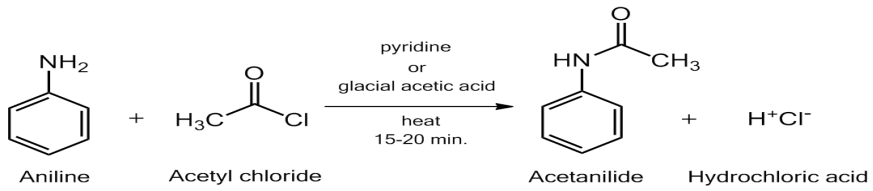


Figure 3. Synthesis of acetanilide from aniline and acetyl chloride.

7.3.3 Procedure

Procedure of this experiment can be subdivided in two parts. The first part covers the synthesis of acetanilide yielding crude product and the second part is recrystallization of

the crude product to obtain pure crystalline form of the acetanilide. Both parts are discussed in following section.

7.3.4 Synthesis

In a 100 mL round bottom flask take 5 mL aniline. In another flask prepare acetylating mixture by mixing 5 mL acetyl chloride and 5 mL dry pyridine. Add the acetylating mixture to the flask containing aniline. Fit an air condensor on the mouth of the flask and reflux the mixture gently on sand bath for 10-15 minutes. Cool the reaction mixture and pour it gently in 150-200 mL ice cold water with stirring. A white solid appears. Filter it and wash it with cold water 2-3 times and dry. This is the crude acetanilide.

If pyridine is not available then you can use this alternate method. In a dry boiling tube take 1 mL of aniline and add 1 mL of glacial acetic acid and mix thoroughly with glass rod. To this mixture add acetyl chloride (1 mL) in small lots. If the boiling tube feels hot and difficult to hold then cool it under tap water. After addition of acetyl chloride heat the mixture for 5 minutes in a boiling hot water bath. Cool the test tube and add ice cold water (approx 10 mL) to the reaction mixture with constant stirring. Now filter the white coloured precipitate (acetanilide) and wash with water till filtrate becomes neutral to litmus.

7.3.5 Recrystallization

The solid product obtained above can be crystallized in hot water to yield white shiny crystalline substance. For recrystallization purpose take the crude solid in a boiling tube and dissolve in minimum amount of hot water with constant heating in hot water bath. After complete dissolution of solid remove the boiling tube from hot water bath and keep aside for cooling for 5 minutes and cool it in ice bath. When sufficient crystals of product are observed, filter them on a Buchner funnel. Allow the product to dry completely and collect the product as white crystalline powder.

7.3.6 Characterization

The obtained white solid crystalline flakes are characterized by determining the melting point. Melting point obtained in the temperature range 113-115°C indicates the formation of desired compound.

7.3.7 Result

Acetanilide was synthesized by condensation of aniline and acetic anhydride.

Appearance = White crystalline flakes

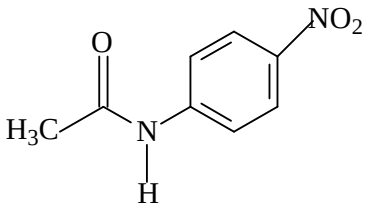
Yield = _____ g

Melting point (before recrystallization) = _____ °C

Melting point (after recrystallization) = _____ °C

7.4 NITROACETANILIDE

4-nitroacetanilide is an important aromatic compound with chemical formula, $C_8H_8N_2O_3$ and molar mass, 180.16 $g \cdot mol^{-1}$. It is nitro derivative of acetanilide and also has two positional isomers, namely, 2-nitroacetanilide and 3-nitroacetanilide. It is brownish white solid which melts at 215 °C. 4-nitroacetanilide is used for preparation of aminoacetanilide and few aromatic dyes. Structural formula of 4-nitroacetanilide is given in **Figure 4**.



para–nitroacetanilide

Figure 4. Structural formula of 4-nitroacetanilide or p-nitroacetanilide ($C_8H_8N_2O_3$).

In laboratory 4-nitroacetanilide is synthesized by nitration of acetanilide using concentrate H_2SO_4 and concentrate HNO_3. This reaction is also called nitration and follows electrophilic aromatic substitution mechanism involving nitronium ion as electrophile.

7.4.1 Preparation of nitroacetanilide

7.4.2 Chemicals and equipments required

Acetanilide, glacial acetic acid, concentrate sulfuric acid, fuming nitric acid, test tubes, conical flask, glass rod, ice bath, beaker, buchner funnel, filter paper, etc

7.4.3 Theory

Direct synthesis of p-nitroacetanilide from aniline using a nitrating mixture is difficult and not recommended. This is because, in the presence of the nitrating mixture, the amino (-NH_2) group of aniline is oxidised to the nitro (-NO_2) group and forms nitro benzene. The amino group of aniline is first protected by acylation to produce acetanilide which is then nitrated to form 4-nitroacetanilide as the major product and 2-nitroacetanilide as the minor product (**Figure 5**). The acetamido (-$NHCOCH_3$) group directs it to ortho and para positions however para position is favoured because the bulky acetamido group shields the ortho position from the attacking species. You should bear in mind that glacial acetic acid is a polar solvent which dissolves acetanilide and the acetate ion is a poor nucleophile so no substitution product is possible.

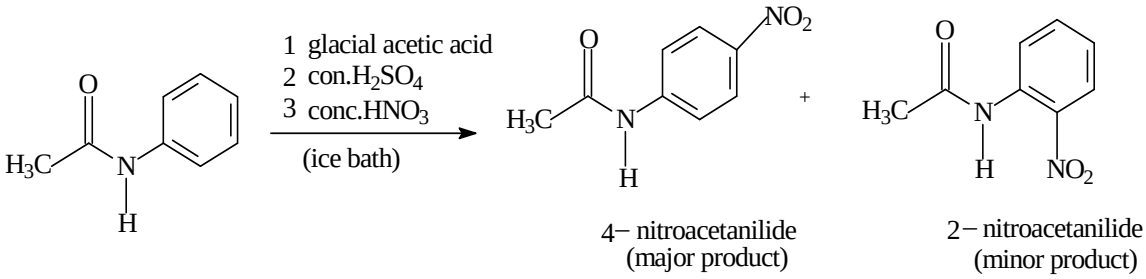


Figure 5. Synthesis of 4-nitroacetanilide or p-nitroacetanilide starting from acetamide.

7.4.4 Procedure

Take 1.6 g of acetanilide and 2.5 mL glacial acetic acid in a conical flask and stir the mixture using a glass rod to dissolve contents. After complete dissolution cool the flask in an ice bath. After cooling the acetanilide solution, carefully add 2.5 mL of pre-cold concentrate sulphuric acid drop by drop into the conical flask. Stir the content for proper mixing and the chill the conical flask by keeping it in an ice bath. Separately prepare nitrating mixture by taking 0.9 ml of fuming nitric acid and 1.25 mL of concentrate sulfuric acid in a test tube and allow it to cool using the ice bath. To the cooled contents in the flask, add the nitrating mixture prepared in the test tube, drop by drop while stirring constantly with the help of a glass rod. While adding the nitrating mixture, the temperature of the mixture in the flask should not rise above 25 °C. Remove the conical flask from the ice bath and allow it to stand for 30min at room temperature. Pour the contents of the flask into a beaker containing 25 mL water and crushed ice. Stir it well

and filter the yellow precipitate of 4-nitroacetanilide with the help of Buchner funnel. The precipitate must be washed thoroughly with cold water and then dried and weighed.

7.4.5 Recrystallization

4-nitroacetanilide can be recrystallized by following a procedure similar to that adopted for acetanilide in the previous experiment.

7.4.6 Characterization

The obtained yellow crystalline solid is characterized by determining the melting point. Pure 4-nitroacetanilide melts at 215℃. You should be very careful while heating nitro aromatic solid compounds. Use very small amounts of solid 4-nitroacetanilide for determination of melting point.

7.4.7 Result

4-nitroacetanilide was synthesized by nitration of acetanilide.

Appearance = Yellow crystalline solid

Yield = _____g

Melting point (before recrystallization) = _____ ℃

Melting point (after recrystallization) = _____ ℃

7.5 NAPHTHYL BENZOATE

Naphthyl benzoate is also called naphthol benzoate is an aromatic ester with considerable biological activities. Molecular formula of naphthyl benzoate is $C_{17}H_{12}O_2$ and its molar mass is 248.28 $g \cdot mol^{-1}$. As presented in **Figure 6**, naphthyl benzoate is benzoic ester derivative of naphthols and hence, has two positional isomers, namely, 2-naphthyl benzoate (or β-naphthol benzoate) and 1-naphthyl benzoate (or α-naphthol benzoate).

The β- isomer is more important for its biological activities. 2-naphthyl benzoate (or β-naphthol benzoate) is white crystalline solid which is practically insoluble in water but readily dissolves in organic solvents including chloroform, dichloromethane, glycerol and hot ethanol. 2-naphthyl benzoate is used as antiseptic agent and as biochemical in proteomics, i.e., research studies involving proteins. It is also used as paraffin hardening

agent. In laboratory 2-naphthyl benzoate is synthesized by refluxing β-naphthol with benzoyl chloride in dichloromethane solvent followed by work up.

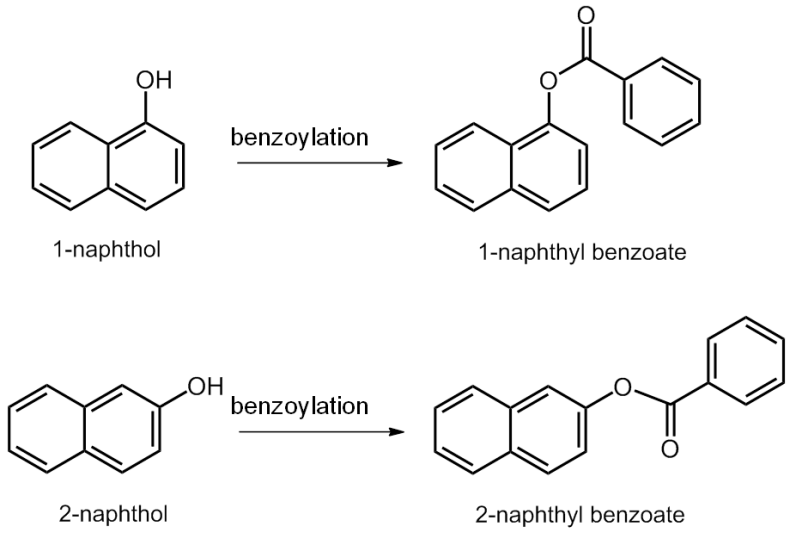


Figure 6. Synthesis of 1- and 2-naphthyl benzoate from 1- and 2-naphthol respectively.

7.5.1 Preparation of naphthyl benzoate

7.5.2 Chemicals and equipments required

β-naphthol, benzoyl chloride, dichloromethane, Test tubes, round bottom flasks, conical flask, glass rod, ice bath, beaker, separating funnel, filter paper, etc

7.5.3 Theory

As presented in **Figure 7**, 2-naphthyl benzoate is synthesized by refluxing β-naphthol with benzoyl chloride in dichloromethane solvent followed by work up as discussed in the section discussing procedure of the preparation.

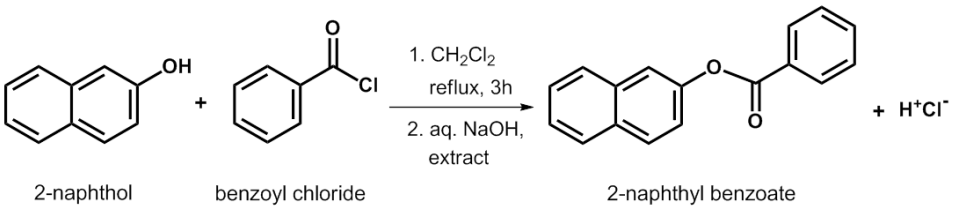


Figure 7. Synthesis of 2-naphthyl benzoate from benzoylation of 2-naphthol.

7.5.4 Procedure

Take 1.0 g of β-naphthol in a 100 mL round bottom flask and add 35 mL of dichloromethane. With gentle stirring with glass rod dissolve the solid completely and to this solution add 1.5 g benzoyl chloride in four to six small portions. Put the water condenser on the mouth of flask and heat at 50 °C on the water bath. Make sure that cold water is circulating in the condenser. After three hours remove the heating to water bath and allow the flask to cool down to room temperature. Transfer the reaction mixture to a separatory funnel of 100 mL capacity and add 10 mL of 0.05 M NaOH solution. Close the stopcock of separating funnel and shake well to extract unreacted β-naphthol to the aqueous (NaOH) phase. Product 2-naphthyl benzoate remains in the organic solvent dichloromethane. Keep the separating funnel undisturbed for separation of aqueous and organic phases. Carefully collect the lower layer (dichloromethane is denser than water, hence settles as lower layer in the separating funnel) in a beaker and gently warm the content to vaporize dichloromethane solvent. On evaporation of solvent you will obtain the desired product from the beaker as a white solid.

7.5.5 Characterization

The obtained white crystalline solid is characterized by determining the melting point. Melting point obtained in the temperature range 107-110°C indicates the formation of 2-naphthyl benzoate.

7.5.6 Result

2-naphthyl benzoate was synthesized by esterification of β-naphthol using benzoyl chloride.

Appearance = White crystalline solid

Yield = _____ g

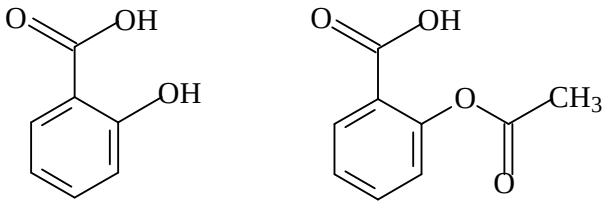
Melting point (before recrystallization) = _____ °C

Melting point (after recrystallization) = _____ °C

7.6 SALICYLIC ACID

Salicylic acid is a colourless crystalline solid substance which is widely used in organic synthesis. Systematic name for salicylic acid is 2-hydroxybenzoic acid. Its

chemical formula is $C_7H_6O_3$ and molecular mass is 138.12 $g \cdot mol^{-1}$. Salicylic acid possesses several medicinal activities for the reason it is identified as one of the most essential medicines by World Health Organization. It is an important ingredient of skin care products, antiseptics and food preservatives. On the other hand, aspirin (acetylsalicylic acid), an acetyl derivative of salicylic acid, is a white crystalline, weakly acidic substance with a melting point of 136 °C. Aspirin is pro drug of salicylic acid and used as analgesic and anti-inflammatory medication. Since, chemically aspirin is ester of salicylic acid, therefore it can be hydrolyzed to obtain salicylic acid.



Salicylic acid Aspirin

Figure 8. Structural formula of salicylic acid and its acetyl derivative, aspirin.

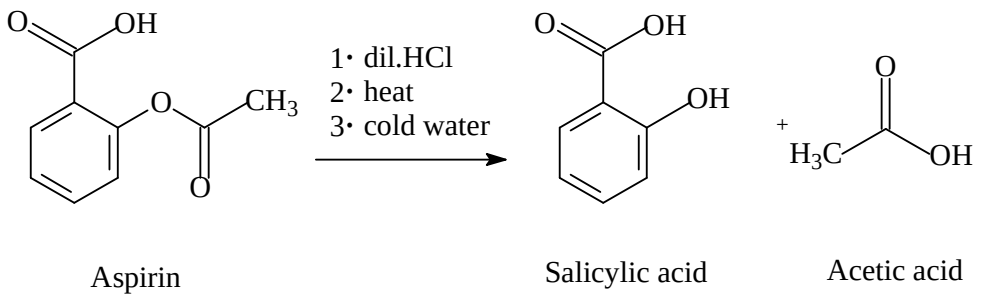
7.6.1 Preparation of salicylic acid from aspirin

7.6.2 Chemicals and equipments required

Aspirin (acetylsalicylic acid), dilute HCl, test tubes, round bottom flasks, conical flask, glass rod, ice bath, condenser, beaker, separating funnel, burner, filter paper, etc

7.6.3 Theory

Hydrolysis of acetylsalicylic acid results in salicylic acid and acetic acid. Ester hydrolysis can be catalyzed by acids or bases. However, acid catalyzed hydrolysis is easier to perform as compared to base catalyzed hydrolysis which requires an additional neutralization step in case of acidic substrates. Therefore, we will follow the acid catalyzed hydrolysis of aspirin to prepare salicylic acid. The reaction is depicted in **Figure 9**.



Aspirin Salicylic acid Acetic acid

Figure 9. Synthesis of salicylic acid from aspirin.

7.6.4 Procedure

Take 5 g of aspirin in a conical flask and dissolve in 50 mL of 20% HCl solution. Heat the contents of conical flask for 30 minutes at 60 °C on a water bath. Be careful that temperature should not rise higher than 60 °C. Progress of reaction can be ascertained by appearance of vinegar like smell from the reaction mixture. After completing the heating step, add 50 mL of ice cold water to the reaction mixture. A white precipitate of salicylic acid will appear. Separate the white precipitate by filtration on a Buchner funnel and do not discard the filtrate at this stage. Rinse the product with 10 mL cold water to remove left over acetic acid. Since salicylic acid is sparingly soluble in water therefore some part of the prepared salicylic acid remains in the filtrate which can be recovered by solvent extraction.

Transfer the filtrate to a separatory funnel of 100 mL capacity and add 50 mL of diethyl ether. Close the stopcock of separatory funnel and shake well to extract salicylic acid to the organic phase. Hydrochloric acid used as catalyst remains in the aqueous layer, while salicylic acid and some part of acetic acid extracts to the organic (ether) layer. Keep the separatory funnel undisturbed for separation of aqueous and organic phases. Carefully take the lower aqueous layer (diethyl ether is lighter than water, hence settles as upper layer in the separating funnel) in a beaker and discard. Now take out the organic layer in a beaker and gently warm the content to vaporize solvent. On evaporation of solvent you will obtain the desired product from the beaker as a white solid.

7.6.5 Recrystallization

Salicylic acid can be recrystallized from hot water. Dissolve the obtained solid substance in minimum amount of hot water (60℃) and then allow cooling down. White needle shaped transparent crystals of salicylic acid will be formed in several hours.

7.6.6 Characterization

The crude and recrystallized salicylic acid samples are characterized by determining the melting point. Melting point of pure salicylic acid is 158.6 ℃. Melting point obtained closer to 158.6℃ indicates the formation of desired compound.

7.6.7 Result

Salicylic acid was synthesized by hydrolysis of aspirin.

Appearance = Transparent crystalline crystals

Yield = _____ g

Melting point (before recrystallization) = _____ ℃

Melting point (after recrystallization) = _____ ℃

7.7 CLAISEN CONDENSATION

The Claisen condensation is reaction of two esters or one ester and a carbonyl compound in presence of a strong base yielding a β-keto ester or a β-diketone respectively. This is an important organic reaction used for formation of a carbon–carbon bond. One of the two reactants must have at least one α-hydrogen for participating in Claisen condensation. This reaction between two esters is called classical Claisen condensation whereas that between one ester and one carbonyl compound is called mixed Claisen condensation.

7.7.1 Claisen condensation between acetophenone and ethyl acetate

7.7.2 Chemicals and equipments required

Acetophenone, ethyl acetate, ether, sodamide, glacial acetic acid, test tubes, round bottom flasks, conical flask, glass rod, ice bath, condenser, beaker, separating funnel, burner, filter paper, etc

7.7.3 Theory

Reaction between acetophenone and ethyl acetate is mixed Claisen condensation reaction. Main product of the reaction is 1-phenylbutane-1,3-dione which is commonly called as 1-benzoylacetone. This compound is used in fragrances. The complete reaction is presented in **Figure 10**. The reaction can be effected in the presence of strong base sodium ethoxide or sodamide. You will be performing the reaction using sodamide as it is easier to handle as compared to sodium ethoxide. Remember sodamide or sodium ethoxide are very sensitive to moisture, therefore all glassware, chemicals and solvents must be 'dry' for Claisen condensation.

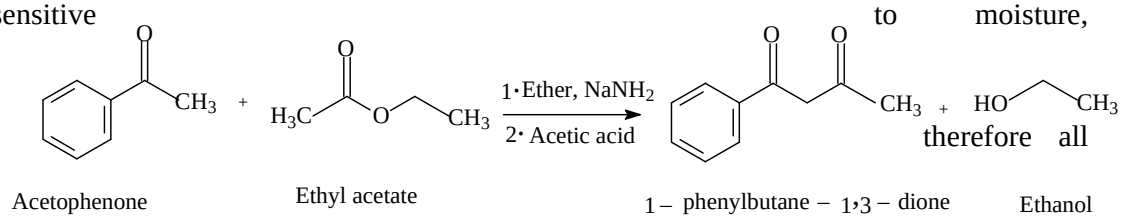


Figure 10. Synthesis of 1-phenylbutane-1,3-dione (or 1-benzoylacetone) by reaction between acetophenone and ethyl acetate.

7.7.4 Procedure

Take 3.0 g of acetophenone and 2.5 g of dry ethyl acetate in a round bottom flask of 100 mL capacity and dissolve in 20 ml of dry diethyl ether. Cool the flask using an ice bath and maintaining the dry condition. To the cold solution of reactants, slowly add 2.0 g of sodamide powder. Allow the contents of flask to react for next 24 hours. On completion of reaction time, pour the reaction mixture on sufficient amount of ice cold water taken in a beaker and dissolve in it using a glass rod. Remove the ether layer from the beaker by allowing evaporation or by bubbling air through the reaction mixture. Add glacial acetic acid in small portions till the pH of the solution is slightly acidic (below the value of 7) and the product, 1-benzoylacetone precipitates out. Filter out the product and wash with water followed by drying and weighing.

7.7.5 Recrystallization

Colourless crystalline solid can be obtained by recrystallizing the crude reaction product with organic solvents.

7.7.6 Characterization

The obtained white solid is characterized by determining the melting point. Melting point of pure 1-benzoylacetone is 61 °C. Hence the observed melting point in temperature range 60-62 °C indicates the formation of desired compound.

7.7.7 Result

1-benzoylacetone was synthesized by Claisen condensation between acetophenone and ethyl acetate.

Appearance = White crystalline

Yield = _____ g

Melting point (before recrystallization) = _____ °C

Melting point (after recrystallization) = _____ °C

7.8 ISOLATION OF CAFFEINE FROM TEA LEAVES

Caffeine is an alkaloid compound found in seeds, nuts and leaves of several plants. It is a white crystalline solid with chemical formula, $C_8H_{10}N_4O_2$. Caffeine tests bitter and act as psychoactive substance to prevent drowsiness in humans.

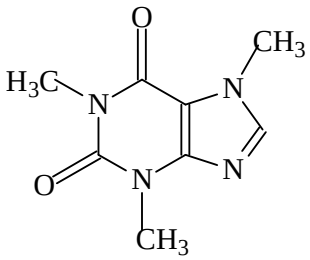
7.8.1 Chemicals and equipments required

Green tea powder (tea dust), distilled water, dichloromethane, sodium carbonate, anhydrous sodium sulfate, beaker, separatory funnel, filter paper, burner etc.

7.8.2 Theory

Caffeine is a purine derivative alkaloid compound (**Figure 11**). Hence it has polar functional groups such as carbonyl. Caffeine is soluble in organic solvents like dichloromethane but interestingly presence of polar groups makes caffeine soluble in water. It is highly soluble in water at high temperatures and less soluble at room temperature. Therefore, extraction of caffeine is effected by boiling the tea leaves in water. Tannin is another class of organic compounds present in tea leaves which is extracted in water during the process. Hence in order to obtain pure caffeine it is necessary to remove tannin. Tannin is phenolic substance which on treatment with sodium carbonate makes water soluble and dichloromethane insoluble salts. However, caffeine remains unaffected

by sodium carbonate. Therefore, extraction of aqueous solution of caffeine and tannin salts with dichloromethane allows selective transfer of caffeine in the organic solvent.



Caffeine

Figure 11. Synthesis of acetanilide from aniline and acetyl chloride.

7.8.3 Procedure

Take 2 g dust of green tea and 1 g sodium carbonate in a 100 mL beaker and 20 mL distilled water. Cover the beaker with watch glass and gently heat for 10 minutes. Carefully filter the solution in another beaker while hot. Allow the filtered solution to cool down to room temperature and then transfer to a separatory funnel. Add 5 mL dichloromethane to the separatory funnel, close the stopcock and swirl gently a few times. Keep the separatory funnel in ring stand to allow separating organic and aqueous layers. Dichloromethane being denser than water settles as lower layer in separatory funnel. Carefully collect the dichloromethane layer in a beaker. Again add 5 mL dichloromethane to the separatory funnel, swirl gently and allow separation of aqueous and organic layers followed by collection of the dichloromethane part in previously collected portion. Dry the combined dichloromethane solution using anhydrous sodium sulfate and transfer the dried solution to a 25 mL beaker. Gently heat the beaker to evaporate the solvent (dichloromethane boils at 39.6 °C) on drying collect the white substance deposited in beaker with the help of a spatula.

7.8.4 Characterization

The obtained white solid is characterized by determining the melting point. Melting point of caffeine is 238 °C.

7.8.5 Result

Caffeine was extracted from green tea dust.

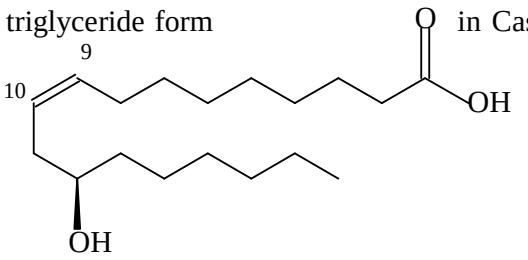
Appearance = White crystalline solid

Yield = _____ g

Melting point = _____ °C

7.9 ISOLATION OF RICINOLEIC ACID FROM CASTOR OIL

Ricinoleic acid is an unsaturated omega-9 fatty acid. It is also categorized as a hydroxy acid. Chemical formula of ricinoleic acid, the major component of castor (*Ricinus communis*) seed oil is $C_{18}H_{34}O_3$. It has several biological activities including analgesic effects. It remains in triglyceride form in Castor oil and hence can be obtained by hydrolysis of castor oil.



Ricinoleic acid

Figure 12. Structural formula of ricinoleic acid. Position of double bond and hydroxyl group is noteworthy.

7.9.1 Chemicals and equipments required

Castor oil, potassium hydroxide, ethanol, distilled water, condenser, beaker, separatory funnel, filter paper, burner etc.

7.9.2 Theory

This experiment involves hydrolysis of triglyceride, *i.e.*, ester hydrolysis. Ester hydrolysis is a reversible process in which ester linkages are broken to yield an acid and an alcohol and *vice versa*. Hydrolysis reaction can be catalyzed by means of an acid or a base. In the present experiment you would use potassium hydroxide as catalyst which facilitates the formation of ricinoleic acid.

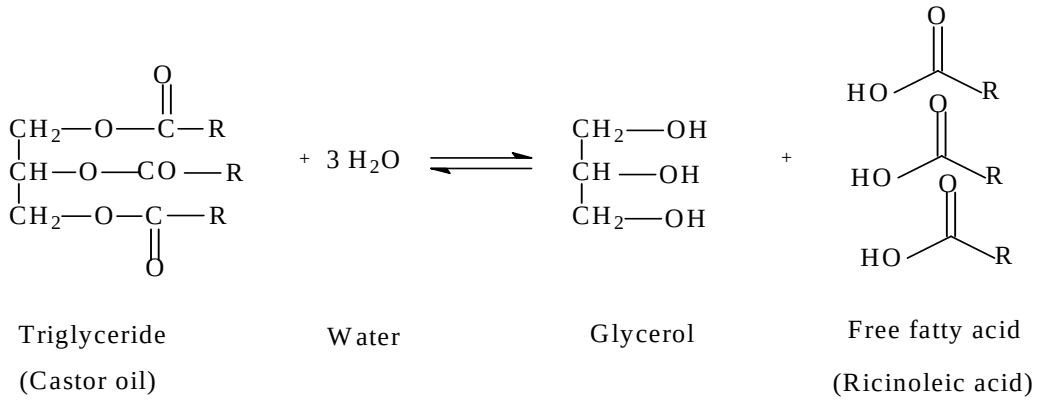


Figure 13. Schematic depiction of hydrolysis of the triglyceride (Castor oil) resulting in glycerol and three molecules of ricinoleic acid.

7.9.3 Procedure

Take 1 g KOH pellets, 1 mL water and 10 mL ethanol in a 100 mL round bottom flask and mix thoroughly to dissolve KOH completely. To this solution, add 5 g or mL castor oil and fit the flask with reflux assembly. Reflux the solution for three hours followed by addition of 30 mL distilled water. Separately dilute 1 mL of concentrate sulphuric to 5 mL in a test tube and gradually add to the flask with stirring. After complete addition of acid mix the contents of flask with a glass rod and then transfer to a separatory funnel. Swirl the separatory funnel and allow the phases to separate. Separated upper layer is ricinoleic acid whereas rest of the mass goes to aqueous layer. Carefully drain down aqueous layer and collect the ricinoleic acid in a test tube.

7.9.4 Result

Ricinoleic acid was isolated from castor oil by hydrolysis method.

Appearance = Yellowish liquid

Yield = _____ g or mL

7.10 SUMMARY

First experiment is the acetylation of aniline which represents one of the very important chemical reactions. You can use the acetylation reaction for the protection of amino groups. Protection of amino group learnt in first experiment is utilized in the second one, which is for the preparation of nitro acetanilide from aniline. You have learnt that direct nitration of aniline is not feasible. Since nitrating reagent reacts with amino group

therefore the strategy you use is first protect amino group by acetylation reaction and then execute nitration reaction. Benzoylation of naphthol yielding naphthyl benzoate is discussed in the third experiment which is another very commonly used reaction in organic chemistry. Protection of functional groups is devised in such a way that whenever required, deprotection of functional group can be done. This strategy is presented in the next experiment: formation of salicylic acid by hydrolysis of aspirin. Condensation of ester and ketone is one of the available reactions for formation of C-C bond which you have learnt about in the fifth experiment. You must have learnt about the extraction and isolation of organic compounds from natural sources in the last two experiments. Therefore, the experiments in this unit have covered a wide range of common organic transformations.

7.11 TERMINAL QUESTION

Short Answer type questions

Q.1 What is acetylation?

Q.2 What is a condensation reaction?

Q.3 Why is recrystallization done?

Q.4 What is the reactive species formed in the nitration of acetanilide to 4-nitroacetanilide?

Q.5 What is nitrating mixture?

Q.6 What happens when we attempt direct nitration of aniline?

Q.7 If the final product synthesized is an water immiscible oily liquid, how will you separate the impurities using a separatory funnel?

Q.8 Name the two isomers of naphthyl benzoate. Which isomer is biologically more useful?

Q.9 Give IUPAC name of aspirin.

Q.10 Name the product formed by condensation of acetophenone and ethylacetate.

Q.11 What precaution should be taken while handling sodamide or sodium ethoxide?

Q.12 What makes caffeine soluble in both organic solvents and water?

Q.13 What strategy should be adopted while extraction of caffeine so as to prevent getting tannin along with caffeine in organic layer?

7.12 ANSWERS

A.1 Introduction of acetyl group to a molecule by replacing a proton is called acetylation.

A.2 Condensation is type of chemical reactions in which two molecules combine to form a larger molecule with loss of a small molecule such as H_2O.

A.3 Recrystallization is done in order to obtain pure compound as crystals since the initial product obtained may contain impurities such as some unreacted starting compounds or side products formed during the course of reaction.

A.4 Nitronium ion as electrophile.

A.5 It is a mixture of concentrate sulfuric and concentrate nitric acid in a 1:1 (v/v) ratio.

A.6 Direct nitration of aniline does not yield nitroaniline instead the anime group oxidizes to nitro group. Hence we get nitrobenzene.

A.7 An oily product can be separated from the impurities if we know the solubility of the product and possible impurities in water or organic solvents. Using a suitable water immiscible organic solvent such as dichloromethane, ethylacetate etc. and water we get two layers of aqueous and organic phases when transferred to separatory funnel. After shaking the contents to mix well for extraction, the two layers are allowed to separate keeping the separatory funnel undisturbed on a stand. Depending upon the density of the organic solvent it will be heavier or lighter than water and thus will form lower layer or upper layer respectively. Discarding the impurities and water soluble reactants in aqueous layer the product can be obtained separately in the organic layer.

A.8 The two isomers of naphthyl benzoate are 2-naphthyl benzoate (or β-naphthol benzoate) and 1-naphthyl benzoate (or α-naphthol benzoate). The β- isomer is more important for its biological activities.

A.9 IUPAC name of aspirin is 2-acetoxybenzoic acid.

A.10 1-phenylbutane-1,3-dione which is commonly called as 1-benzoylacetone.

A.11 Sodamide or sodium ethoxide are very sensitive to moisture, therefore all glassware, chemicals and solvents must be 'dry' for Claisen condensation.

A.12 Presence of polar groups makes caffeine soluble in water along with organic solvents.

A.13 In order to obtain pure caffeine it is necessary to remove tannin. Tannin is phenolic substance which on treatment with sodium carbonate makes water soluble and dichloromethane insoluble salts. Caffeine remains unaffected by sodium carbonate. Therefore, extraction of aqueous solution of caffeine and tannin salts with dichloromethane allows selective transfer of caffeine in the organic solvent.

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UNIT 8: ESTIMATION METHODS

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8.1 OBJECTIVES

Estimation methods discussed in this chapter are the quantitative organic analysis techniques which are helpful to ascertain composition and purity of an organic compound. Many organic molecules have pronounced acidic or basic properties and high reactivity at the same time others are neutral and inert. This contrasting chemical behavior depends on the functional groups a molecule bears. Hence, knowing the degree to which a particular functional group is present in a compound becomes crucial to understand the properties of molecules. Since there are a large number of functional groups in organic chemistry hence for obvious reasons there are even a large number of estimation methods. In this chapter you would learn about the estimation of few commonly encountered functional groups. Thus, this chapter deals with estimation of sugars, amino acids, hydroxyl group and unsaturation. Most valued commonly used procedure is presented for each of these categories. Vivid details of experimental procedures and calculations are given so that you must be confident in laboratory while performing the experiment.

8.2 QUANTITQTIVE ESTIMATION OF SUGAR (GLUCOSE) USING FEHLING'S SOLUTION

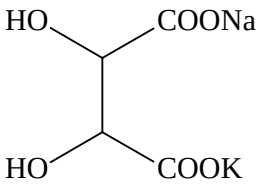
8.2.1 Chemicals and equipments required

Glucose - 1.5 g, copper sulphate - 7 g, sodium potassium tartarate - 34.6 g, sodium hydroxide - 12 g, burette, conical flasks, burner, glass rod etc.

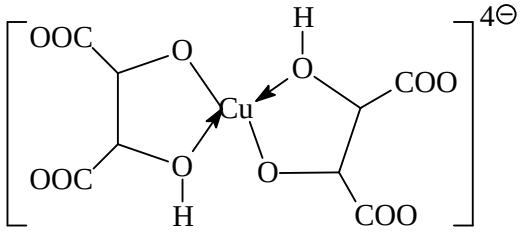
8.2.2 Theory

Fehling's solution is used to differentiate water soluble aldehyde and ketone functional groups and to test for monosaccharides such as glucose and fructose. Fehling's solution is always prepared fresh in the laboratory before the experiment since it loses its composition when stored for long duration. It can be used to determine whether a carbonyl-containing compound is an aldehyde or a ketone (only aliphatic aldehydes). It is made as two separate

solutions; Fehling's A and Fehling's B solution. Fehling's A is a blue aqueous solution of copper (II) sulphate pentahydrate crystals, while Fehling's B is a solution of aqueous potassium sodium tartrate (also known as Rochelle salt) and a strong alkali such as sodium hydroxide. On taking equal volume of the two solutions we get dark blue coloured Fehling's solution which is due to the formation of bistartratocuprate (II) complex. This is the active reagent of the Fehling's solution and acts as an oxidizing agent.



Rochelle salt



Active complex of Fehling solution

Figure 1. Structure of Rochelle salt and active Cu(II) complex species of Fehling's solution.

8.2.3 Procedure

(i) Preparation of Fehling A and B

A) Fehling A: - Dissolve 7 g of copper sulphate in distilled water. Transfer the solution in 100 cc measuring flask. Wash the container with distilled water. Transfer the washing to measuring flask and make upto the mark.

B) Fehling B: - Dissolve 34.6 gm of sodium potassium tartarate and 12 g of sodium hydroxide in boiling distilled water. Transfer the solution in 100cc measuring flask. Wash the container with distilled water. Transfer the washing to measuring flask and make upto the mark.

(ii) Preparation of Fehling solution:- Fehling A + Fehling B

(iii) Preparation of standard glucose solution

Weigh accurately a pure sample of glucose and first dissolve in about 10cc of distilled water taken in a 250 cc measuring flask. Now make upto mark with distilled water.

(iv) Titration of standard glucose solution

Pipette out 10cc of Fehling solution in a conical flask and 80cc of distilled water. Boil the contents and add gradually the standard glucose solution taken in a burette with continuous shaking, till the blue colour of the solution disappears. Keep the conical flask on burner during the addition of glucose solution till the temperature in thermometer reads 70 ℃ that is keep below boiling. Maintain the temperature closer to 70 ℃ throughout the titration. Keep adding glucose solution till the solution loses its blue colour with some red precipitate (Figure 2). Repeat the process till two concordant readings are obtained. Record the readings in table 1

(v) Titration of unknown glucose solution

Same method is used (as described above) for titration of unknown glucose solution. Record the readings in table 2

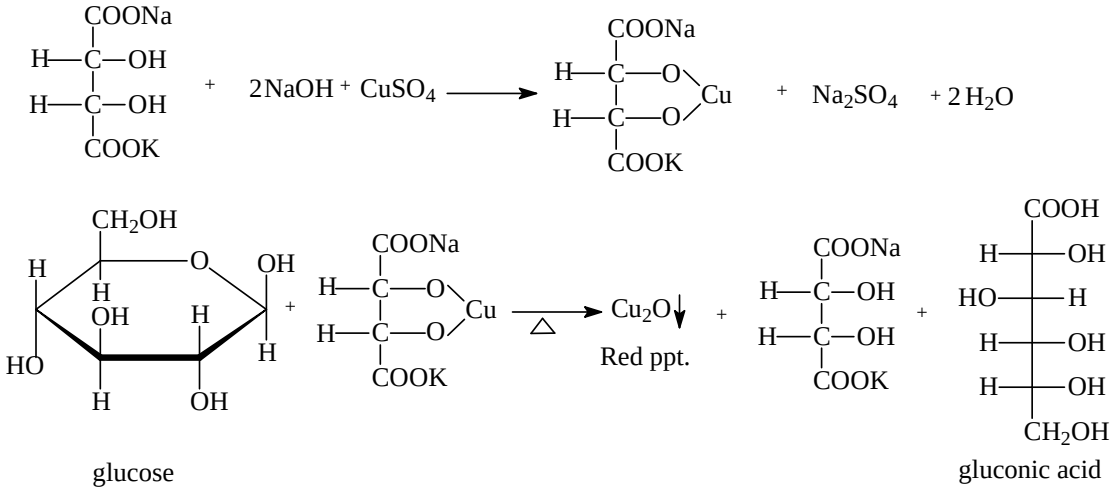


Figure 2: *Reaction of glucose with Fehling solution*

8.2.4 Observation

Weight of weighing tube =…….g

Weight of weighing tube + glucose =……g

Weight of glucose=…….g

Table 1 Titration with known glucose solution –

S.N.	Fehling solution in cc	Reading of burrete		Glucose solution in cc (known)
		Initial reading	Final reading	
1.				
2.				
3.				
4.				

Table 2 Titration with known glucose solution

S.N.	Fehling solution in cc	Reading of burrete		Glucose solution in cc (unknown)
		Initial reading	Final reading	
1.				
2.				
3.				
4.				

8.2.5 Calculation

$$\text{Strength of glucose solution} = \frac{4{\cdot}0 \times 1{\cdot}5 \times \text{volume of known glucose solution}}{\text{volume of unknown glucose solution}}$$

8.2.6 Result

The strength of unknown glucose solution =…….g/L

8.3 QUANTITATIVE ESTIMATION OF AMINO ACID (GLYCINE) USING SORENSON FORMOL TITRATION

8.3.1 Chemicals and equipments required

Amino acid, glycine 2g, NaOH 1g 40% formaldehyde 50 mL, phenolphthalein indicator, solution, conical flask, volumetric flask, burette etc.

8.3.2 Theory

Amino acids like glycine which contains equal number of amino and carboxylic groups can not be estimated directly by titrating with satndars NaOH solution, due to the formation of zwitter ions in aqueous solutions. However the estimation is done by first treating the amino acid with excess of neutralized HCHO solution (which react with amino groups of the amino acid, leaving the carboxylic group free) and then titrating with standard $NaOH \longrightarrow \overset{\ominus}{O}H + Na^{\oplus}$ NaOH solution.

$$H_3\overset{\oplus}{N}CH_2COO^{\ominus} + \overset{\ominus}{O}H \rightleftharpoons H_2N.CH_2COO^{\ominus} + H_2O$$

Zwitter ion

$$H_2N.CH_2COO^{\ominus} + HCHO \longrightarrow CH_2{=}N.CH_2COO^{\ominus} + H_2O$$

$$CH_2{=}N.CH_2COO^{\ominus} + Na^{\oplus} \longrightarrow CH_2{=}N.CH_2COONa$$

8.3.3 Procedure

(i) Preparation of standard glycine solution: Weigh prciselly 2 g of glycine and dissolve it in 10mL distilled water. Transfer the solution to 250mL measuring flask. Wash the container with more distilled waterand transfer the washingalso to the measauring flask now make up the volume of flask by adding distilled water up to the mark acid (glycine) and make solution in distilled water in a 250 mL volumetric flask. Make up the volume up to the mark on the neck of flask.

(ii) Preparation of neutral formaldehyde solution: Take 50 mL of 40% formaldehyde in a conical flask and add 8-10 drops of phenolphthalein indicator. To it add 0.1N NaOH solution from the burette till the solution becomes faint pink in colour (do not record this reading). This step is necessary to carry out before titration because formaldehyde contains some amount of formic acid which needs to be neutralized.

(iii) Titration of standard glycine solution: In a conical flask pipette out 25 mL of glycine solution and add 2-5 drops of phenolphthalein and gradually add 0.1N NaOH from burette till faint pink colour is developed (do not record this reading). This process abstracts a proton from quaternary ammonium group of amino acid to form free amino groups if the amino acid was present as zwitter ion. This step is necessary to carry out before titration because amino acid solutions are rarely neutral. Add 10.mL of neytral formalin solution. The pink colour of solution immediately disappears. Not the initial reading of the burrete and titrate the solution with Standard NaOH solution till pink colour is restored. Repeat the process and take at least two concordant readings.Record the readings in table 1

(iv) Titration of unknown glycine solution:

Same procedure as in step (iii) is followed for unknown solution. Record the readings in table 2

8.3.4 Observation

Table 1 known glycine solution:

S.N.	Vol. of glycine sol. In mL	Reading of the burette		Vol. of N/10 solution used up
		Initial	Final	
1.	25			
2.	25			
3.	25			
4.	25			

Table 2 unknown glycine solution:

S.N.	Vol. of glycine sol. In mL	Reading of the burette		Vol. of N/10 solution used up
		Initial	Final	
1.	25			

2.	25			
3.	25			
4.	25			

8.3.5 Calculations

Weight of weighing tube = ----------g

Wt. of weighing tube + glycine-------g

Wt. of glycine =--------- (-) ---------- = -------g

Strength of glycine

$$\text{Strength of unknown glycine solution} = \frac{4{\cdot}0 \times 2{\cdot}0 \times \text{volume of known glycine solution}}{\text{volume of unknown glycine solution}}$$

8.3.6 Result

The strength of unknown glycine solution is……g/L

8.4 QUANTITATIVE *ESTIMATION OF HYDROXYL GROUP*

8.4.1 Chemicals and equipments required

Acetic anhydride, alcohol or phenol sample, dry pyridine, phenolphthalein indicator, 0.5N NaOH, condenser, conical flask, burette etc.

8.4.2 Theory

The commonly used procedure is preparation of acetyl derivative and estimation of acid formed upon hydrolysis. Acetylation of hydroxy compounds (e.g. phenol, n-hexanol, cyclohexanol, glucose, mannitol, benzyl alcohol, cresol etc) is done by using excess acetic anhydride in pyridine. The acetic acid formed in the reaction is removed by combination with pyridine. Excess anhydride is hydrolyzed with water and the acetic acid formed is titrated with sodium hydroxide solution in order to determine unreacted acetic anhydride.

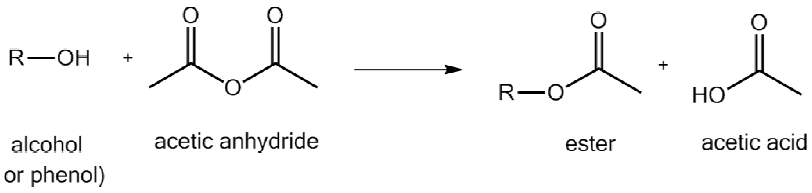


Figure 4. Reaction of one mole of OH group with one mole of acetic anhydride produces one mole of acetic acid (and one mole of ester).

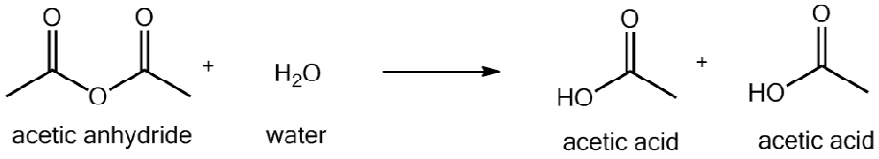


*Figure **5.** Reaction of one mole of acetic anhydride produces two moles of acetic acid on reaction with water.*

8.4.3 Reagents

A. Acetylating mixture: Throughly mix one volume of acetic anhydride with three volume of pyridine.

B. N/2 alcoholic NaOH solution: Prepare saturated solution of NaOH in water (about 18-20 N). Take 7mL of this solution in a 250 mL of measuring flask and make up it to 250 mLadding ethanol or methanol. Standarsize this solution with either standard N/2 oxalic acid orusing phenolphthalein as an indicator

8.4.4 Procedure

Acetic anhydride is very sensitive to moisture and water therefore, following experiment should be performed with due care to avoid unwanted exposure of reagents and solutions to the atmosphere. First step involves preparation of acetylating mixture by mixing 10 mL (~10 g) of acetic anhydride and 10 mL (~10 g) of dry pyridine in a conical flask (Note that excess of acetic anhydride should be used if more than one hydroxyl group are present in given sample). After preparing, fill the acetylating mixture in a burette and immediately put a cork on it to avoid exposure to environment. In a clean and dry 250 mL conical flask take accurately weighed 1-1.5 g of supplied sample of alcohol or phenol in a 100 mLround bottom flask. Add 10 mL of acetylating mixture from the burette to the conical flask containing alcohol or phenol. Remember that you will require removing the cork put on

the burette before draining the acetylating mixture. Put the cork immediately back to the burette after use. Fit a water condenser to the conical and heat the mixture at 70°C for one hour. This treatment will acetylate all the alcohol or phenol present in the conical flask. The residual acetic anhydride present in the conical is decomposed by adding 10 to 15 mL of cold water. Now add 2 or 3 drops of phenolphthalein indicator and titrate the contents with 0.5N NaOH solution already filled in another burette. For blank experiment, take 10 mL of acetylating mixture in a conical flask and without adding the alcohol or phenol perform the exactly same procedure as described above. Record the readings in tables 1 and 2

8.4.5 Observations

Table 1 Titration of reaction mixture against standardised NaOH

SN	Volume of reaction mixture (mL)	Reading of the burette (mL)		Volum of NaOH Used up (mL)
		Initial	Final	

Table 2 Titration of reaction mixture against standardised NaOH

SN	Volume of Blank mixture (mL)	Reading of the burette (mL)		Volum of NaOH Used up (mL)
		Initial	Final	

8.4.6 Calculations

Weight of sample = W g
Volume of NaOH used with the sample =V_1 mL
Volume of NaOH used with the blank = V_2 mL
Normality of NaOH solution =N/x

1000 mL N NaOH $\equiv$ 1 g mole NaOH $\equiv$ 1 g mole $CH_3COOH \equiv$ 1 OH group

$(V_2 - V_1)$ mL of N/x NaOH $\equiv$ $\frac{(V_2 - V_1)}{1000}$ x N/x hydroxyl group

W g of the hydroxyl compound contains

$$= \frac{(V_2 - V_1)}{1000} \text{ x N/x hydroxyl group}$$

100 g of the hydroxyl compound contain

$$= \frac{(V_2 - V_1)}{1000 \cdot W} \text{ x N/x} \cdot 100 = \frac{(V_2 - V_1)}{10 \cdot W} \text{ x N/x}$$

Thus the percentage of hydroxyl group in the sample of an unknown compound

$$= \frac{(V_2 - V_1)}{10 \cdot W} \text{ x N/x}$$

If molecular weight of the hydroxyl compound is known, Say it is M, then number of OH groups present in the compound will be:

$$= \frac{(V_2 - V_1)\ M}{10 \cdot W} \text{ x N/x}$$

8.4.7 Result

The supplied alcohol (or phenol) sample contains _____ hydroxyl groups.

8.5 ESTIMATION OF UNSATURATION FROM IODINE VALUE USING RICINOLEIC ACID

8.5.1 Chemicals and equipments required

Distilled water, glacial acetic acid, potassium iodide solution (prepared by dissolving 150 g solid KI in water and dilution to one litre), carbon tetrachloride, starch indicator solution (prepared by making a paste of 10 g of soluble starch in cold distilled water and adding it

to 1 L boiling water with stirring; salicylic acid 1.25 g is added as preservative and kept in refrigerator at 4 to 10 °C), 0.1N standard thiosulfate solution (prepared by dissolving 24.8 g of $Na_2S_2O_3.5H_2O$ in water and diluting it up to one litre; the solution is standardized by titrating it against acidified standard dichromate solution) and Wij's solution which can be prepared or purchased. Potassium dichromate, iodine trichloride, glacial acetic acid, pipette, volumetric flask etc.

8.5.2 Theory

Ricinoleic acid is an unsaturated omega-9 fatty acid also possessing a hydroxyl group. It is a major component obtained from castor seed oil. Iodine value is defined as the measure of unsaturation of fats and oils and their potential to get oxidized. It is expressed as the number of grams of iodine absorbed per 100 gm of fat/oil sample. The sample is treated with an excess of halogenating agent (Wij's or Hanus's solution). The amount of iodine absorbed is determined by back titration with standard sodium thiosulphate solution.

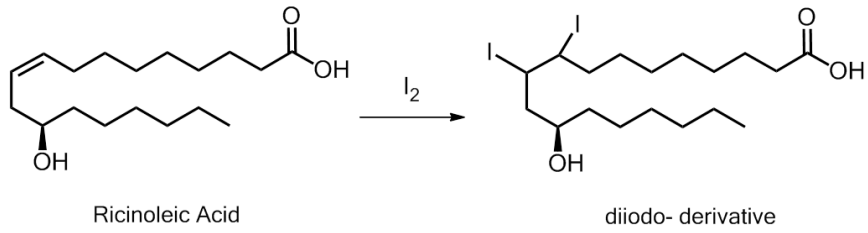


Figure 6. Addition of iodine molecule to the double bond present in Ricinoleic acid.

8.5.3 Procedure

(i) Standardization of thiosulfate solution: Take a finely ground and dried sample of potassium dichromate (4.903 g) in a one litre volumetric flask and dissolve it in minimum amount of water and then make up the volume to 1L. Thus a 0.1N solution of potassium dichromate is obtained. Pipette out 25 mL of this solution in a 250 mL conical flask, add 5 mL of conc. HCl and 10 mL of 15% potassium iodide solution with continuous stirring. The mixture is allowed to stand for 5-10 minutes; 100 mL of water is then added and the mixture is then titrated with the thiosulfate solution, stirring continuously until the yellow colour disappeared. Now add starch indicator 1-2 mL and titrate again till blue colour disappears.

(ii) Preparation of Wij's solution: Dissolve 7.9 g of iodine trichloride in 100 mL of glacial acetic acid in a beaker. Heat the solution gently on a water bath and then cool to

room temperature. In a 250 mL conical flask take 8.9 g of iodine and dissolve in warm acetic acid. Mix the two solutions in 1 L measuring flask and make up the volume to the mark on the neck of the flask by using glacial acetic acid.

Take 0.1 g of sample oil/fat in a 250 mL flask with a stopper. Add 20 mL of carbon tetrachloride or chloroform and shake well. To this add 25 mL of Wij's solution stopper the flask and shake vigorously. Allow the flask to stand in dark for thirty minutes. After this time period add 20 mL of KI solution and dilute the solution with 100 mL of freshly boiled and cooled water. Titrate this solution immediately against 0.1N thiosulfate solution gradually and with stirring. Titration is done till yellow colour of the solution disappears. Now 1-2 mL of starch solution is added and titrated till blue colour of the solution just disappears. A blank titration is carried out simultaneously. The same procedure and same reagents are used only the oil is omitted.

8.5.4 Calculation Iodine value is expressed as the amount of iodine (in grams) absorbed per 100 grams of sample. According to formula below-

$$\frac{(V_b - V_s) \times N \times 126.9 \times 100}{w \times 1000}$$

w = weight of sample in gram

V_b = Volume of $Na_2S_2O_3$ used in blank titration

V_s = Volume of $Na_2S_2O_3$ used in sample titration

N = Normality of the $Na_2S_2O_3$ solution

8.5.5 Result

Iodine value of given sample is _____ g.

(Note: Express your calculated value to nearest whole number. Make sure that the results of duplicate experiments should not vary by more than 14 g iodine per 100 g of sample. If your results indicate so, repeat the experiment again with utmost care.)

8.6 SUMMARY

In the above exercises you learnt estimation of some vital compounds or functional groups encountered in a given organic chemistry. You were made familiar with important aspects for an accurate estimation. Preparation of several standard solutions and titration using blank solutions are also discussed in procedures. Importantly, preparation of very useful Fehling's and Wij's solution was done. Simple calculations were done for quantitative estimation. These estimation methods can be used to detect amount of unsaturation in a given sample of fat or presence of sugar in urine. You learnt to carry out neutralization of zwitter ionic amino acids, acetylation of hydroxyl group, halogenation reaction at the double bond etc reactions as discussed in different experiments.

8.7 TERMINAL QUESTION

Short Answer type questions

Q.1 What is the change in oxidation state of copper when glucose is tested by using Fehling's solution?

Q.2 What causes the formation of red precipitate when glucose is estimated using Fehling's solution?

Q.3 Why is it important to neutralize formaldehyde solution prior to titration for estimation of amino acid?

Q.4 What is a blank titration and its use?

Q. 5 Why some solutions are standardized prior to their use?

Q.6 What is a standard solution?

8.8 ANSWERS

A.1 Cu^{+2} in sodium potassium tartarate is reduced to Cu^{+1} in Cu_2O.

A.2 Formation of Cu_2O gives the red precipitate.

A.3 Formaldehyde contains traces of formic acid which requires to be neutralized before doing experiment. Hence, it is titrated with alkali to neutralize it.

A.4 In a blank titration the titration is carried out with a known concentration of titrant into a solvent having no analyte (*i.e.,* the substance whose concentration is to be determined). The only difference from the regular titration is the absence of analyte. The process helps to know the amount of reactive substance within the plain solvent to be determined and hence allows determination of the error in future titration experiments using this solvent.

A.5 Standardization is done to know the real concentration of the solution which is being made for a titration experiment even though we have added a known amount of solute to a fixed volume of solvent to prepare this solution. This is so because say for example we wish to make a 0.1 N NaOH solution. But this NaOH was kept in bottle for some time and may have reacted with some species in air (CO_2) or while weighing it may have captured some moisture. So the weight which we measured is not exactly what we had to take. Thus this solution is titrated using an indicator to know the exact concentration of the solution made.

A.6 A standard solution is a solution containing a accurately known concentration of a substance. A known weight of solute is dissolved to make a specific volume of standard solution. Standard solutions are used to determine the concentrations of other solutions in titrations.

8.9 REFERENCES

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UNIT 9: MULTI STEP SYNTHESIS

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9.1 OBJECTIVE

Multistep synthesis is the conversion of a commonly available organic molecule into desired products using organic reactions. It means that you will require devising a sequence of organic reactions that will lead from a simple starting compound to a desired product compound. Apparently, multistep syntheses require more than one step. It means that one or more intermediate compounds are formed along the way. On completion of the exercises given in this unit you would be aware of fundamental skills of organic synthesis, how to execute organic reactions in laboratory and the use of different reaction setups etc.

Multistep synthesis problems are often very challenging. Hence, mental reasoning about the solution is very important in solving these types of problems. Multistep syntheses of four important compounds representing diverse classes of organic compounds are presented in this chapter. This will present you a picture of importance of organic chemistry in industry and household. The reactions involved in four multistep syntheses will boost your confidence as a synthetic chemist.

9.2 ADIPIC ACID

Adipic acid or hexanedioic acid is a dicarboxylic acid with the formula $(CH_2)_4(COOH)_2$ and molar mass, 146.14 $g \cdot mol^{-1}$. It is an odourless solid at room temperature and possesses white crystalline appearance. Its melting point is 152.1 °C. Adipic acid is highly soluble in methanol, ethanol, moderately soluble in acetone and cyclohexane whereas practically insoluble in benzene, petroleum ether and acetic acid. Adipic acid does not occur in nature. Several billion kilogram of this compound is synthesized annually around the world because of its use for the synthesis of nylon. Structural formula of adipic acid is given in **Figure 1**.

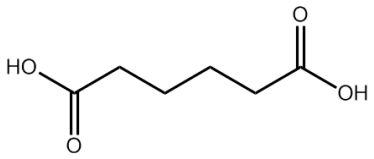


Figure 1. Structural formula of adipic acid ($C_6H_{10}O_4$)

Multistep synthesis of adipic acid involves two steps, first is the oxidation of cyclohexanol to cyclohexanone and the second one is oxidation of cyclohexanone to adipic acid. There are methods available to synthesize adipic acid by direct oxidation of cyclohexanol using strong oxidizing agents. Multistep syntheses of adipic acid is discussed in following section.

9.2.1 Synthesis adipic acid from cyclohexanol

9.2.2 Chemicals and equipments required

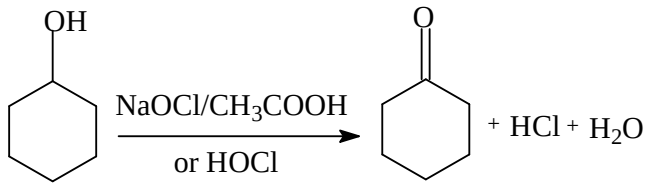
Adipic acid, conc. HNO_3, 10% NaOH solution, glacial acetic acid, 5% NaOCl solution, saturated sodium bisulfite solution, potassium iodide, starch, anhydrous sodium carbonate, sodium dichromate, concentrate sulphuric acid, sodium chloride, round bottom flask, dropping funnel, thermometer, separatory funnel etc.

9.2.3 Theory

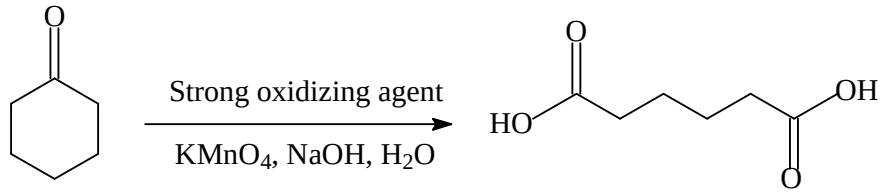
Adipic acid or hexanedioic acid is primarily used in the synthesis of nylon 6,6 for fibres and plastics. It can be synthesized by two methods. First method involves two steps (step 1) oxidation of cyclohexanol to cyclohexanone; (step 2) oxidation of cyclohexanone to yield adipic acid. In the second method, adipic acid can be directly synthesized by oxidation of cyclohexanol to nylon 6,6 *via* cyclohexanone in a single step. It must be remembered that cyclohexanone is a ketone bearing alpha-hydrogen and thus shows keto enol tautomerism.

9.2.4 Procedure

In this section synthesis of adipic acid by two step oxidation is discussed **(Figure 2)**. Cyclohexanol is oxidized to cyclohexanone using sodium hypochlorite and in the second step cyclohexanone is oxidized to adipic acid using potassium permanganate. In the oxidation of cyclohexanol to cyclohexanone sodium hypochlorite and acetic acid are used which generate hypochlorous acid, the active oxidizing agent.



Oxidation of cyclohexanol to cyclohexanone



Oxidation of cyclohexanone to adipic acid

Figure 2. Steps involved in the synthesis of adipic acid from cyclohexanol via cyclohexanone

9.2.5 Synthesis

Step I Synthesis of cyclohexanone from cyclohexanol

Method i: Take 10 mL of cyclohexanol in a 250 mL conical flask and add 15 mL glacial acetic acid. Add dropwise 75 mL of 5% NaOCl solution to the flask while keeping it mildly warm at about 40-50^{o} C. Use thermometer to maintain the temperature. Keep stirring the solution with glass rod and again keep it back in ice bath. Again add dropwise 75 mL of NaOCl solution and check with potassium iodide-starch paper. If the paper does not turn blue-violet add some more of NaOCl solution (1-5 mL) and check again. Allow the solution to return to room temperature and wait for 15 minutes. Add a saturated sodium bisulfite solution until a negative potassium iodide-starch test is obtained. To remove acetic acid add anhydrous sodium carbonate with stirring until foaming ceases. Now add 8 g of NaCl and stir for ten minutes to further salt out cyclohexanone. Decant the mixture into a separatory funnel and add ether or dichloromethane to extract cyclohexanone. Collect the organic portion in a conical flask and dry by using anhydrous magnesium sulfate. Decant this solution using a funnel with cotton plug into a conical flask. Remove ether by heating over a water bath. The residue left should be distilled in a distillation assembly set at 154-156 ℃ to get the cyclohexanone fraction.

Method ii: Weigh 20 g of $Na_2Cr_2O_7$; add 100 mL water and 9.5 mL conc. H_2SO_4 in a 250 mL conical flask. Shake and cool the resulting orange red solution (colour due to chromic acid formed) in ice cold water to 15 ^oC; use thermometer. Pour the dichromate solution into another flask containing 10 mL of cyclohexanol. Stir the contents vigorously and keep this flask in ice bath since the reaction is exothermic. When the temperature stops rising allow the flask to stand at room temperature for 30 minutes. Transfer the reaction mixture to a 250 mL round bottom flask and add 100 mL water and few boiling chips. Set up the distillation assembly to distil the mixture till 70 mL of the distillate is collected. Now extract this distillate with ether in a separatory funnel and add saturated NaCl solution. Stopper the funnel and shake well; keep releasing the pressure developed inside funnel at intervals. Allow the funnel to stand for some time till the organic and aqueous layers separate out. Collect the organic layer in a conical flask. Wash the aqueous layer with 20 mL ether at least twice. Collect the combined ether extracts and add anhydrous magnesium sulfate for drying. Filter and remove the ether by heating on water bath. Do not heat directly as ether is highly flammable. Distil the left over residue and collect the fraction at 154-156 °C.

Step II Preparation of adipic acid from cyclohexanone: Weigh 8.0 g of solid potassium permanganate and dissolve in 30-50 mL of H_2O in a 250 ml conical flask. Add 8 to 10 mL cyclohexanone prepared above to the flask. Heat the mixture on hot plate to 30 °C. Add 1 mL of 3M NaOH solution. Stir the reaction mixture for 15-20 minutes at 45 °C. Heat the reaction mixture till you notice formation of black manganese dioxide. Perform a spot test by dipping a stirring rod in the mixture and applying to a piece of filter paper. If the paper turns purple, then excess permanganate needs to be reduced. For this purpose add a small portion of sodium bisulfite (20 drops), stir and take spot test again. Perform this until you get no purple colour on filter paper. Filter the mixture on vacuum filter to remove manganese dioxide. Wash with 5 mL warm water. Transfer the filtrate to a 250 mL beaker and heat on a hot plate so as to reduce the volume to 10-15 mL. The hot solution is acidified with conc. HCl (1 mL) pH 1-2; check with litmus paper. Further add 1.5 mL of acid. Allow the solution to cool and then place in ice bath for crystallization. Collect the product by vacuum filtration.

9.2.6 Characterization

The obtained white solid crystalline product is characterized by determining the melting point. Melting point obtained in the temperature range 152-155°C indicates the formation of desired compound.

9.2.7 Result: Record the weight of the dried crystals as the actual yield

Appearance = White crystalline flakes

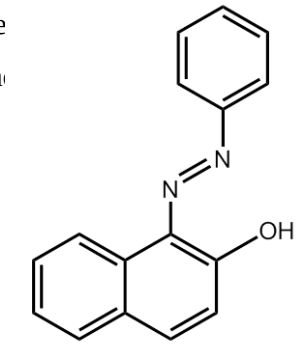
Yield = _____ g

Melting point = _____ °C

9.3 AZO DYE AND SUDAN-I

Azo dyes are one of the most important colourants used in the textile industry. As the name suggests these compounds contain an azo group that is –N=N– which links two sp^2 hybridized carbon atoms. Azo dyes are brightly coloured due to the presence of extended conjugation. These are very cost effective and moderately fastening dyes.

Sudan-I or 1-phenylazo-2- naphthol or 1-(phenyldiazenyl) naphthalen-2-ol (**Figure 3**) is a lysochrome i.e. in hystochemical staining it is used for staining lipids. It has an orange-red appearance. It is used to color substances such as waxes, oils, petrol, solvents and polishes. Sudan-I was also being used to colour foodstuffs such as curry powder and chilli powder. However its use in colouring food items has been banned now in many countries because it has bee ry 3 carcinogen by the International Agency for Research on Can



Sudan I or
1-phenyl-azo-2-naphthol

Figure 3. Structural formula of azo dye, Sudan-I ($C_{16}H_{12}N_2O$)

9.3.1 Synthesis of azo dye from acetanilide via aniline

9.3.2 Chemicals and equipments required

Aniline, concentrate hydrochloric acid, sodium nitrite, β-naphthol, sodium hydroxide, conical flask, test tube, ice bath etc.

9.3.3 Theory

An azo dye is defined by having an azo linkage (-N=N-) as part of its chromophore. Azo dyes are synthesized in two steps. First, synthesis of diazonium salt from primary amine and nitrous acid (HNO_2) prepared from sodium nitrite ($NaNO_2$) and a HCl (**Figure 4 & 5**). Second, coupling of the diazonium salt with a strongly activated aromatic system such as β-naphthol (**Figure 6**). An azo coupling is a reaction between a diazonium compound and an aniline, phenol or other aromatic compound which produces an azo compound. Since here the staring compound is acetanilide we have to first carry out an extra step of hydrolyzing acetanilide to aniline (primary amine) followed by diazotization and coupling. Due to the easy availability of starting compounds here azo dye Sudan-I is synthesized.

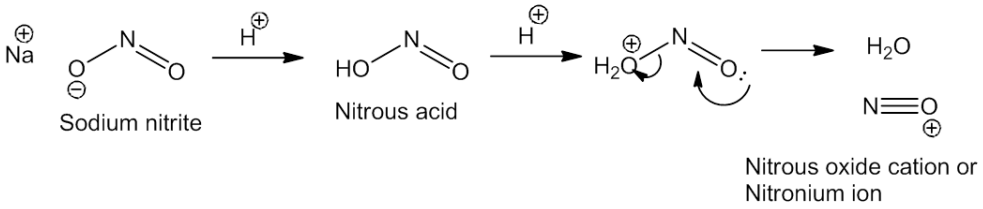


Figure 4. Mechanism for generation of nitronium ion

9.3.4 Procedure

Part A: Hydrolysis of Acetanilide: Take 2 g of acetanilide in a 50 mL round bottom flask and add 5 mL water and 5 mL concentrated hydrochloric acid. Fit a cold water condenser to the mouth of flask and place the assembly on a sand bath. Heat the reaction mixture gently (50-60 °C) for 10 minutes and then strongly (~100 °C) for one hour. Heating acetanilide with acid causes hydrolysis reaction to give aniline and acetic acid. Aniline converts to quaternary ammonium chloride salt (anilinium chloride) in presence of hydrochloric acid. Prepared anilinium chloride can be directly used for the second step. Allow the reaction mixture to cool down to room temperature. After reaching the room temperature, place the flask in an ice bath for further cooling.

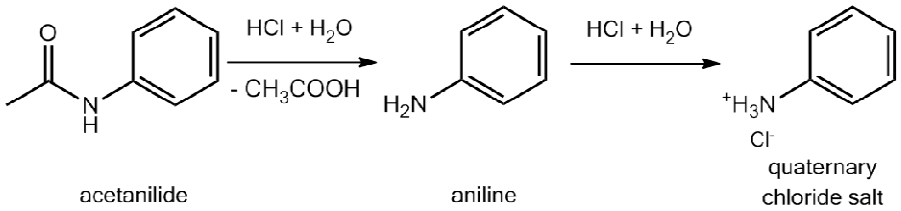


Figure 5. *Acid catalyzed hydrolysis of acetanilide*

Part B: Synthesis of azo dye (Sudan-I) by diazotization reaction: Take 5 mL 10% $NaNO_2$ in a test tube and chill it in ice bath. Take 0.6 g of β-naphthol, 4 mL 10% NaOH and 10 mL distilled water in a separate beaker. Stir the contents of beaker well till homogeneous solution appears and then chill in ice water bath. When all mixtures are chilled to nearly 0 °C add $NaNO_2$ solution with the help of dropper to the flask containing anilinium chloride (obtained by Part A as discussed above). Stir the mixture thoroughly. Transfer the mixture from flask to beaker containing β-naphthol, NaOH and water. Stir continuously to avoid accumulation of red clumps. Keep the mixture in ice water bath and continue stir using glass rod for about 5 minutes. Filter the precipitate using vacuum pump and wash with cold water to obtain the azo dye.

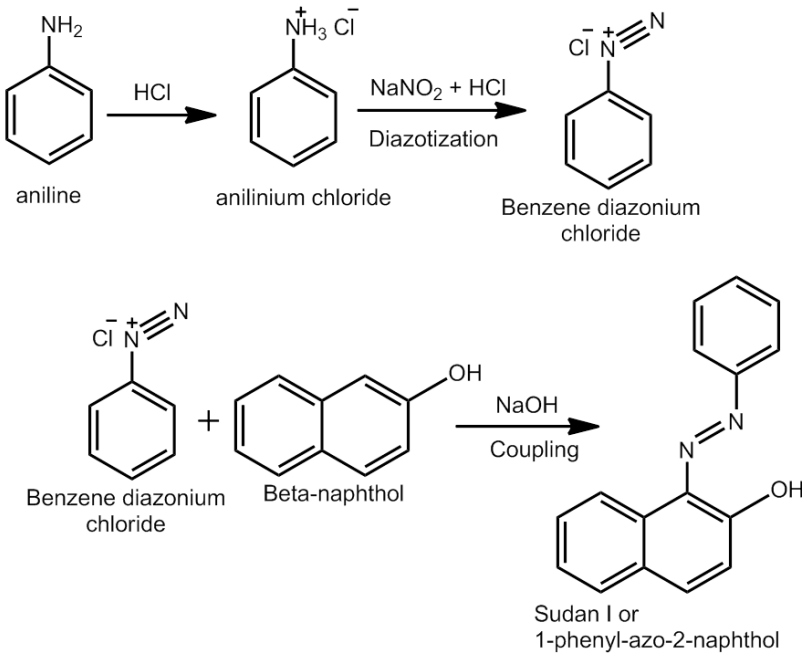


Figure 6. *Synthesis of azo dye Sudan-I from anilinium chloride*

9.3.5 Recrystallization

Dry the product and recrystallize in ethanol. Vacuum filter the crystals and wash with cold ethanol. Dry the crystals weigh and record the yield of the product.

9.3.6 Characterization

The orange red solid crystalline compound is characterized by determining the melting point. Melting point obtained in the temperature range 131-133°C indicates the formation of desired compound.

9.3.7 Result

The azo dye was synthesized by hydrolysis of acetanilide to aniline followed by diazotization and coupling reactions.

Appearance = Orange red crystalline powder

Yield = _____ g

Melting point = _____ °C

9.4 POLYMER INTRODUCTION

Polymers are macromolecules which have their molecular structure built from several smaller repeating monomer units. There are both synthetic and natural polymers. Polymers are grown from small monomer units which are bonded together by covalent bonds. In laboratory polymers are grown by two methods namely step-growth polymerization (polyesters, polyamides etc) and chain growth polymerization (polyethylene).

9.4.1 Synthesis of nylon 6, 6

9.4.2 Chemicals and equipments required

0.35 M aqueous hexamethylenediamine, 5l% (v/v) adipoyl chloride in cyclohexane solvent, 20% (w/v) aqueous sodium hydroxide, beaker, glass rod, watch glass etc.

9.4.3 Theory

Polymers are macromolecules which are built from smaller molecular subunits known as monomers. The term Nylon refers to a family of synthetic polymers which are synthesized

from the reaction of diamine with diacids (or the acid chloride analog). The numbering system for acid (in this case "6-6") refers to the number of carbons in the monomer which came from the diamine and the diacid respectively. Nylon 6,6 (**Figure 7**) is a polyamide and the polymeric chain grows by step-growth polymerization. In this type of polymerization the monomer units combine step by step to first form dimmers then trimers and eventually a long chain polymer.

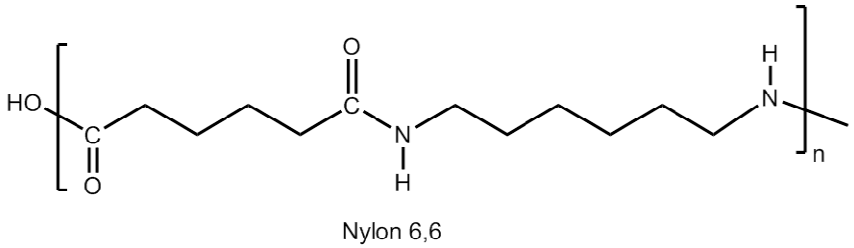


Figure 7. Structural formula of Nylon 6,6

9.4.4 Procedure

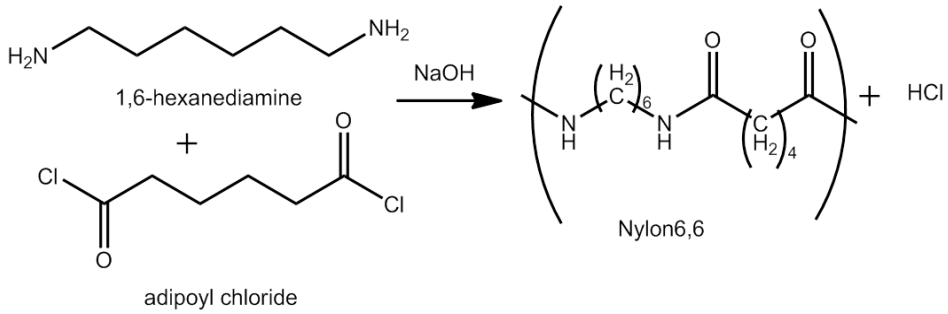


Figure 8. Synthesis of Nylon 6,6

Nylon 6-6 is formed from a condensation reaction between hexamethylenediamine and adipoyl chloride (**Figure 8**). Since the reaction occurs at the interface of two immiscible solutions it is called interfacial polymerization. It is a polyamide used as fibre in applications such as carpeting and clothing.

9.4.5 Synthesis

Weigh 1.5 gram of 1,6-hexanediamine and dissolve in 25 mL of water in a beaker (gives 0.35 M aq. hexamethylenediamaine solution). Take 1 mL of adipoyl chloride and 19 mL of cyclohexane in a 50 mL beaker and mix them by stirring with glass rod (gives 5 vol% adipoyl chloride). Weigh 5 g of sodium hydroxide pellets and dissolve in 20 g of water

(gives 20 wt% aqueous sodium hydroxide) in another 50 mL beaker. Add 10 drops of sodium hydroxide solution to a separate beaker containing 10 mL of hexamethylenediamine solution (say beaker A). Cover the remaining beakers containing solutions with a watch glass. Take out 10 mL of prepared adipoyl chloride solution in another beaker (say beaker B). Carefully add adipoyl chloride solution from beaker B to the beaker A (solution of hexamethylenediamine and sodium hydroxide) along the wall of latter. A polymer film is formed immediately at the interface of the two solutions. Use forceps to break the nylon free and pull the wire upwards as a continuously forming rope. Dry it on filter paper and wash it with water and acetone and dry again.

9.4.6 Result

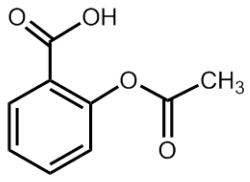
Nylon 6,6 was synthesized by condensation reaction between hexamethylenediamine and adipoyl chloride.

Appearance = off white fibers

Yield = _____ g

9.5 ASPIRIN

Aspirin (acetyl salicylic acid or 2-acetoxybenzoic acid; **Figure 9**) was first derived from salicylic acid which is present in bark of the willow tree (*Salix alba*). Aspirin is one of the most widely sold over-the-counter drug. It has the ability to reduce fever (antipyretic), to reduce pain (analgesic), and to reduce swelling, soreness, and redness (anti-inflammatory agent).



Aspirin or 2-Acetoxybenzoic acid

Figure 9. Structural formula of aspirin ($C_9H_8O_4$)

9.5.1 Synthesis of aspirin

9.5.2 Chemicals and equipments required

Salicylic acid, acetic anhydride, concentrate sulfuric acid, ice cold water, conical flask, beaker, Buchner funnel etc.

9.5.3 Theory

Aspirin is synthesized by acetylation of salicylic acid using acid as a catalyst. That is an acetyl group is introduced into the hydroxyl group.

9.5.4 Procedure

Aspirin can be synthesized in laboratory by reaction of salicylic acid with acetic anhydride, using concentrated sulfuric acid as a catalyst (**Figure 10**). Phosphoric acid is generally used as the catalyst but since it is a very hazardous chemical so it is avoided.

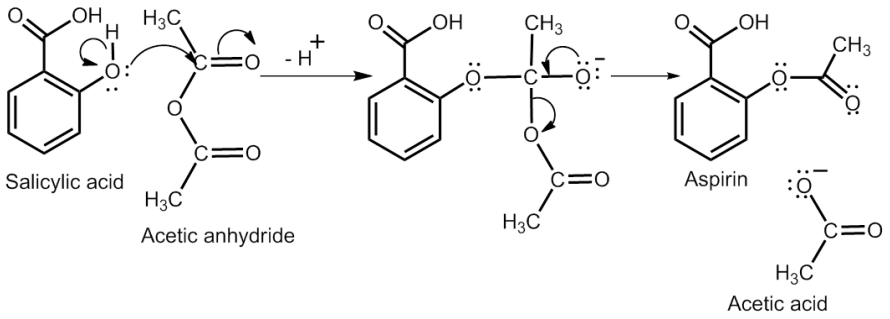


Figure 10. Probable mechanism involved in the synthesis of aspirin from salicylic acid and acetic anhydride

9.5.5 Synthesis

Weigh 4.0 g of salicylic acid and put in a conical flask. Carefully add 6 mL of acetic anhydride to the flask. With extreme caution add five drops of concentrated sulfuric acid to the flask. Heat the contents of the flask for 20 minutes with continuous stirring on a hot water bath. The entire solid must completely dissolve. Remove the flask from water bath and allow it to cool to room temperature. As cooling proceeds formation of crystals should occur; do not disturb the flask during this time. After crystal formation ceases add 40 mL of ice cold water to the flask. Water dissolves unreacted acetic anhydride and and cause precipitation of insoluble aspirin. Collect the crystals by filtration using Buchner funnel. Wash them with cold water and then ethanol. Dry the crystalline sample and weigh. If

crystal formation does not occur spontaneously on cooling then pour the solution in a 250 mL beaker and add 40 mL of ice water and mix thoroughly. Now place the beaker in ice water and let it sit undisturbed until crystals have grown.

9.5.6 Recrystallization

The crude product obtained above often contains impurities such as the starting products and products from the side reactions. To get the pure compound we need to carry out the process of recrystallization of the crude product. Dissolve 2-4 g of the product in 20 mL ethyl alcohol in a 125 mL conical flask. Warm the flask contents on water bath to speed up dissolution of the compound. Do not use direct flame to heat the flask since it contains ethyl alcohol which highly flammable. If any solid impurity still remains then filter the solution. Add 30 mL of warm water to the flask and keep it aside to cool. Soon colourless crystals of aspirin are obtained which can be collected by filtration.

9.5.7 Characterization

The colorless needles like crystal are characterized by determining the melting point. Melting point obtained in the temperature range 135-138 °C indicates the formation of desired compound.

9.5.8 Result

Aspirin was synthesized by by reaction of salicylic acid with acetic anhydride.

Appearance = Colourless needle like crystals

Yield = _____ g

Melting point = _____ °C

9.6 SUMMARY

In this section multi step synthesis that is involving more than two steps were done. These incorporated synthesis of some very important compounds such as adipic acid, nylon, azo dye and aspirin which are now used commercially world over. Adipic acid is used in synthesis of polymers and azo dyes are used widely used colourant. Discovery of nylon changed the scenario of textile industry and is known to be a landmark discovery. Similarly, laboratory synthesis of aspirin is an important discovery in the field of

medicine. Aspirin is one of the most widely used drugs by the masses. Thus these are important reactions for gaining an insight into commercial synthesis of the above products.

In these experiments you learnt to carry out important organic transformations such as diazotization, coupling and condensation reactions; oxidation reaction of cyclohexanol and cyclohexanone. These reactions are very useful in a number of organic transformations.

9.7 TERMINAL QUESTION

Short Answer type questions

Q.1 What precautions should be taken while working in a chemical laboratory?

Q.2 What is the reactive species in the process of diazotization?

Q.3 What is an acetyl group and an acetate group?

Q.4 IUPAC name of adipic acid

Q.5 How is nitrous acid generated for diazotization reaction?

Q.6 Nylon 6,6 is formed by interfacial polymerization. What does this mean?

9.8 ANSWERS

A.1 The following precautions must always be taken

i. Wear lab coat at all times.

ii. Use goggles wherever needed.

iii. All chemicals must be handled with gloves on because most of them are corrosive, may cause itching while some may cause severe damage to skin.

iv. Acids should always be handled with utmost care.

v. Substances which are sensitive to moisture and flammable must be used carefully in inert atmosphere and the glassware/ solvents being used should be completely dry

vi. Before using any chemical for an experiment consult the MSDS (Material Safety Data Sheet) sheet for its detailed information.

vii While reducing the volume of a reaction mixture always bear in mind the solvents present in the mixture. Those solvents which have low boiling point or are flammable

must be warmed gently only on water bath and temperature should be monitored using a thermometer.

A.2 Nitrous acid

A.3 CH_3CO is acetyl group and $(CH_3CO)O$ is acetate group.

A.4 Hexanedioic acid.

A.5 It is generated *in situ* from sodium nitrite and a strong acid, such as hydrochloric acid or sulfuric acid.

A.6 During the synthesis of Nylon 6,6 the polymer is formed at the interface of two layers *viz.* organic layer and aqueous layer hence it is called interfacial polymerization.

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UNIT 10: PHASE EQUILIBRIA

CONTENTS:

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10.3 ICST: to construct the phase diagram of phenol-water system
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10.3.4 Observations and calculations
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10.4.4 Observations
10.4.5 Result
10.5 Summary
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10.7 Answers

10.1 OBJECTIVES

After reading this unit you should be able to

(a) Explain the phase separation of liquid mixtures due to partial miscibility.
(b) Explain the effect of temperature and composition on the solubility limit of two partially miscible liquids.
(c) Define critical solution temperature (CST).
(d) Construct a phase diagram of a two component condensed system of a liquid pair (phenol and water).
(e) Interpret a phase diagram of a two component condensed system (phenol and water).
(f) Explain the effect of impurities on Critical Solution Temperature (CST).

10.2 INTRODUCTION

Two liquids can be mixed together to form one of the following systems.

(a) The two liquids are completely miscible like alcohol and water.

(b) The two liquids are partially miscible like phenol and water.

(c) The two liquids are practically immiscible like carbon disulphide and water .

These systems are called condensed systems in which the vapour phase is ignored and only solid and/or liquid phases are considered. The pressure is considered to be 1 atm while the temperature and concentration are the only variables which can be changed independently.

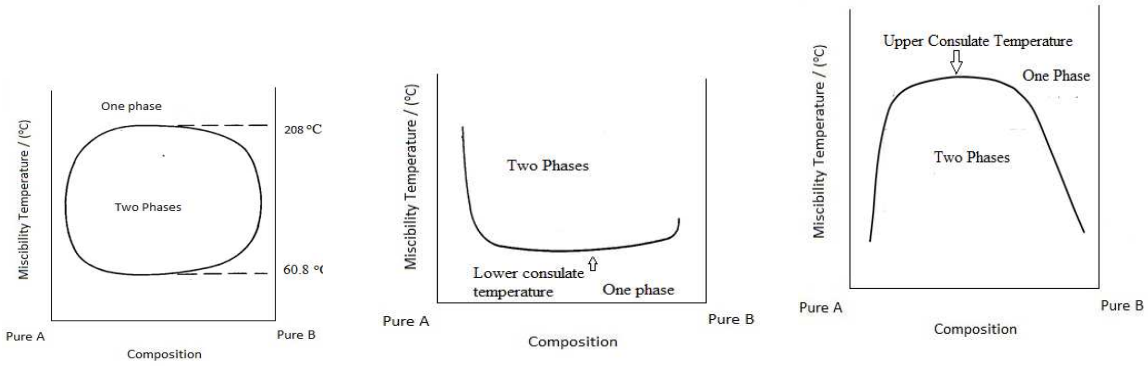


Figure 1. Liquid pairs exhibiting upper and lower consulate temperatures.

The condensed phase rule for such a two system is given by P+F=C+1

Where P is the number of phases, F is the number of degrees of freedom and C is the number of components. Two partially miscible liquids may become completely miscible at a higher temperature and the two phases become one homogeneous phase. This miscibility temperature is different for different compositions of the mixture. The highest miscibility temperature is called the upper critical solution temperature. Above this temperature all compositions of this mixture are completely miscible. Lower critical solution temperature is the lowest temperature below which the components are miscible in all proportions. Liquid pairs exhibiting upper and lower consulate temperatures are depicted in Fig. 1.

10.3 ICST: TO CONSTRUCT THE PHASE DIAGRAM OF PHENOL-WATER SYSTEM

10.3.1 Chemicals and apparatus required

Phenol- 8 g and distilled water. Test tube, beaker (250 cm^3), measuring cylinder, cork stopper carrying a thermometer, an aluminium stirrer and a beaker.

10.3.2 Principle:

The phenol-water system is an example of partially miscible liquids. When a temperature-composition diagram of the phenol-water system is drawn, the CST temperature is represented by a maximum in the mutual solubility curve. This is also called the upper consulate temperature. The temperature-composition diagram of phenol–water system is shown in Fig. 2

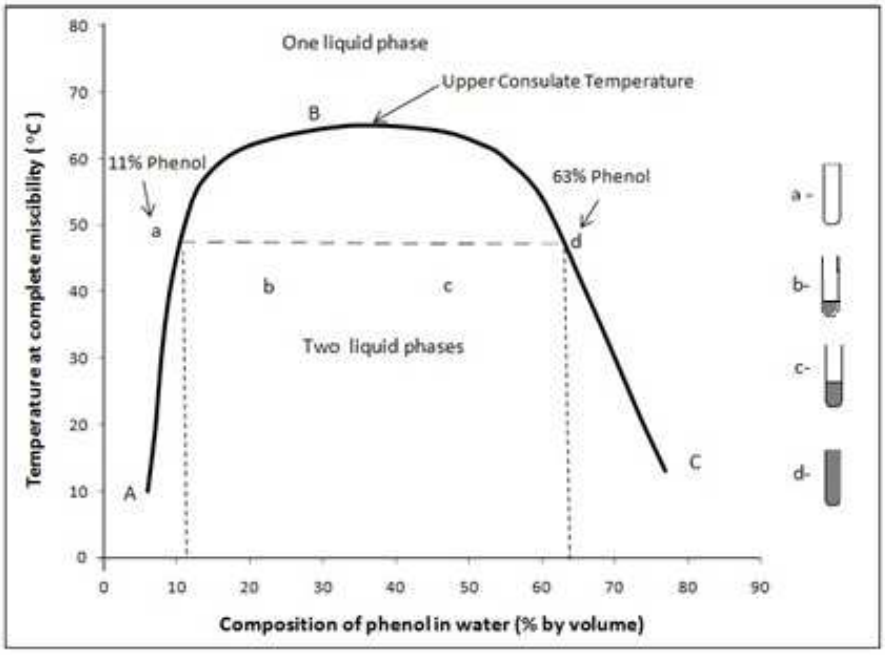


Figure2. Temperature-composition diagram of phenol–water system

The miscibility temperature at each composition is plotted to give curve ABC. At origin, the system is 100% water. Adding known increments of phenol to a fixed weight of water, maintaining the temperature at 50^{o}C, will result in the formation of a single liquid phase (water with dissolved phenol). This continues till point *a*. After point *a*, a minute amount

of a second phase appears. The concentration of phenol at this point is 11% by weight of phenol in water.

As the quantity of phenol is increased the amount of phenol-rich phase increases and the amount of water-rich phase decreases. Once the total concentration of phenol exceeds 63% at 50^{o}C a single phenol rich liquid phase is formed; point d in Fig. 2. If we prepared a system containing 24% by weight of phenol and 76% by weight of water, at equilibrium we will have two liquid phases. The upper layer would have a composition rich in water while the lower layer would have a composition rich in phenol.

Within the area ABC two liquid phases are in equilibrium with each other. One phase is water saturated with phenol and the other is phenol saturated with water. Outside the ABC curve, there is only one phase. Any point on the curve ABC represents the saturated homogeneous phase. This is a condensed system of two components. The phase rule may be expressed as F=C-P+1. Outside the area enclosed by the curve, number of phases, P, is 1 and the number of degrees of freedom, F, is 2.

10.3.3 Procedure

1. Take 9 dry test tubes and label them 1 to 9. Weigh 1, 2, 3, 4, 5, 6, 7, 8 and 9 g of phenol and transfer each to a test tube. Add 9, 8, 7, 6, 5, 4, 3, 2, and 1 cm^3 of water in each test tube such that the total weight of the mixture in each test tube remains 10 g. This gives you a composition range of 10-90% by weight of phenol.
2. Stopper the tube with a cork carrying a thermometer and a stirrer.
3. Keep the first tube with 90% by weight of phenol in a beaker containing water. Stir the contents. You will observe turbidity. Heat the beaker gradually. Stir the contents of the tube until turbidity disappears forming a homogeneous layer. Note the temperature when this occurs.
4. The mixture is allowed to cool with constant stirring. The temperature at which two layers appear or turbidity appears again is noted. The mean of the these two temperatures gives the miscibility temperature of the phenol–water mixture.
5. The procedure is repeated with the second test tube containing 80% by weight of phenol. The miscibility temperature is noted for this mixture.
6. Repeat the procedure for mixture containing 70, 60, 50, 40, 30 and 20% by weight of phenol.
7. Record your observations as shown in Table 1.

8. Plot temperature of complete miscibility against weight % of phenol in water. This gives the phase diagram of phenol-water system. The critical solution temperature of phenol-water system and the critical composition can be obtained from the phase diagram.

10.3.4 Observations and calculations:

Table1. Temperature of complete miscibility of mixtures of varying weight percentage of phenol in water

Wt. % Phenol	Phenol (g)	Volume of water (cm^3)	Temperature of complete miscibility (^oC)		Mean miscibility Temperature (^oC)
			Heating	Cooling	

10.3.5 Result

The critical solution temperature of phenol-water system = ^oC

The critical composition = % phenol in water .

10.4 STUDY OF EFFECT OF NaCl/SUCCINIC ACID ON CST OF PHENOL-WATER SYSTEM

10.4.1 Chemicals and apparatus required

Phenol-8 g, succinic acid and distilled water.Test tube, cork stopper carrying a thermometer, an aluminium stirrer and a beaker.

10.4.2 Principle

Presence of impurities in the phenol-water mixture affects the critical solution temperature. If the impurity is soluble in both the liquids, the CST is lowered. The impurity keeps distributing itself between the two conjugate solutions and increases the

mutual solubility of the liquids. An example is when succinic acid is added to the phenol-water system. If the impurity added is soluble only in one of the liquids then the CST is raised for eg. addition of NaCl or KCl raises the CST of the phenol-water system.

10.4.3 Procedure

1. Prepare 250 cm^3 of 0.2 M succinic acid solution.
2. Transfer 10, 20, 30, 40 and 50 cm^3 of this solution into five dry 100 cm^3 volumetric flasks and make up with distilled water to get 0.02, 0.04, 0.06, 0.08 and 0.10 molar solutions of succinic acid, respectively.
3. Determine the miscibility temperature using 5 g of phenol and 5 cm^3 of 0.02 molar succinic acid solution.
4. Repeat the experiment using 5 g of fresh phenol and 5 cm^3 of each of the other concentrations and also an unknown solution. Record your readings as shown in Table 2 and Table 3.
5. Plot a graph of miscibility temperature against concentration of phenol-water system for each concentration of succinic acid (Fig.3). Determine the CST of phenol-water system for each concentration of succinic acid. Determine the CST of the given solution of unknown concentration also.
6. Plot a graph of CST against concentration of succinic acid (Fig.4). A linear plot is obtained. The concentration of unknown solution of succinic acid is obtained from the above graph by extending a straight line from the CST of unknown solution of succinic acid on Y axis and dropping a perpendicular from the point where this meets the straight line to the X axis.

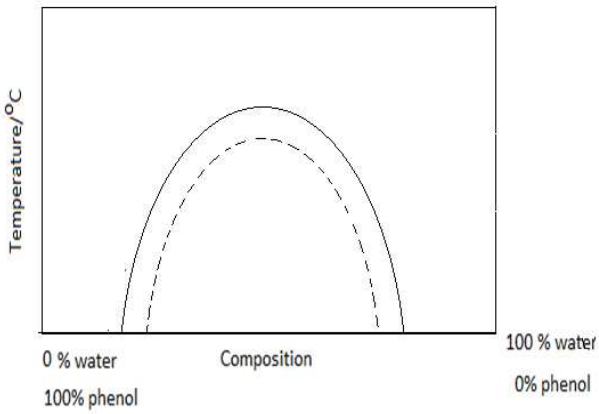


Figure 3. Effect of NaCl/succinic acid on CST of phenol-water system

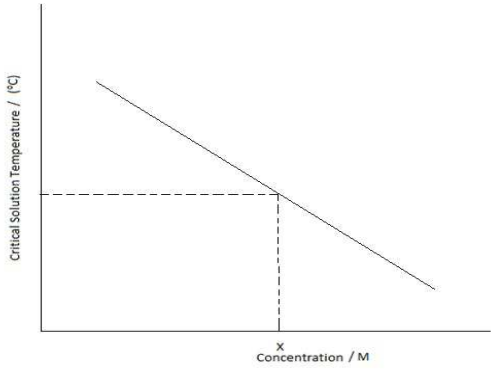


Figure 4. Plot of CST of a Phenol-Water system against concentration of succinic acid

10.4.4 Observations

Table 2. Miscibility Temperature of Phenol-Water system for each concentration of succinic acid solution

Concentration(M) of succinic acid solution	Wt % Phenol	Miscibility temperature (^oC)
0.02		
0.04		
0.06		
0.08		
0.10		

Table 3. Critical Solution Temperature (^oC) of phenol-water system for each concentration of succinic acid solution

Concentration (M)	0.02	0.04	0.06	0.08	0.10	unknown
Critical Solution Temperature						

(^{o}C)						

10.4.5 Result

The critical solution temperature of phenol-water system containing succinic acid is …….

The concentration of succinic acid in phenol-water system containing unknown amount of succinic acid is ……..

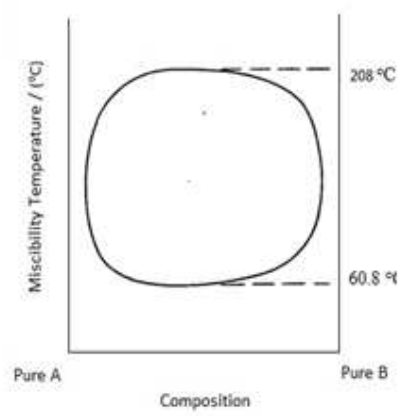
10.5 SUMMARY

In this unit you have studied that the phase separation in partially miscible liquid pairs depends on temperature and composition of the liquid mixture. Critical solution temperature is the highest or lowest point on the mutual solubility curve of liquid mixtures. The upper critical solution temperature (upper consolute temperature) is the highest temperature at which phase separation occurs. Above this temperature, the two components are fully miscible. Some systems show a lower critical solution temperature (lower consolute temperature), below which they mix in all proportions and above which they form two phases. An example is water and triethylamine. A plot of miscibility temperature versus composition gives miscibility curve of phenol-water system. The area under the curve has two phases coexisting while only one phase exists in the area that is not enclosed by the curve in the phase diagram. Presence of impurities affects the critical solution temperature eg. presence of succinic acid increases the CST of phenol-water system.

10.6 TERMINAL QUESTIONS

1. Which phase is ignored in a condensed system of water-phenol?
2. Define critical solution temperature.
3. Define degree of freedom.
4. Can partially miscible liquid pairs have more than one critical temperature? Give an example.
5. What is another name for Critical Solution Temperature in phenol and water system?

6. If we prepared a system containing 24% by weight of phenol and 76% by weight of water, at equilibrium which two layers will coexist?
7. What factor affects the solubility of two partially miscible liquids in a condensed system?
8. How does impurity affect the CST of a pair of two partially miscible liquids?
9. What is the maximum number of phases that can co-exist in a single-component condensed system, if degree of freedom is zero?
10. How many phases exist in the region enclosed within the curve in the given diagram?



10.7 ANSWERS

1. The vapor phase is ignored and only solid and/or liquid phases are considered.
2. Critical solution temperature is the highest temperature after which a pair of partially miscible liquids becomes completely miscible.
3. Degree of freedom is defined as the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium.
4. Yes. An example is nicotine-water system. It has a lower critical solution temperature of 61^{o}C and an upper critical solution temperature of 210 ^{o}C.
5. The upper consulate temperature.
6. The upper layer would have a saturated solution of phenol in water while the lower layer would have a saturated solution of water in phenol.
7. Temperature

8. If foreign substance is soluble in only one of the two components or the solubility of foreign substance is very different from the two components, the mutual solubility of the mixture will decrease and causes the upper critical solution temperature to raised and lower critical solution temperature is lowered. For example, the addition of foreign substances like salts can reduce the miscibility of water and phenol. This will cause the water molecules to hydrate the salt ions, reducing the tendency of water molecules to solvate the phenol. On the other hand, if the foreign substance has same solubility in both components, the mutual solubility of mixture will increase and the upper critical solution temperature will be lowered and the lower critical solution temperature will be raised. For instance, when succinic acid is added to phenol-water mixture.
9. The phase rule may be expressed as F=C-P+1.

   0= 1- P+1

   P = 2
10. Two.

UNIT 11: PARTITION COEFFICIENT

CONTENTS:

11.1 Objectives

11.2 Introduction

11.3 Determination of partition coefficient of iodine in water/ tetrachloromethane

11.3.1 Chemicals and apparatus required

11.3.2 Principle

11.3.3 Procedure

11.3.4 Observation

11.3.5 Calculations

11.3.6 Result

11.4 Determination of association factor of benzoic acid in benzene by distribution method

11.4.1 Chemicals required and apparatus required:

11.4.2 Principle

11.4.3 Procedure

11.4.4 Observations

11.4.5 Calculations

11.4.6 Result

11.5 Summary

11.6 Terminal questions

11.7 Answers

11.1 OBJECTIVES

After studying this unit you should be able to

1. Understand the concept of partition equilibrium of a solute between two phases.
2. Define Nernst distribution.

3. Calculation of partition coefficient of a solute distributed between two phases.
4. Determine the distribution coefficient of iodine between water and CCl_4 at room temperature.
5. Determine the distribution coefficient of benzoic acid between water and toluene at room temperature.

11.2 INTRODUCTION

Partition equilibrium is the phenomenon of a solute distributing itself between two distinct phases in contact with one another, Fig.1. The two phases could be gas and liquid or two immiscible liquids. According to Nernst distribution law, when a liquid or solid substance is added to a mixture of two immiscible liquids, the ratio of the concentration of solute distributed between two immiscible solvents at a given temperature is a constant and does not depend on the amount of the solute used i.e.

$K_D = C_1$(Phase 1)/C_2 (Phase 2)

Where C_1 and C_2 are concentration of similar molecular species in the two immiscible liquids 1 and 2 at a constant temperature. K_D is called the partition coefficient or distribution coefficient.

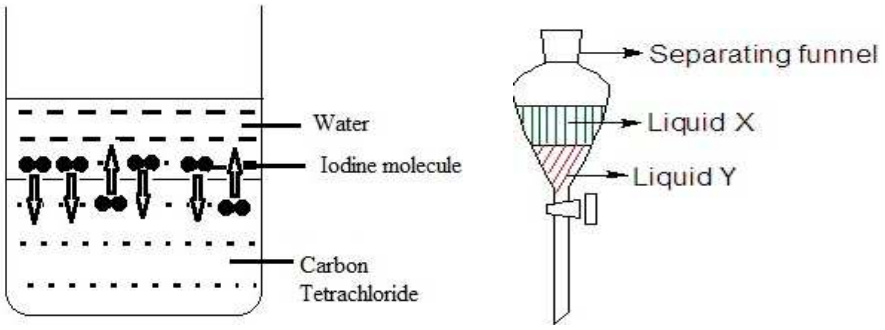


Figure.1. Distribution of iodine between H_2O (X) and CCl_4 (Y)

If more of the solute is added to the system, the solute will distribute itself between the immiscible liquids so that the ratio of the solute concentration remains the same at constant temperature independent of the total quantity of solute in the same molecular state. The important condition for the above law to hold is that the solute is in the same molecular state in both the liquid phases.

Validity of the law:

1. Temperature and pressure should remain constant throught the experiment.

2. Equilibrium stae should have been attained.

3. Neither solution should have reached the saturation state

4. The two liquids should be immiscible.

5. The molecular stae of the solute should be the same in both the layers

11.3 DETERMINATION OF PARTITION COEFFICIENT OF IODINE IN WATER/ TETRACHLOROMETHANE

11.3.1 Chemicals and apparatus required

Potassium dichromate, sodium thiosulphate (0.1N and 0.01N), potassium iodide, starch indicator, iodine, CCl_4 and distilled water. Well stoppered reagent bottles (150 cm^3), burette, pipettes, conical flasks and porcelain troughs.

11.3.2 Principle

This experiment is an example of a partition system involving distribution of I_2 between an aqueous phase and a water immiscible organic phase namely carbon tetrachloride.

$I_{2\,(aq)} \rightleftharpoons I_{2\,(CCl4)}$

$K = [I_{2\,(aq)}]/ [I_{2\,(CCl4)}] = 0.0116$

Solvent CCl_4 remains in the lower layer as it is denser than water. The non-polar I_2 is more soluble in the nonpolar organic solvent than in the highly polar solvent, water. The amount of I_2 in both the layers is analysed by titrating aliquots pipetted out from each layer with standardized sodium thiosulphate using starch as indicator.

11.3.3 Procedure

1. Label three bottles I, II and III. Make the following mixtures in each bottle as given in Table 1 and shake the bottles in a mechanical shaker for about an hour. Place the bottles in a water trough for 20 minutes to attain equilibrium.

Table 1. List of Amount of iodine in CCl4 and water to make various mixtures

Bottle No.	Contents
I	20 cm^3 of saturated solution of iodine in CCl_4 + 200 cm^3 of distilled water
II	25 cm^3 of saturated solution of iodine in CCl_4 + 250 cm^3 of distilled water
III	30 cm^3 of saturated solution of iodine in CCl_4 + 300 cm^3 of distilled water

2. Standardize thiosulphate solution with the help of standard potassium dichromate solution and repeat the titrations for concordant readings as shown in Table 2.
3. Pipette out 5 $cm^3$of the CCl_4 layer from bottle I into a conical flask and add 20 cm^3 of distilled water. Add 2 cm^3 of 10% KI solution. Titrate this solution against a previously standardized 0.1N thiosulphate solution using starch as indicator. The end point is the disappearance of blue colour. Repeat the experiment to get concordant values. Record your readings as shown in Table 3.
4. Now pipette out 25 cm^3 of the aqueous layer from bottle I. Titrate this solution against a previously standardized 0.1N thiosulphate solution using starch as indicator. The end point is the disappearance of blue colour. Repeat the experiment to get concordant values. Record your readings as shown in Table 4.
5. Tabulate your readings as shown in Table 5 to determine K_D.
6. Repeat the above procedure for bottle II and III.

11.3.4 Observation:

Table 2. Titre values for standardization of sodium thiosulphate

Volume of $K_2Cr_2O_7$ cm^3	Burette reading /cm^3		Volume of sodium thiosulphate/ cm^3
	Initial	Final	

20			
20			

Table 3. Titre values for titration of Iodine present in organic layer with thiosulphate in bottle I

Bottle	Volume of CCl_4 layer/ cm^3	Burette Reading / cm^3		Volume of Thiosulphate cm^3
		Initial	Final	
I				
II				
III				

Table 4 Titre values for titration of Iodine present in aquueous layer with thiosulphate in bottle I

Bottle	Volume of aqueous layer cm^3	Burette Reading/ cm^3		Volume of Thiosulphate cm^3
		Initial	Final	
I				
II				
III				

Table 5 Determination of dissociation constant K_D

Bottle	Layer	Volume of Thio cm^3	Strength of I_2	$K_D = C_1/C_2$
I	CCl_4			
	Aqueous			
II	CCl_4			
	Aqueous			

III	CCl_4			
	Aqueous			

11.3.5 Calculations

A. Standardisation of sodium thiosulphate solution

$N_1 \times V_1 = N_2 \times V_2$

N_1= concentration of $K_2Cr_2O_7$

V_1= volume of $K_2Cr_2O_7$

N_2= concentration of sodium thiosulphate

V_2= volume of sodium thiosulphate

$N_2 = \frac{N_1 \times V_1}{V_2}$

B. Aqueous Phase

$I_2 + 2\ S_2O_3^{2-} \rightleftharpoons 2I^- + S_4O_6^{2-}$

$N_1 \times V_1 = N_2 \times V_2$

N_1= concentration of I_2 in the aqueous layer

V_1= volume of I_2 in the aqueous layer

N_2= concentration of thiosulphate solution

V_2= volume of thiosulphate solution used in titration of aqueous layer

The volume of sodium thiosulphate consumed in the titration is equivalent to the amount of iodine present.

Equivalent weight of iodine =

Concentration of iodine in aqueous layer, $[I_2]_{H2O}$ = …. N

C. Organic Phase

$N_1 \times V_1 = N_2 \times V_2$

N_1= concentration of I_2 in the organic layer

V_1= volume of I_2 in the organic layer

N_2= concentration of thiosulphate solution

V_2= volume of thiosulphate solution used in titration of organic layer

Concentration of iodine in organic layer, $[I_2]_{CCl4}$ = …. N

The volume of sodium thiosulphate consumed in the titration is equivalent to the amount of iodine present.

$K_D = N [I_2]_{H2O}/N[I_2]_{CCl4}$

11.3.6 Result:

The distribution coefficient of iodine between CCl_4 and water is found to be…….

11.4 DETERMINATION OF ASSOCIATION FACTOR OF BENZOIC ACID IN BENZENE BY DISTRIBUTION METHOD

11.4.1 Chemicals required and apparatus required

Benzoic acid, benzene, sodium hydroxide solutions (0.1 N and 0.02 N), phenolphthalein indicator and distilled water. Well stoppered reagent bottles (150 cm^3), burette, pipettes, conical flasks, and porcelain troughs.

11.4.2 Principle

According to Nernst distribution law, the ratio of the concentration of solute distributed between two immiscible solvents at a given temperature is a constant irrespective of the total amount of the substance. The distribution law breaks down in cases when the solute does not have the same molecular species in the two solvents. An example of such a system is the distribution of benzoic acid in water and toluene.

The hydrogen bonds formed between benzoic acid molecules are stronger than the interaction between benzoic acid and toluene molecules. Therefore the toluene cannot solvate each molecule of benzoic acid efficiently and therefore benzoic acid tends to form large amounts of dimers when dissolved in toluene, Fig. 2. The amount of unassociated

benzoic acid molecules is relatively less in toluene. In aqueous solution, the hydrogen bonds formed between benzoic acid with water molecules are stronger than bonds formed between benzoic acid molecules. Therefore in aqueous solution, benzoic acid doesnot associate. Also, dissociation of benzoic acid in water can be ignored since benzoic acid is a weak acid ($K_a = 6.3 \times 10^{-5}$ mol dm^{-3}).

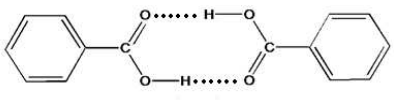


Figure.2. Dimer of benzoic acid

Let C_1 be the concentration of unassociated benzoic acid in water. And C_2 be the concentration of benzoic acid in solvent in which it associates to form mainly dimers. In this solvent there will be an equilibrium between the associated and simple miolecules. Let C_2 (1-α) and $C_2\alpha$ be the concentration of simple and associated molecules of benzoic acid in the second solvent respectively which are in equilibrium with each other.

In aqueous solution, there is no association. Also, dissociation of acid can be ignored since benzoic acid is a weak acid ($K_a = 6.3 \times 10^{-5}$ mol dm^{-3}).

If α is the association coefficient of benzoic acid in toluene, then

$2C_6H_5COOH$ (water) ⇌ $(C_6H_5COOH)_2$ (toluene)

C_2 (1-α) ½ $C_2\alpha$

$$K = \frac{\frac{1}{2}C_2\alpha}{[C_2(1-\alpha)]^2}$$

$[C_6H_5COOH]_{total}$ = $[C_6H_5COOH]_{free}$ + $[C_6H_5COOH]_{associated}$

C_2 C_2 (1-α) C_2 α

C_6H_5COOH (toluene) ⇌ C_6H_5COOH (aqueous)

$C_2(1-\alpha)$ C_1

$$K_D = \frac{C_1}{C_2(1-\alpha)}$$

$$K = \frac{\frac{1}{2}C_2\alpha}{[C_2(1-\alpha)]^2}$$

α is a constant at fixed temperature

$$\Rightarrow C_2(1-\alpha) = \sqrt{\frac{C_2\alpha}{2K}} = K^{'}\sqrt{C_2}$$

$$\Rightarrow K_D = \frac{C_1}{C_2(1-\alpha)} = \frac{C_1}{K^{'}\sqrt{C_2}}$$

$$\Rightarrow \frac{C_1}{\sqrt{C_2}} = K_D K^{'} = K^{''}$$

$C_1/\sqrt{C_2}$ = Constant

11.4.3 Procedure

1. Weigh 1 g of benzoic acid and transfer it to a well stopper reagent bottle.
2. Add 100 cm^3 of water and 50 cm^3 of benzene into the same bottle.
3. Shake the contents for 30 minutes and leave the bottle in a water trough for 20 minutes for attainment of equilibrium.
4. Now pipette out 5cm^3 of benzene layer into a conical flask containing about 10 cm^3 of water. Titrate this against 0.1N sodium hydroxide solution using phenolphthalein as the indicator.
5. *Pipette out 20 $cm^3$of the water layer and titrate against standard 0.02 N sodium* hydroxide solution.
6. Tabulate your readings as shown in Table 6.
7. Repeat the above procedure by taking 2 g of benzoic acid.
8. Repeat the procedure for other bottles also and calculate $C_1/\sqrt{C_2}$ as given in Table 7

11.4.4 Observations

Table 6. Bottle I Titre readings for benzoic acid versus sodium hydroxide in organic and aqueous layer

Volume of benzene	Volume of NaOH	Volume of aqueous	Volume of NaOH

layer /cm^3	cm^3	layer/ cm^3	cm^3
		20	
		20	

Table 7. Tabulation to calculate $C_1/\sqrt{C_2}$

C_1 (M)	C_2 (M)	C_1/C_2	$C_1/\sqrt{C_2}$

11.4.5 Calculations

Concentration of benzoic acid in aqueous layer C_1 = ……..M

Concentration of benzoic acid in toluene layer C_2 = ……..Moles/2

K = $C_1/\sqrt{C_2}$ =……

11.4.6 Result

The association factor of benzoic acid in benzene /water system is ..... .

11.5 SUMMARY

A number of varying mixtures of solute in two immiscible solvents were made in reagent bottles, shaken and left to attain equilibrium. The concentration of the solute in each layer was determined by titration with a suitable titrant using appropriate indicator. According to Nernst distribution law, the partition coefficient of the solute is the ratio of concentration of solute in solvent 1 to solvent 2 at constant temperature. Two cases were studied. In the first case i.e. distribution of iodine between water and CCl_4, the molecular species in both solvents is similar. In the second case (distribution of benzoic acid in water and toluene) the solute associates to form dimer in the organic solvent. Corrections were applied in order to determine partition coefficient of free benzoic acid in water and toluene. Then K = $C_1/\sqrt{C_2}$, where K is a constant combining the partition coefficient and the association constant and C_1 is the concentration of unassociated benzoic acid in water.

11.6 TERMINAL QUESTIONS

1. State the principle of partition equilibrium.
2. Name the law which governs the distribution coefficient of solute between two immiscible solvents.
3. A weakly acidic drug would be expected to have a higher distribution coefficient from an acidic aqueous solution. Explain.
4. How can partition coefficients be useful in considering drug absorption across the gastrointestinal tract ?
5. State the relationship between distribution coefficient and distribution law. What is the condition for distribution coefficient K_D to be equal to the distribution ratio?
6. Define hydrogen bonding.
7. What would be the effect of a salt on the distribution of acetic acid between water and ethyl acetate?
8. What is the difference between distribution of iodine between water and CCl_4 and distribution of benzoic acid between water and toluene?
9. A monocarboxylic acid, A, dimerises in benzene. How would you represent the partitioning of acid A between water and benzene?
10. What is the colour of a solution of iodine dissolved in CCl_4?

11.7 ANSWERS

1. Partition equilibrium is the phenomenon of a solute distributing itself between two distinct phases in contact with one another. The two phases could be two immiscible liquids.
2. Nernst distribution law.
3. A partition coefficient considers only a single specific form of a drug whereas the distribution coefficient considers the total analytical concentration. Under acidic conditions a weakly acidic drug would have a greater proportion in the unionised form whereas the opposite would be true for a basic drug. As the unionised form will typically prefer the hydrophobic phase the distribution coefficient for the acidic drug will be higher from acidic conditions
4. Partition coefficients are useful for indicating whether passive diffusion of a drug across a membrane is possible. Partition coefficients can be used to understand

whether drug can passively diffuse across a membrane such as the gastrointestinal tract. This is because the drug molecule must first partition from the gastrointestinal fluid into the lipid environment of the membrane and then partition out the other side of the membrane in to an aqueous environment.

5. $K_D = [X]_{org} / [X]_{aq}$

   Now consider the extraction of benzoic acid from an aqueous solution by addition of ether. Benzoic acid is slightly ionized in aqueous solution. So some benzoic acid exists in ionic form in water phase. So quantitative separation is not possible. A term called distribution ratio, D, takes solute in all its forms in the two phases.

   $C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$

   The ionization constant, K_a, is given as

   $K_a = \{ [C_6H_5COO^-]_{aq} + [H^+]_{aq} \} / [C_6H_5COOH]_{aq}$

   $D = [C_6H_5COOH]_{org} / [C_6H_5COOH + C_6H_5COO^-]_{aq}$

   The relation between D and K_D is then given by

   $D = K_D / \{1 + (K_a / [H^+]_{aq})\}$

   Therefore when $[H^+]_{aq} >> K_a$, D is nearly equal to K_D.

6. It is an electrostatic force of attraction between a hydrogen atom covalently bonded to a highly electronegative atom like oxygen, nitrogen or fluorine and another highly electronegative atom nearby.
7. It will decrease the solubility of ethyl acetate in the aqueous phase.
8. In the first case the solute, I_2, is present in the same form in both the solvents while in the second case the solute, benzoic acid, dimerises in the organic solvent.
9. $A_{benzene} \overset{k_1}{\rightleftharpoons} \frac{1}{2} A_2$

   $K_D \downarrow\uparrow$

   A_{water}

   Where, k_1 is dimerisation constant and K_D is the partition coefficient.

10. Violet.

UNIT 12: PHASE DIAGRAM OF SIMPLE EUTECTIC SYSTEM

CONTENTS:

12.1 Objectives
12.2 Introduction
12.3 To construct phase diagram for a two component eutectic system of resorcinol and benzoic acid
12.3.1 Chemicals and apparatus required
12.3.2 Principle
12.3.3 Procedure
12.3.4 Observations
12.3.5 Results
12.4 To conduct phase diagram for a two component eutectic system of naphthalene and benzoic acid
12.4.1 Chemicals and apparatus required
12.4.2 Procedure
12.4.3 Observations
12.4.4 Result
12.5. Summary
12.6 Terminal questions
12.7 Answers

12.1 OBJECTIVES

After completing this unit you should be able to understand

1. A two component binary solid-liquid simple eutectic phase.
2. Meaning of eutectic point and eutectic composition.
3. Reduced phase law.
4. Effect of amount of one component say B on the melting point of another component say A in case of a

system comprising of A and B, where A and B are immiscible when solids and miscible in the liquid or melt phase and vice-versa.

5. The concept of latent heat of fusion.

12.2 INTRODUCTION

A solid/liquid system with the gas phase absent is called a condensed system. The experiments are carried out at constant pressure (usually atmospheric pressure). The reduced phase rule applicable to such system is F=C-P+1. T_e is the minimum temperature that can be reached by the system with solid A, B and solution in equilibrium. This temperature is called *eutectic temperature*. At this point, F = 3 - P = 3 - 3 = 0. The general phase diagram of such a two component condensed system is shown in the Fig.1. The two components A and B are completely miscible in the liquid state and their solution on cooling yields only pure A or pure B as solid phases.

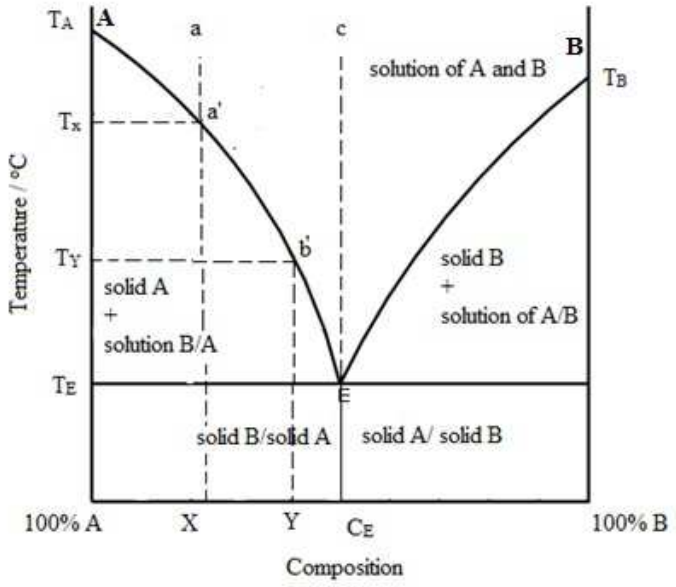


Fig. 1. Diagram of a simple eutectic system.

The area above the curve AE and BE represents the two components A and B as liquid solutions of varying compositions.

F = C-P+1 = 2-1+1 = 2

The degree of freedom is two which means that to define the system at any point above the curve AE and BE, both temperature and composition have to be specified

On cooling, the A/B solution at a point *a* in the area above ABC, the cooling line meets the curve AE say at a'. At this point, A separates as solid and the equilibrium shifts down along the curve AE. The change of composition and temperature continues till the eutectic point E is reached, when solid B separates. Thus in the area below AE and above T_E, there exists two phases viz solid A and solution A/B and the system is bivariant.

Curve AE: The freezing point curve of A.

The point T_A represents the freezing point of A. Along the curve AE the freezing point of A falls by the addition of B to A.

Solid A ⇔ Solution

Curve BE: The freezing point curve of B.

The point T_B shows the freezing point of B. Along the curve BE the freezing point falls by the addition of A to B. Along this curve solid B is in equilibrium with the liquid solution of A in B.

Solid B ⇔ Solution

F = C- P+1 = 2-2+1 = 1

The degree of freedom is one and the system is monovariant. Point E represents the eutectic point. The two curves AE and BE meet at E. At this point both solids A and B are in equilibrium in the solution phase comprising of A and B.

F = C-P+1 = 2-3+1=0

Thus the system at E is non-variant. The corresponding composition and temperature at C are known as eutectic composition and eutectic temperature.

Similarly cooling of solution B/A on the other side of eutectic, on reaching area BE yields solid B/solution system. Thus the area below BE upto T_E line would represent solid B and solution.

If the solution just above the eutectic point c is cooled a solid mixture (eutectic mixture) of eutectic component C_E will be obtained straightaway.

The entire area below T_E line represents solid A/solid B.

12.3 TO CONSTRUCT PHASE DIAGRAM FOR A TWO COMPONENT EUTECTIC SYSTEM OF RESORCINOL AND BENZOIC ACID

12.3.1 Chemicals and apparatus required

Benzoic acid (m.p: 121.4^{0}C) and resorcinol (m.p.: 110^{0}C), 11 test tubes, one boiling tube with a cork to carry a thermometer, a bath of liquid paraffin in a beaker, a wire stirrer and an iron stand with lamp, a tripod stand with wire gauge, a bunsen burner.

12.3.2 Principle

Cooling curves and phase diagram:

Cooling curve of a eutectic system of component A and B are obtained by cooling a molten mixture of the components and plotting a curve between temperature and time as shown in Fig.2. The curve is characterized by two features called a break and a halt. The cooling curve is continuous till the solid phase B starts separating at point b. The rate of cooling decreases and a break is observed at this point in the curve. This break represents the freezing point. The cooling continues and solid B keeps separating. At c the other component A also starts solidifying. The cooling temperature shows a halt along cd line. The temperature is constant along this line as the composition of the system is constant and it represents the eutectic temperature of the mixture taken. After the point d there is progressive cooling of the solidified mass.

To obtain a phase diagram, cooling curves of mixtures with different compositions of A and B are obtained as shown in Fig.3. The eutectic temperature remains the same for each mixture. A mixture with eutectic composition shows no break point in its cooling curve and only a halt is observed at the eutectic temperature. Plot a temperature-composition graph by plotting the freezing point/ break temperature of different mixtures on the Y axis and their respective composition on the X-axis.

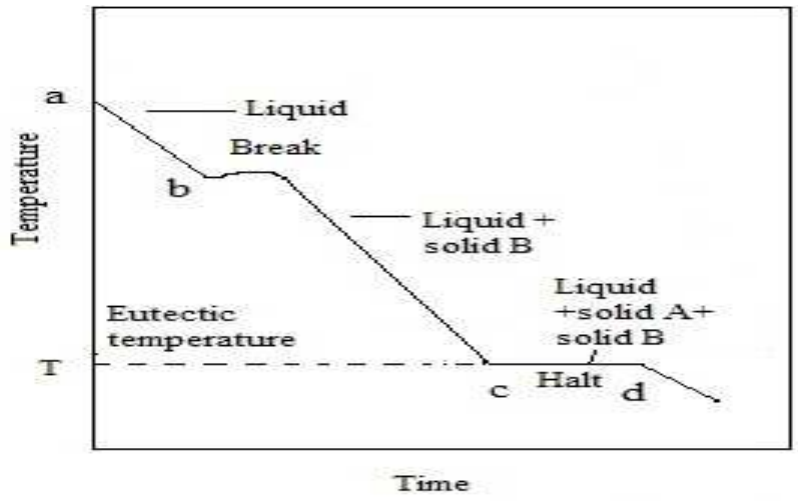


Figure 2: Cooling curve of a binary eutectic system

Figure. 3. Cooling curves for a mixture rich in compound A (1), for a mixture rich in compound B (2), and for a mixture with the eutectic composition (2).

12.3.3 Procedure

Set up the apparatus as in Figure.4. Prepare the following mixtures of A & B components by weighing the required amounts as given in Table 1.

Table 1. Amount of A & B components to be taken for preparing mixtures of A & B

Test Tube	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
A /g	10	9	8	7	6	5	4	3	2	1	0
B/g	0	1	2	3	4	5	6	7	8	9	10

1. Take pure component in a test tube containing a stirrer and a thermometer. Place this test tube in a water bath. Melt the pure component in the test tube and allow it to cool. Stir the mixture as it cools. Note the freezing temperature of the pure component with the thermometer.
2. Place the test tube with the first mixture in the water bath and melt the mixture. When a homogeneous liquid phase is obtained remove the tube from the bath. Wipe it clear and allow it to cool while taking the temperature after every 15-30 seconds. The temperature falls till solid A (benzoic acid) or B (resorcinol) or solid solution begins to form. Temperature should be noted until a constant temperature is reached.
3. Repeat the experiment with the with same procedure remaining mixtures. The eutectic temperature is determined by finding the eutectic freezing region for rest of the nine compositions.
4. Note down the first break temperature in every curve against wt % or mole fraction. Also note the halt temperature in every curve and enter against the wt% or mole fraction as shown in Table 2.
5. The phase diagram is obtained by making plots of break and halt temperatures against composition. Therefore plot a graph of melting point of pure compound and the nine break temperatures versus wt% or mole fraction of benzoic acid. The halt temperatures would be the same for all nine cases.

6. The curve so obtained is the phase diagram of benzoic acid- resorcinol system. Note down the eutectic temperature and composition from this curve.

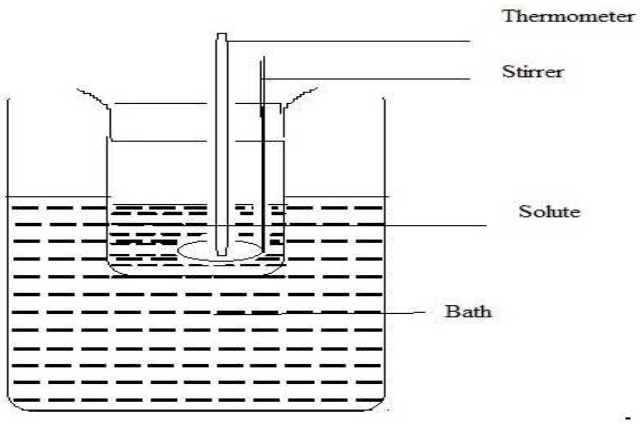


Figure. 4. Schematic set up of apparatus for determination of eutectic temperature and eutectic composition of resorcinol and benzoic acid system

12.3.4 Observations

Table 2. Amount of A & B components to be taken for preparing mixtures of A & B

S.N	Weight of B (g)	Wt % of A	Break Temperature (°C)	Halt Temperature (°C)

12.3.5 Results

The eutectic temperature of the system =……..^{o}C

The eutectic composition of the system =……wt. % A and ……wt. % B

12.4 TO CONDUCT PHASE DIAGRAM FOR A TWO COMPONENT EUTECTIC SYSTEM OF NAPHTHALENE AND BENZOIC ACID

12.4.1 Chemicals and apparatus required

Naphthalene (m.p: 80^{o}C) and benzoic acid (m.p: 120 ^{o}C),10 test tubes, one boiling tube with a cork to carry a test thermometer, suitable thermometer (360°), a bath of liquid paraffin in a beaker, a wire stirrer and an iron stand with lamp, a tripod stand with wire gauge, a bunsen burner.

12.4.2 Procedure

Set up the apparatus as in Figure. 1. Prepare the following mixtures of A & B components by weighing the required amounts as shown in Table 3.

Table 3. Amount of A & B components to be taken for preparing mixtures of A & B

A (Naphthalene) (g)	10	9	8	7	6	5	4	3	2	1	0
B (Benzoic acid) (g)	0	1	2	3	4	5	6	7	8	9	10

1. Take pure component in a test tube containing a stirrer and a thermometer. Place the test tube in a water bath. Melt the pure component in the test tube. Allow it to cool. Stir the mixture as it cools. Note the freezing temperature of the pure component with the thermometer.
2. Place the test tube with the first mixture in the water bath and melt the mixture. When a homogeneous liquid phase is obtained remove the tube from the bath. Wipe it clear and allow it to cool while taking the temperature every 15 seconds. The temperature falls till solid A or B or solid solution begins to form. Temperature should be noted until a constant temperature is reached.

3. Repeat the experiment with the remaining mixtures. The eutectic temperature is determined by finding the eutectic freezing region for rest of the nine compositions.
4. Note down the first break temperature in every curve against wt % or mole fraction. Also note the halt temperature in every curve and enter against the wt% or mole fraction as shown in Table 4.
5. The phase diagram is obtained by making plots of break and halt temperatures against composition. Therefore plot a graph of melting point of pure compound and the nine break temperatures versus wt% or mole fraction of benzoic acid. The halt temperatures would be the same for all nine cases.
6. The curve so obtained is the phase diagram of benzoic acid- naphthalene system. Note down the eutectic temperature and composition from this curve.

12.4.3 Observations

Table 4. Amount of A & B components to be taken for preparing mixtures of A & B

S.N.	Weight of A (g)	Weight of B (g)	Wt. % of A	Break Temperature (°C)	Halt Temperature (°C)

12.4.4 Result

The eutectic temperature of the system =……..^{o}C

The eutectic composition of the system =……Wt. % A and ……Wt. % B

12.5 SUMMARY

Binary eutectic mixtures with components A and B were chosen such that both components are immiscible in solid phase and miscible in liquid phase. They do not react

with each other. The cooling curves of A and B were obtained by adding in steps B in melt of pure A (amount of B less than A) and plotting melting point of the mixture (freezing point).The process is repeated by stirring with pure B and adding A in steps and plotting the melting point of each mixture against the composition of A in the mixture. This gives the complete phase diagram of a simple eutectic system. From the phase diagram the eutectic temperature and eutectic composition was determined.

12.6 TERMINAL QUESTIONS

1. Define a phase.
2. Define a component? How many components and phases are present in an aqueous solution of salt?
3. What is a phase diagram?
4. Define a binary eutectic mixture?
5. What is a liquidus line and solidus line?
6. What is the eutectic temperature and eutectic composition of a two component eutectic system of naphthalene and benzoic acid?
7. What is a eutectic point?
8. What does a horizontal arrest in a cooling curve represent?
9. What is the difference between a eutectic and a eutectoid mixture?
10. What is Pattinson's process?

12.7 *ANSWERS*

1. A phase is a physically distinct region that has same composition and chemical property within its boundary.
2. The elements or compounds which are present in the mixture are called its components. An aqueous solution of a salt has two components; water and salt. The number of phases is one.
3. A phase diagram is a plot between physical state of the substance with its temperature and/or pressure.
4. Binary eutectic mixture is a solid solution of two components which has the lowest freezing point of all the possible mixtures of the components.

5. The liquidious line separates the all melt phase from the melt and solid phase. The solidus line separates the melt and crystal region from the all solid region.
6. The eutectic temperature of a two component eutectic system of naphthalene and benzoic acid is 67-69 ^{o}C and eutectic composition is 30 mol % benzoic acid B.
7. The eutectic is the point at which all three phases can exist simultaneously i.e. solid A, solid B and melt.
8. Invariant reaction.
9. Eutectic mixture gives rise to a liquid in equilibrium with two solid phases whereas a eutectoid mixture results in a solid phase in equilibrium with two other solid phases.
10. Pattinson's process is a method of desilverising lead.

UNIT 13: pH TITRATION

CONTENT:

13.1Objectives

13.2 Introduction

13.2.1 Titration of strong acid (HCl) with strong base (NaOH)

13.2.2 Titration of weak acid (CH_3COOH) with strong base (NaOH)

13.3 Determination of the strength of a given unknown solution of hydrochloric acid by pH titration of the hydrochloric acid with sodium hydroxide

13.3.1 Chemicals and apparatus required

13.3.2 Principle

13.3.3 Procedure

13.3.4 Observations

13.3.5 Calculation

13.3.6 Results

13.4 Summary

13.5 Terminal questions

13.6 Answers

13.7 References

13.1 OBJECTIVES

After completing this unit you should be able to

1. Calculate pH for various combinations of strong and weak acid-base pairs.

2. Locate the end point from the graph of pH of solution versus volume of base added.

3. Determine the strength of an acid by potentiometric titrations.

13.2 INTRODUCTION

Acid base titrations are basically neutralization titrations. Acids and bases ionize in water.

$HA \longrightarrow H^+ + A^-$

$BOH \longrightarrow B^+ + OH^-$

$H^+ + A^- + OH^- + B^+ \longrightarrow B^+ + A^- + H_2O$

The extent of hydrolysis of the salt BA formed from neutralization between the acid and base decides the pH of the solution at equivalence point.

The pH of a solution is given as

$pH = - \log [H^+]$

pH titration is the process of adding either base from the burette to a known volume of acid (alkalimetry) in a beaker and measuring the pH of the solution at each addition or vice versa (acidimetry). In a titration of an acid with a base, the pH of the solution before titration is low. On addition of aliquots of base to the acid, the pH starts increasing. Near the end point a sharp increase in pH occurs. When a plot of pH versus volume of base is constructed you obtain a pH curve. After the end point, addition of the base does not change pH and results in a plateau in the curve. The pH curves for strong acid-strong base, strong acid-weak base, weak acid-strong base and weak acid-weak base are depicted in Fig 1. However, it is difficult to locate the end point in weak acid-weak base titrations by potentiometric method.

13.2.1 Titration of strong acid (HCl) with strong base (NaOH)

In titration of a strong acid (HCl) with a strong base (NaOH) the salt formed by neutralization reaction does not hydrolyse in water. Hence the solution at the equivalent point is neutral.

Initially the pH keeps increasing slowly as the base is added. After the end point the concentration of the base (NaOH) is in excess and a sharp increase in pH is noted.

$[H^+] = [HCl]$

The pH is given by

$pH = 14 – pOH$

In the case of a strong acid versus strong base, at equivalence point $[H^+] = [OH^-]$

The ionic product of water = $K_w = [H^+] [OH^-] = 10^{-14}$

$K_w = [H^+]^2$

$(K_w)^{1/2} = [H^+]$

$[H^+]$ = [HCl]

$pH = -\log [H^+] = -\log (K_w)^{1/2} = -\frac{1}{2} \log K_w = -\frac{1}{2} \log 10^{-14} = \frac{1}{2} \times 14 \times \log 10 = 7$

(log 10 = 1)

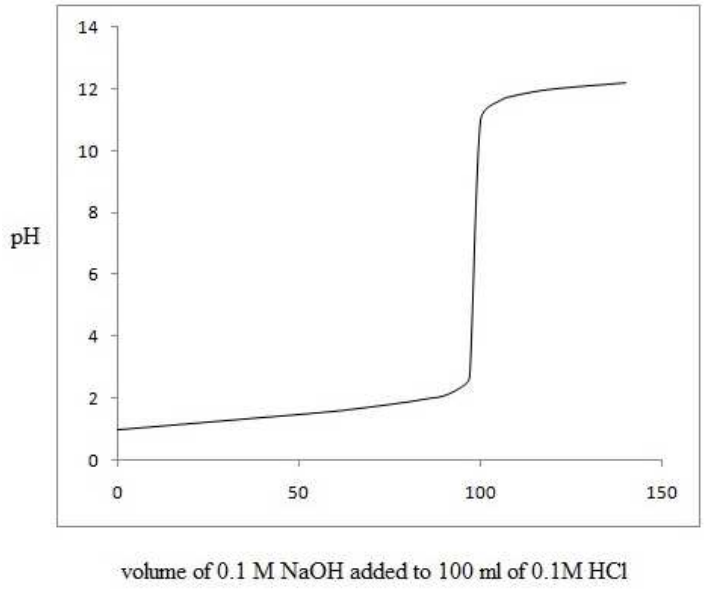


Figure 1. (a) pH titration curve of strong acid (HCl) vs strong base (NaOH)

13.2.2 Titration of weak acid (CH_3COOH) vs strong base (NaOH)

In case of weak acid

$[H^+] = \{K_a \text{ [acetic acid]}\}^{1/2}$

$CH_3COOH + OH^- \rightleftharpoons H_2O + CH_3COO^-$

Addition of NaOH converts a portion of acetic acid to its conjugate base. This solution of a weak acid and its conjugate base forms a buffer for which the pH of the solution is calculated by Hendersen equation .

At equivalence pH is more than 7

pH = pKa + log [Conjugate base] / [Weak acid]

After the equivalence point, NaOH is present in excess and pH rises to about 12..

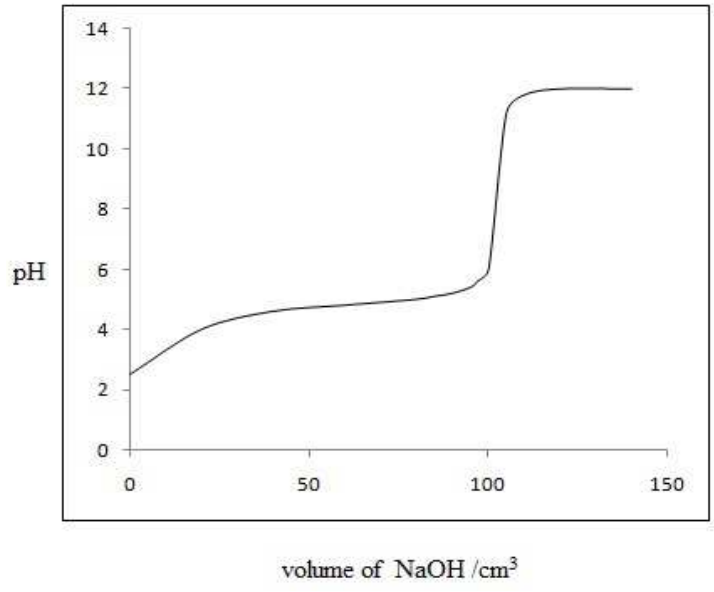


Figure. 1. (b) pH titration curve of weak acid (CH_3COOH) vs strong base (NaOH)

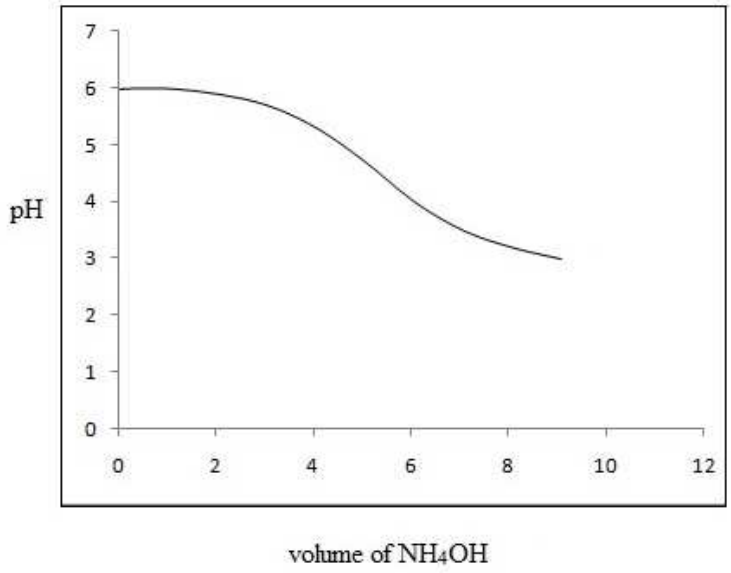


Figure 1. (c) pH titration curve of weak acid (CH_3COOH) vs weak base (NH_4OH)

13.3 DETERMINATION OF THE STRENGTH OF A GIVEN UNKNOWN SOLUTION OF HYDROCHLORIC ACID BY PH TITRATION OF THE HYDROCHLORIC ACID WITH SODIUM HYDROXIDE

13.3.1 Chemicals and apparatus required

HCl, NaOH and distilled water,**:** Beaker (250 cm^3), burette (50 cm^3), burette stand, pH meter and pH electrode.

13.3.2 Principle

In titration of a strong acid (HCl) with a strong base (NaOH) the salt formed by neutralization reaction does not hydrolyse in water. Hence the solution at the equivalence point is neutral.

Initially the pH keeps increasing as the base is added. After the end point the concentration of the base (NaOH) is in excess.

$[H^+] = [HCl]$

The pH is given by

pH = 14 – pOH

In the case of a strong acid versus strong base, at equivalence point $[H^+] = [OH^-]$

The ionic product of water = $K_w = [H^+] [OH^-] = 10^{-14}$

$K_w = [H^+]^2$

$(K_w)^{1/2} = [H^+]$

$[H^+] = [HCl]$

$$pH = -\log [H^+] = -\log (K_w)^{1/2} = -\frac{1}{2} \log K_w = -\frac{1}{2} \log 10^{-14} = \frac{1}{2} \times 14 \times \log 10 = 7$$

(log 10 = 1)

13.3.3 Procedure

1. Prepare 1M NaOH by weighing 4 g of NaOH and dissolving it in 100 cm^3 of distilled water.

2. Fill the burette with standardized 1M NaOH solution.
3. Standardize the pH meter (Follow the specific instructions for the pH meter that you have in your laboratory)
4. Now pour 50 cm^3 of given solution of HCl in a 250 cm^3 beaker. Dip the pH probe in the solution and measure and record the pH of the solution before any NaOH has been added.
5. Proceed to add aliquots of 1cm^3 standardized 1M NaOH. Take the burette reading and also record the pH reading after each addition.
6. When you notice that the pH starts to change rapidly, reduce the aliquots of the additions of NaOH to 0.5 cm^3 and then to single drops. Continue adding NaOH till the pH reaches 12.
7. Tabulate your data as given in Table 1 and construct a graph of pH versus volume of NaOH solution added from the burette (Fig.2). Locate the end point from inflexion point.

   Incorporate the volume of NaOH consumed for neutralizing the acid in the formula

   $V_1 N_1 = V_2 N_2$ to determine the normality of hydrochloric acid.

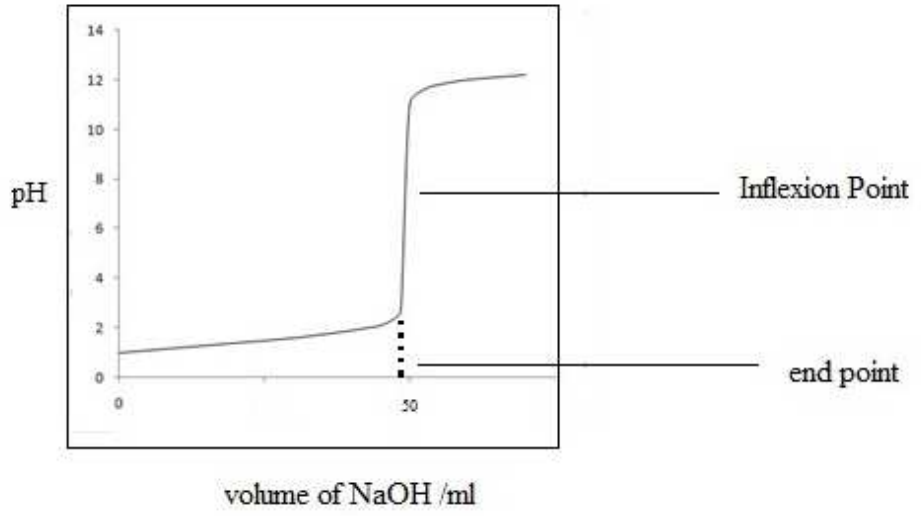


Figure 2. pH titration curve of strong acid (1M HCl) vs strong base (1M NaOH)

13.3.4 Observations

Table 1. Titre values for HCl versus NaOH titration

S. N.	Burette Reading/ cm^3		Volume of NaOH /cm^3
	Initial	Burette	

13.3.5 Calculation

$V_1 N_1 = V_2 N_2$

V_1 = volume of NaOH

N_1 = normality of NaOH

V_2 = volume of HCl

N_2 = normality of HCl

Strength of HCl = Normality of HCl (N_2) × Equivalent weight of HCl (36)

13.3.6 Results

The strength of given solution of hydrochloric acid is …… g/litre

13.4 SUMMARY

Quantitative analysis by potentiometric titration method for an acid base neutralization reaction involves recording the pH after each addition of a standard solution of a base to a known volume of an acid of unknown strength. The pH of the solution depends on the ionisability of the acid and base in water and the extent of hydrolysis of the salt formed from the neutralization of the acid by the base. A graph of pH versus volume of base added to the acid is constructed. The end point is located from the point of inflexion which is a point where the pH of the solution changes rapidly. A perpendicular drawn from point of inflexion to X axis gives the volume of base required to neutralize the volume of acid taken in the beaker. This value is incorporated in the equation

$V_1N_1=V_2N_2$ to determine the normality of the acid . The strength of the acid is calculated by the formula, Strength of acid =Normality of Acid x Equivalent weight of acid.

13.5 TERMINAL QUESTIONS

1. Define acidimetry and alkalimetry.
2. What is a standard solution?
3. Give two examples of a primary standard.
4. What is equivalence point in an acid base titration?
5. How do you express acidity of a base and basicity of an acid?
6. What factors affect the form of a pH curve?
7. When will be the pH =0, < 7 and > 7 at equivalent point in an acid base reaction?
8. How do you express the pH of acetic acid?
9. Calculate the weight of NaOH required neutralizing 25 cm^3 of 1N HCl.
10. In an experiment 50 cm^3 of 0.1N HCl is titrated against 0.1N NaOH. Calculate the pH of the solution after addition of 40 cm^3 of NaOH.

13.6 ANSWERS

1. The process of addition of a standard acid from a burette to a known volume of base in a conical flask is called acidimetry. The process of addition of a standard base from a burette to a known volume of acid in a conical flask is called acidimetry.
2. A standard solution is a reagent of known concentration.
3. Oxalic acid and sodium carbonate.
4. Equivalence point is a stage where the reaction between acid and base undergoes completion theoretically.
5. Acidity of a base = Molecular weight / Equivalent weight
   Basicity of an acid=Molecular weight / Equivalent weight
6. The following factors affects the shape of pH curve
   i. The extent of ionization of acid or base.
   ii. The molalities of the solution used in the titration and
   iii. Acidity of the base and basicity of the acid.
7. In an acid base titration if the salt formed between strong acid and strong base does not hydrolyse then pH =0 at equivalence point.

In an acid base titration if the salt formed between strong acid and weak base, the salt hydrolyses to give an acidic solution then pH < 7 at equivalence point.

In an acid base titration if the salt formed between weak acid and strong base, the salt hydrolyses to give a basic solution then pH > 7 at equivalence point.

8. $pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$

9. Let w = weight NaOH in gm

   Equivalent weight of NaOH = Molecular weight of NaOH = 40

   $\frac{w}{E} \times 1000 = V_{HCl}N_{HCl}$

   $w = V_{HCl}N_{HCl} \times \frac{E}{1000}$

   $w = 25 \times 1 \times \frac{40}{1000} = 1g$

10. Given

    $V = 50$ ml, $N_{HCl} = 0.1N$, $N_{NaOH} = 0.1N$

    Apply the formula $V_{NaOH} N_{NaOH} = V_{HCl} N_{HCl}$

    $V_{NaOH} = (V_{HCl} N_{HCl}) / N_{NaOH}$

    $V_{NaOH} = (50 \times 0.1)/ 0.1$

    Let y = 40 ml

    When volume of NaOH (y ml) is less than that required at equivalence point, then

    [Excess acid]= $[(V \times N_A) - (y \times N_g)] / (V + y)$

    $= 50 \times 0.1 – 40 \times 0.1/ 50+40 = 0.011$

    pH = -log[excess HCl]

    $= -\log [1.1 \times 10^{-2}]$

    $= 2 - \log 1.1$

    pH = 2- 0.04 = 1.96

13.7 REFERENCES

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UNIT 14: CONDUCTOMETRIC TITRATIONS

CONTENTS:

14.1 Objectives

14.2 Introduction

14.3 Acid-base titration: strong acid (HCl) versus strong base (NaOH)

14.3.1 Chemicalsand apparatus required

14.3.2 Principle

14.3.3 Procedure

14.3.4 Observations

14.3.5 Calculations

14.3.6 Result

14.4 Precipitation titration: KCl against $AgNO_3$

14.4.1 Chemicals and apparatus required

14.4.2 Principle

14.4.3 Procedure

14.4.4 Observations

14.4.5 Calculations:

14.5 Summary

14.6 Terminal questions

14.7 Answers

14.1 OBJECTIVES

1. To determine the equivalence point from a conductance vs. volume graph
2. To understand the role of equivalent conductance of each ion in the reaction towards the appearance of the conductance vs. volume graphs.

14.2 INTRODUCTION

Conductometric titration is an elerctroanalytical method for quantitative determination of an analyte. Titration is a procedure to determine the strength of an unknown solution (titrand) by reacting it with a solution of known concentration. The point where all the unknown solution reacts with the standard solution is called the equivalence point.The strength (g/L) of the unknown solution is calculated from the volume of the titrant consumed in the reaction, the titrant concentration and the volume of the solution of unknown strength.

The principle is based on the fact that during conductometric titration, one of the ions is replaced by the other ion which differs in its mobility and conductance. The conductivity of a solution depends on ions and factors like concentration, mobility and valency of the ions, degree of dissociation of the electrolyte and temperature. The concentration of an electrolyte analyte will decrease as it reacts with the titrant. This will vary the conductance of the solution with addition of the titrant. Before titration the solute consists of a different set of ions. During titration the concentration of these ions in the solution changes. After the equivalence point, a different set of ions result in the conductance through solution. Near equivalence point , the conductance will change sharply. A plot of conductance versus volume of titrant added will give the volume of titrant used to react with the total species in the unknown solution. Neutralization reactions as well as precipitation reactions can be studied by conductometric titrations. The following combinations may be studied using same procedure.

a) Titration of strong acid with strong base e.g. HCl with NaOH .

During titration of strong acid with strong base e.g. HCl with NaOH, the highly mobile H^+ ions are replaced by less mobile Na^+ ions. The OH^- ions combine with H^+ ions to form water. Therefore the conductance of the solution keeps decreasing. After neutralisation of the acid by the base further addition of base makes OH^- in excess. Since the mobility of OH^- is appreciable the conductance of the solution again increases after end point. The titration graph of strong acid with strong base is shown in Figure 1 (a).

b) Titration of weak acid with strong base e.g. CH_3COOH with NaOH.

In the titration of weak acid with a strong base, the conductance first decreases as the salt formed suppresses the ionisation of the acid. The salt formed CH_3COONa is more

ionisable than the weak acid. As the amount of salt increases, the conductance of the solution begins to increase. After the equivalence point the base is in excess and OH^- begin to conduct. This increases the conductance more rapidly. The titration graph of weak acid with strong base is shown in Figure 1 (b).

c) Titration of strong acid with weak base e.g. HCl with NH_4OH.

During titration of strong acid with strong base e.g. HCl with NH_4OH, the highly mobile H^+ ions are replaced by less mobile NH_4^+ ions. The OH^- ions combine with H^+ ions to form water. The conductance of the solution at decreases till equivalence point. After neutralisation the ionisation of the added base is supressed by the presence of its salt. Hence,the conductance of the solution remains constant after equivalence point. The titration graph of strong acid with weak base is shown in Figure 1 (c).

d) Titration of weak acid with weak base e.g. CH_3COOH with NH_4OH.

The nature of curve before equivalence point is similsr to the curve obtained by titrating weak acid against strong base. After the equivalance point conductance virtually remains same as the weak base which is being added in feebly ionized acid and therefore is not much conducting Figure 1 (d).

(e) Mixture of a strong acid and a weak Acid vs. a strong base or a weak base.

In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar Figure 1 (e).

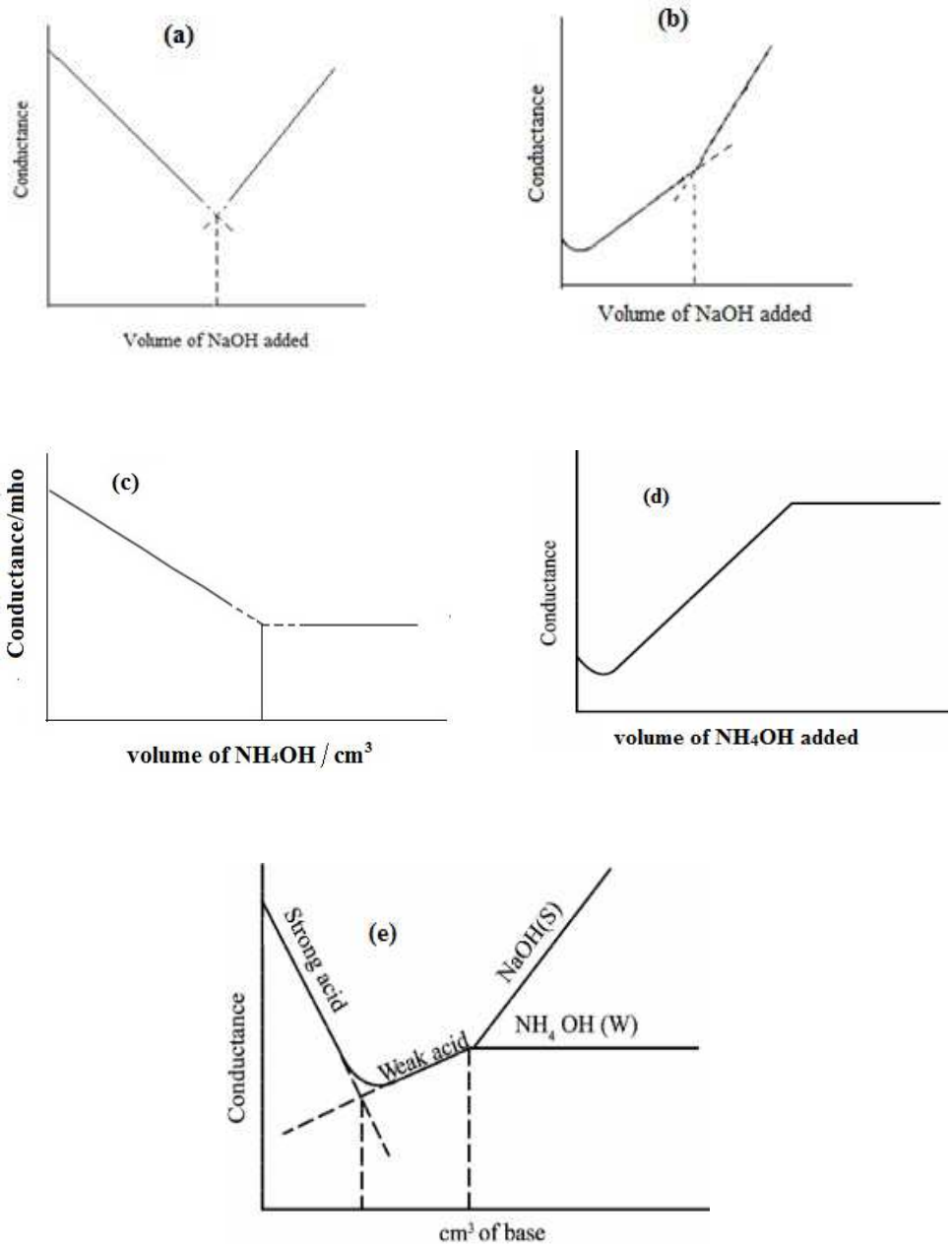


Figure.1. Plot of conductometric acid base titrations (a) Titration of strong acid with strong base.g. HCl with NaOH (b) Titration of weak acid with strong base e.g. CH_3COOH with NaOH and (c) Titration of strong acid with weak base e.g. HCl with NH_4OH (d) Titration of weak acid with weak base e.g. CH_3COOH with NH_4OH (e) Mixture of a strong acid and a weak acid vs. a strong base or a weak base.

14.3 ACID-BASE TITRATION: STRONG ACID (HCl) VERSUS STRONG BASE (NaOH)

14.3.1 Chemicalsand apparatus required

HCl, NaOH, oxalic acid, phenolphthalein and conductivity water.Conductometer, electrodes, temperature sensor rod, wipes to clean the electrode, beakers (250 cm^3), measuring cylinder, burette and conical flask (100 cm^3).

14.3.2 Principle

The conductance of HCl solution is high due to the presence of highly mobile H^+. As NaOH is added to the acid, the H^+ are replaced by Na^+ which have relatively low ionic conductivity.

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow H_2O + Na^+ + Cl^-$$

H^+ ions form water with OH^-. Water remains undissociated in the solution. After the equivalence point, the solution contains excess of OH^- ions which have high conductance and a rapid increase in conductance is noticed.

14.3.3 Procedure

1. Arrange the equipment assembly by attaching the electrode and temperature sensor rod with the conductometer.
2. Weigh 4 g of NaOH in 100 ml to make an appropriate 1N NaOH.
3. Prepare 1 N oxalic acid by weighing 6.3 g oxalic acid in 100 cm3 standard volumetric flask. Sodium hydroxide is then standardized with 1N oxalic acid using phenolphthalein indicator.
4. Clamp a burette filled with standardized 1N NaOH solution.
5. Transfer 50 cm^3 of given solution of HCl acid into a beaker. Dip the electrode and temperature sensor in the solution. The level of solution should be enough to cover the the electrodes. Add standard NaOH from the burette in steps of 0.5 $cm^{3.}$ Stir the solution well before noting the conductance.
6. Near the equivalence point the conductance of the solution increases rapidly. Continue the titration to add another 10 cm^3 in steps of 0.5 $cm^{3.}$ Consider this as a pilot titration.

7. Repeat the titration. This time add NaOH in steps of 0.1 cm^3 near the equivalence point and continue adding another 10 cm^3 after the equivalence point.
8. Record your readings as shown in Table 1.
9. Plot a graph of conductance against volume of NaOH added to locate the equivalence point, Figure.2. The equivalence point is determined by extrapolating the two lines till they intersect. The point of intersection is the equivalence point.

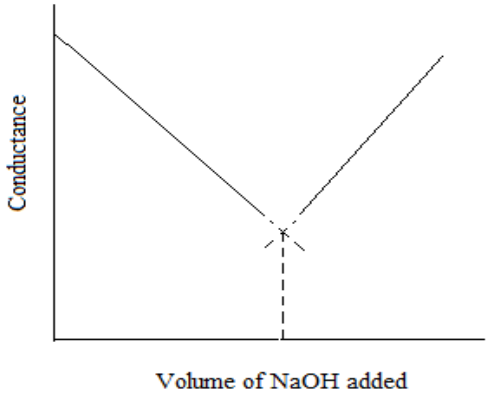


Figure 2. Graph of conductance against volume of NaOH

14.3.4 Observations

Table 1. Titre values for titration of HCl against NaOH

S.N.	Volume of HCl (cm^3)	Volume of NaOH (cm^3) Burette Reading		Conductance (mho)
		Initial	Final	

14.3.5 Calculations

$N_1V_1=N_2V_2$

N_1= Normality of HCl

N_2= Normality of NaOH

V_1=Volume of HCl

V_2= Volume of NaOH required to neutralize HCl

Strength of HCl = Normality of HCl × equivalent weight of HCl (36)

14.3.6 Result

The strength of given HCl solution is .....g/L.

14.4 PRECIPITATION TITRATION: KCl AGAINST $AgNO_3$.

14.4.1 Chemicals and apparatus required

$AgNO_3$, NaCl, K_2CrO_4, KCl and conductivity water.Conductometer, electrodes, temperature sensor rod, wipes to clean the electrode, beakers (250 cm^3), measuring cylinder, burette and conical flask (100 cm^3).

14.4.2 Principle

Precipitation titration can be monitored conveniently by conductivity measurements. In this titration the product is an insoluble substance. An example of precipitation titration is the titration of potassium chloride with silver nitrate. One of the product is a white precipitate of silver chloride.

$AgNO_3 + KCl \longrightarrow AgCl\downarrow + KNO_3$

Silver nitrate potassium chloride silver chloride potassium nitrate

In this experiment we measure the change in electric conductance of the solution on adding increasing amounts of $AgNO_3$

Conductance (G) is the reciprocal of the electrical resistance. G = 1/R (Siemens)

Conductivity: $\kappa = G \times C$, where C is the cell constant, whose unit is cm^{-1}.

Molar conductivity Λ_m of a solution with concentration of *M* molar is given by

$\Lambda_m = c/(\kappa \times 1000)$

14.4.3 Procedure

1. Arrange the equipment assembly by attaching the electrode and temperature sensor rod with the conductometer.

2. Prepare 1N $AgNO_3$ by weighing 42.46 g and making up the solution in a 250 cm^3 standard volumetric flask with conductivity water.
3. Standardize your $AgNO_3$ solution with NaCl. Prepare 1N NaCl solution by dissolving 5.8 g of NaCl crystals in 100 cm^3 of conductivity water. Then pipette out 10 cm^3 of standard 1N NaCl solution in a 250 cm^3 conical flask. Add few drops of potassium chromate solution. Fill a burette with the $AgNO_3$ solution. Titrate till the colour of the solution in the conical flask changes from white (colour of AgCl) to red. Use the formula $V_1\ N_1 = V_2\ N_2$ to obtain the normality of $AgNO_3$ solution. Tabulate your observations in table 1
4. Clamp a burette filled with standardized 1N $AgNO_3$ solution.
5. Transfer 50 cm^3 of given KCl solution into a beaker. Dip the electrode and temperature sensor in the solution. The level of solution should be enough to cover the electrodes. Add 1N $AgNO_3$ from the burette in steps of 0.5 cm^3. Stir the solution well before noting the conductance.
6. Near the equivalence point the conductance of the solution increases rapidly. Continue the titration to add another 10 cm^3 in steps of 0.5 cm^3. Consider this as a pilot titration.
7. Repeat the titration. This time add $AgNO_3$ in steps of 0.1 cm^3 near the equivalence point and continue adding another 10 cm^3 after the equivalence point. Tabulate your readings as given in Table1 and Table 2.
8. Plot a graph of conductance against volume of $AgNO_3$ added to locate the equivalence volume of $AgNO_3$ added, Fig, 2. The equivalence point is determined by extrapolating the two lines till they intersect. The point of intersection is the equivalence point.

14.4.4 Observations

Table 1. Titre values for titration of KCl against $AgNO_3$

S.N.	Volume of KCl (cm^3)	Volume of $AgNO_3$ (cm^3) Burette Reading		Conductance (mho)
		Initial	Final	

Table 2 Table for plotting graph of conductance versus volume of $AgNO_3$

S. N.	Volume of $AgNO_3$ (cm^3)	Conductance(mho)

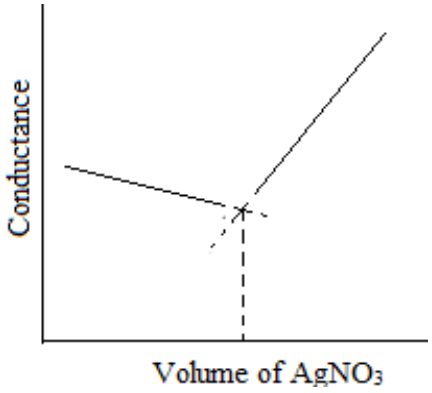


Figure 2. Graph of precipitation titration of KCl against $AgNO_3$

14.4.5 Calculations:

$N_1V_1=N_2V_2$

Strength of KCl = Normality of KCl × Equivalent weight of KCl (74.5 g)

Result: The strength of given KCl solution is .....g/L.

14.5 SUMMARY

Conductomeric titrations can be used to find the amount of an electrolyte analyte present in a given solution. During conductometric titration, one of the ions initially present in the solution of the analyte (titrand) participates in a neutralization or

precipitation reaction and is replaced by another ion from the titrant which differs in its conductance. The concentration of the analyte will decrease as it reacts with the titrant. This will vary the conductance of the solution. Near equivalence point, the conductance will change sharply. A graph between conductance and volume of titrant added is plotted. The point of intersection of the two lines so obtained gives the volume of titrant consumed till equivalence point. The normality of the titrant is found by using the formula

$N_1V_1=N_2V_2$

The strength of the given analyte solution = Normality of the given analyte solution x Equivalent weight of the analyte

In neutralization reaction the appearance of the graph depends on the strength of the acid and the base used in the titration.

14.6 TERMINAL QUESTIONS

1. Name the different types of conductances.
2. What is the relationship between specific conductance and equivalent conductance?
3. Give four factors which affect the conductivity of an electrolyte?
4. What is the principle behind conductometric titrations?
5. What is the purpose of adding a few drops of potassium chromate in NaCl solution during standardization of $AgNO_3$?
6. Give the graph for conductometric titration of CH_3COOH with NH_4OH.
7. Explain the appearance of the graph for conductometric titration of CH_3COOH with NH_4OH.
8. What is the effect of dilution on specific conductance and equivalent conductance of an electrolyte?
9. Why the normality of the titrand is should be kept atleast 10 times more than the normality of the titrand in conductometric titrations?
10. Rank H^+, Na^+ and K^+ in order of their increasing ionic mobility in water.

14.7 ANSWERS

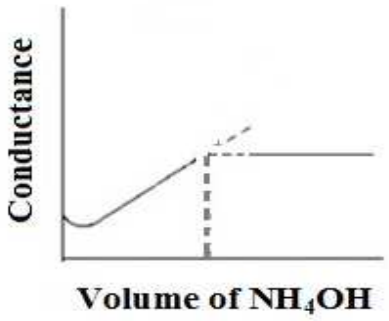
1. Specific conductance, equivalent conductance and molar conductance.

2. $\Lambda_{eq} = \frac{1000 \times \kappa}{c}$,

   where Λ_{eq} is the equivalent conductance, κ is the specific conductance and c is concentration expressed in normality.

3. The conductivity of an electrolytic solution depends on degree of dissociation of the electrolyte, mobility of the ions and valency of the ions and temperature.
4. During conductometric titration, one of the ions initially present in the solution participates in the reaction and is replaced by another ion from the titrant which differs in its conductance. The concentration of an electrolyte analyte will decrease as it reacts with the titrant. This will vary the conductance of the solution. Near equivalence point, the conductance will change sharply.
5. Potassium chromate is used as an indicator for the titration of NaCl with $AgNO_3$. It forms a reddish brown coloured precipitate of silver chromate after all the NaCl is consumed by $AgNO_3$.

   $2AgNO_3 + K_2CrO_4 \longrightarrow Ag_2CrO_4 + 2KNO_3$
6. The graph of conductometric titration of a weak acid (CH_3COOH)with a weak base (NH_4OH) will appear as shown below



7. In the conductometric titration of CH_3COOH with NH_4OH, the conductance first decreases but soon increases due to salt formation and after the equivalence point remains constant.
8. Specific conductance decreases with dilution while equivalent conducxtance increases with dilution for an electrolyte.
9. Dilution increases the mobility of ions and hence the conductance of an electrolyte. When the normality of the titrant is kept atleast 10 times more than the normality of the titrand the error due to dilution is kept to minimum.

10. $H^+ > Na^+ > K^+$

UNIT 15: POTENTIOMETRIC TITRATIONS

CONTENTS:

15.1Objectives

15.2 Introduction

15.3 Titration of a strong acid with a strong base

15.3.1 Chemicals required and apparatus required

15.3.2 Principle

15.3.3 Procedure

15.3.4 Observation

15.3.5 Results

15.4 Determination the amount of fe (ii) present in the given solution by potentiometric titration.

15.4.1 Chemicals and apparatus required

15.4.2 Principle

15.4.3 Procedure

15.4.4 Observations

15.4.5 Calculations

15.4.6 Result

14.5 Summary

15.6 Terminal questions

15.7 Answers

15.1 OBJECTIVES

After completion of this unit you should be able to

1. Know the relationship between an electrode potential (half cell) and its dependence on the concentration of species which reacts at it reversibly (Nernst equation).

2. Know the difference between an indicator and a reference electrode.
3. The representation of half cells.
4. Behaviour of emf near equivalence point
5. To locate the equivalence point in potentiometric titrations.

15.2 INTRODUCTION

In potentiometic titrations the potential of an electrochemical cell is measured on adding a titrant to a titrand in steps. A schematic diagram of a potentiometeric set up is shown in Figure1. The cell consists of an indicator electrode and a reference electrode. The potential of the reference electrode is constant. The potential developed at the indicator electrode helps to quantify the amount of an analyte.

Consider equilibrium between the metal atoms on an indicator electrode and its ions in solution

$M(s) \longrightarrow M^{+} + ne^{-1}$ (oxidation)

A potential develops between the electrode and the surrounding solution. The magnitude of the potential difference depends on the nature of metal, concentration of the metal and temperature The more negative the value of the standard electrode potential of a metal the greater its tendency to give its electrons or get oxidized.

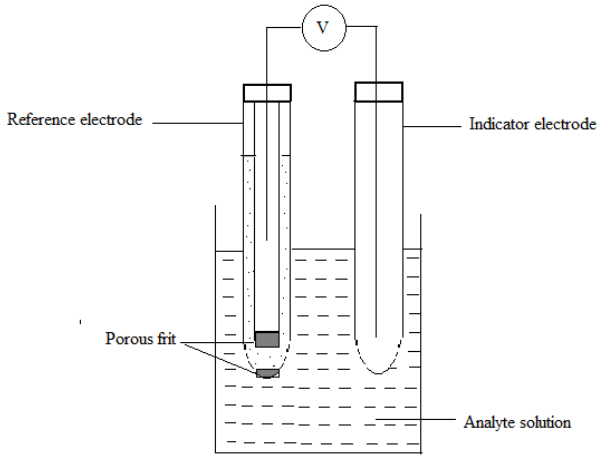


Figure 1. Schematic diagram of a potentiometeric set up

The standard emf of a combination of any two half cells can be determined as follows

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$

The metal with more negative standard electrode potential is made the anode.

The relationship between Gibbs energy of the cell reaction, ΔG, and the emf of the cell, E, is given as

$\Delta G = -nFE$

Where n is the number of electrons exchanged in the cell reaction and F is Faradays constant

The Nernst equation gives the relationship between E_{cell}, E^o_{cell} and ratio of oxidized to reduced species .

$E_{cell} = E^o_{cell} + \frac{RT}{nF} \ln [Ox]/[Red]$

The Nernst equation states that the potential of an electrode depends on the concentration of reduced and oxidized forms of the ions. When the concentration of these ions changes, the electrode potential also changes. Such reactions are useful for dilute solutions or solutions where the end point cannot be detected by indicators.

Near the end point the rate of change of emf is greatest. The end point can be determined by plotting emf against volume of titrant added, Figure 2. A perpendicular drawn at half the height of the inflexion curve gives the end point. The end point can also be determined from a first derivative curve, Figure 3.

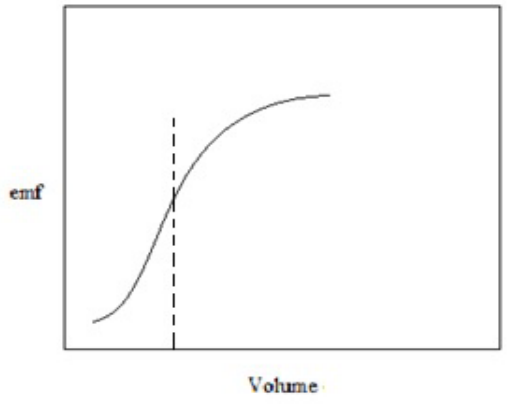


Figure2. Plot of Emf vs Volume

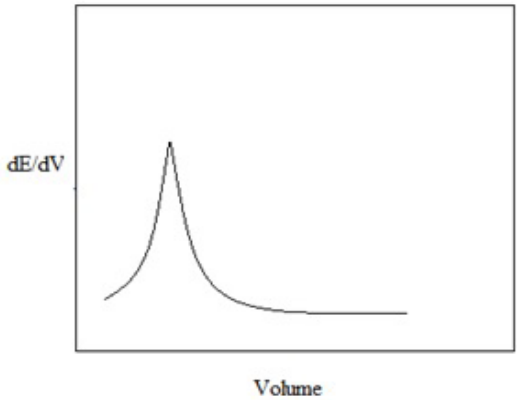


Figure3. Plot of first derivative of Emf vs Volume

15.3 TITRATION OF A STRONG ACID WITH A STRONG BASE

15.3.1 Chemicals required and apparatus required

0.1 N HCl, standardized 0.1 N NaOH solution and quinhydrone, potentiometer with platinum electrode and calomel electrode, beaker, burette.

15.3.2 Principle

Quinhydrone is an equimolar mixture of quinine and hydroquinone.

The cell constructed for H^+ reversible system is

Pt/ acid + (QH)//calomel

The reduction potential of quinhydrone and the emf of the cell will depend on the pH of the solution. On adding small aliquots of a base, the emf of the cell drops gradually and near the equivalence point a large decrease in emf occurs. After the equivalence point, the emf changes again.

15.3.3 Procedure

1. Pipette out 20 cm^3 of 0.1 N HCl acids into a beaker.
2. Add a pinch of quinhydrone and place a platinum electrode in the solution.
3. Connect the calomel electrode through a salt bridge.
4. Titrate the solution with standardized 0.1N NaOH from the burette and determine the emf after every 1 cm^3 addition. Tabulate your readings as shown in Table 1.
5. Draw a plot of emf against volume of NaOH added (Figure 4).The volume of NaOH at the point of intersection is the volume of NaOH used to neutralize the total HCl solution present in the beaker. You can also plot a graph of dE/dV against volume of NaOH added, Figure 5, from the data in Table 2 to get the equivalent point The volume where the the maxima is reached is the equivalence point of the titration.

15.3.4 Observation

Table 1. Titre values of sodium hydroxide and corresponding EMF at each addition of sodium hydroxide

S.N.	Volume of NaOH (cm^3)	Emf, E (V)

Table 2. Table for plot of Emf vs volume of sodium hydroxide and first derivativeof Emf vs volume of sodium hydroxide

S.N.	Volume of NaOH (cm^3)	Emf (V)	ΔE (V)	ΔV (ml)	ΔE/ΔV (V/cm^3)

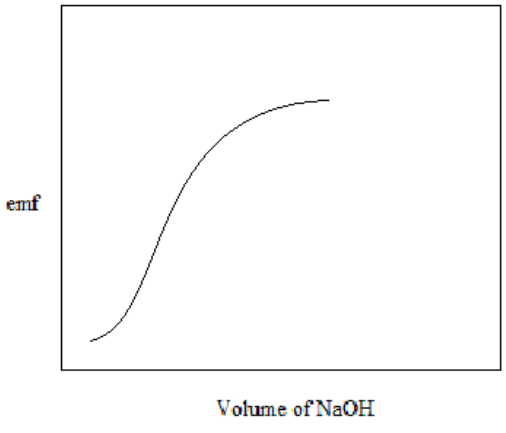


Figure. 4. Pot of Emf vs Volume of sodium Volume of hydroxide

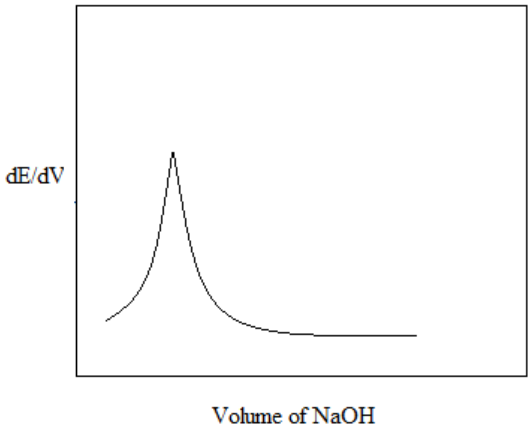


Figure. 5. Pot of first derivative of Emf vs sodium hydroxide

15.3.5 Results

i. The volume of base (NaOH) required neutralizing the acid is…….ml.

ii. The strength of HCl is ……..g/lt.

15.4 DETERMINATION THE AMOUNT OF FE (II) PRESENT IN THE GIVEN SOLUTION BY POTENTIOMETRIC TITRATION

15.4.1 Chemicals and apparatus required required

Potassium dichromate, ferrous ammonium sulphate and sulphuric acid, potentiometer, platinum electrode, calomel electrode, beaker and burette.

15.4.2 Principle

In a potentiometric titration the cell emf changes rapidly in the neighbourhood of the end point of the titration. In this experiment Fe (II) is titrated against $K_2Cr_2O_7$. The Fe (II)-$K_2Cr_2O_7$ redox system is represented as follows

$$Fe^{2+} + 4H_2SO_4 + K_2Cr_2O_7 \longrightarrow Fe^{3+} + K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

The potential E of the indicator electrode is given by

$$E = E^o + \frac{0.0591}{n} \log \{[Fe^{3+}]/[Fe^{2+}]\}$$

Where E^o is the standard reduction potential of the system (0.77V). The potential of the indicator electrode depends on the ratio of oxidized species (Fe^{3+}) to the reduced species (Fe^{2+}). The reaction is

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

The cell can be represented as

Calomel// Fe^{3+}, Fe^{2+}/Pt

The calomel electrode is the reference electrode and platinum electrode serves as the indicator electrode. During the titration $K_2Cr_2O_7$ oxidises Fe^{2+} to Fe^{3+}. This changes the relative concentration of $Fe3^+/Fe^{2+}$. Near the vicinity of the end point, the potential changes rapidly.

15.4.3 Procedure

1. Prepare 0.1N solution of K2Cr2O7 by dissolving 0.49g of K2Cr2O7 crystals in 100 cm^3 of distilled water.

2. Transfer 20 cm^3 of the Fe II solution in a clean beaker. Add 25 cm^3 of 2.5 M H_2SO_4 and 50 cm^3 of distilled water.
3. Standard $K_2Cr_2O_7$ solution is added from the burette in small aliquots (1 cm^3). The emf is recorded after each addition. At the end point there is a rapid increase in emf due to absence of Fe^{2+}. The end point is noted.
4. Repeat the experiment. This time add the titrant, $K_2Cr_2O_7$ solution, in steps of 0.1 cm^3 near the end point. Record your observations as shown in Table 3.
5. Plot a graph between emf and the volume of dichromate added. The inflexion point gives the volume of titrant at the end point.
6. A plot of $\Delta E/\Delta V$ versus volume of $K_2Cr_2O_7$ solution gives the exact volume of dichromate used till the equivalent point.

15.4.4 Observations

Table 3. Table for plot of Emf vs volume of K2Cr2O7 and first derivative of Emf vs volume of $K_2Cr_2O_7$

S.N.	Volume of $K_2Cr_2O_7$ (cm^3)	EMF V	ΔE V	$\Delta E/\Delta V$ V/ cm^3

15.4.5 Calculations

$N_1V_1 = N_2V_2$

N_1= Normality of Fe (II)

V_1= Volume of Fe (II)

N_2= Normality of $K_2Cr_2O_7$

V_2= Volume of $K_2Cr_2O_7$

Strength of Fe (II) = Normality of Fe(II) x Equivalent weight of Fe(II) (27.92 g)

15.4.6 Result

The amount of Fe(II) present in the whole of the given solution is…… g.

15.5 SUMMARY

Potentiometry is an electroanalytical method that relates the change in concentration of ions in equilibrium with each other and in contact with an electrode to the emf of the electrode. Near the end point in neutralization or redox reactions a sharp change is observed in the emf of the electrode. A plot of emf versus volume of titrant added helps to locate the end point from the inflexion point. A first derivative curve of $\Delta E/\Delta V$ versus volume of titrant can also help determine the end point of the reaction. The volume of the titrant obtained is used to calculate the strength of the titrand.

15.6 TERMINAL QUESTIONS

1. What kind of reactions can be best studied by potentiometry?
2. Where can you find the nature of a metal ion to undergo oxidation? How is it listed ?
3. What is meant by ion selective electrodes in potentiometry?
4. How would you depict a silver-silver chloride electrode?
5. What indicator electrodes can be used for acid base potentiometric titrations?
6. What is the purpose of quinhydrone electrode in acid-base potentiometric titrations ?
7. Name the electrolyte solution within the glass electrode of a potentiometer?
8. What is meant by alkaline error?
9. Identify the reactions at anode and cathode in a solution containing $Cr_2O_7^{2-}/Cr^{3+}$ and Fe^{3+}/Fe^{2+} equilibrium rections with a saturated calomel electrode and platinum electrode.
10. What will be the potential at equivalence point if 0.02 M $Fe(CN)_6^{4-}$ is titrated against 0.1M Ce^{4+} ?

15.7 ANSWERS

1. Reactions where the ions are reversible to an electrode and solutions are dilute or the end point due to acid-base neutralization, redox reactions or precipitation reactions cannot be known by an indicator.

2. The nature of a metal ion to undergo oxidation can be found in the electrochemical series. The electrochemical series is built by arranging various redox equilibria in order of their standard electrode potentials. At standard conditions of temperature and pressure (STP) the potential of the metal electrode is called its standard electrode potential. The more negative the value of the standard electrode potential of a metal the greater its tendency to give its electrons or get oxidized. The metals are listed in increasing order of standard reduction electrode potential.
3. An ion selective electrode acts as a sensor for a particular ion in a solution. It converts the activity of an ion to electrode potential. It consists of a membrane that is sensitive to one particular ion and therefore to the changes in its concentration. The membrane could be made of glass, an ionic crystal or a liquid. An example is a glass electrode which is sensitive to H^+ ions.
4. Ag(s)/ AgCl $(_S)$/Cl^-
5. Glass electrode or quinhydrone electrode.
6. The reduction potential of quinhydrone and the emf of the cell will depend on the pH of the solution. Quinhydrone + $2H^+$ $\rightleftharpoons$ Quinol
7. Saturated KCl.
8. At higher pH values a glass electrode can show lower pH due to exchange of alkali metal ions present in the solution by the glass membrane.
9. $Fe^{2+} \longrightarrow Fe^{3+}$ oxidation (anode)

   $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ reduction (cathode)
10. In both the reactions one electron is exchanged

    $E^o_{Ce^{4+}/Ce^{3+}} = 1.61$ V and $E^o_{Fe(CN)_6^{3-}} / E^o_{Fe(CN)_6^{4-}} = 0.36$ V

    $E_{equivalence} = \frac{1.61 + 0.36}{2} = 0.98$ V

UNIT 16: KINETICS

CONTENTS:

16.1 Objectives

16.2 Introduction

16.3 To determine the kinetics of acid-catalyzed hydrolysis of methyl acetate

16.3.1 Chemicals and apparatus required

16.3.2 Principle

16.3.3 Procedure

16.3.4 Calculations

16.3.5 Result

16.4 To determine alkaline hydrolysis of ethyl acetate by conductometry

16.4.1 Chemicals and apparatus required

16.4.2 Principle

16.4.3 Procedure

16.4.4 Result

16.5 Clock reaction

16.5.1 Aim

16.5.2 Principle

16.5.1 Effect of reactant concentration on the rate of reaction

16.5.1.1 Chemicals and apparatus required

16.5.1.2 Procedure

16.5.1.3 Observations

16.5.2 Effect of temperature

16.5.2.1 Procedure

16.5.2.2 Calculations

16.5.2.3 Result

16.5.3. Effect of ionic strength

16.5.3.1 Result

16.6 Iodination of acetone by colorimetry

16.6.1 Chemicals required and apparatus required

16.6.2 Principle

16.6.3 Procedure

16.6.4 Observations
16.6.5 Result
16.7 Summary
16.8 Terminal questions
16.9 Answers

16.1 OBJECTIVES

After reading this unit you should be able to

1. Learn some terms and concepts in chemical kinetics like chemical reaction, mechanism, reactant, product, rate, rate law and rate constant.
2. To obtain the order of an acid catalysed reaction experimentally by volumetric titrations.
3. Monitor the progress of a base catalysed reaction by conductivity measurements
4. Use of spectrophotometric technique to determine the rate constant and the order of iodination of acetone .
5. Calculating the activation energy of iodination of acetone by studying the effect of temperature change on the rate constant.

16.2 INTRODUCTION

Kinetics of a chemical reaction is the rate of formation of products or disappearance of reactants. Rate of a reaction is the amount of substance reacted or produced per unit time.

Rate law is an equation which relates the reaction rate with the concentration of the reactantsa constant called the rate constant.

Order of a reaction with respect to a given substance is the exponent to which the concentration term of the substance in the rate law is raised. The total order of a reaction is the sum of all the exponents to which concentration terms are raised in a rate law.

The order of a reaction is determined experimentally. This unit describes experiments where the rate constant of a reaction is determined by volumetric, conductometric and colorimetric methods.

The factors that affect the rate of a reaction are initial concentration of reactants, temperature and catalyst. Temperature dependence of rate constant is given by Arrehenius equation.

$k = A \exp^{(-E/RT)}$

Activation energy is obtained from the above expression by obtaining rate constants at two different temperatures. Iodination of acetone is taken as a representative reaction to study the activation energy of a reaction. To determine the order in the rate law for iodine clock reaction you would be using the method of initial rates

16.3 TO DETERMINE THE KINETICS OF ACID-CATALYZED HYDROLYSIS OF METHYL ACETATE

16.3.1 Chemicals and apparatus required

0.05 N NaOH, methyl acetate, 0.5 N hydrochloric acid, phenolphthalein indicator and ice., bottles (250 cm^3), pipettes (5 cm^3), burette (50 cm^3), conical flasks (100 $cm^{3)}$, stop watch, and a thermostat.

16.3.2 Principle

Acid-catalyzed hydrolysis of methyl acetate takes place according to the reaction

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

The reaction is catalysed by HCl. Water is taken in excess so that the rate of the reaction depends only on the concentration of the ester. Such a reaction is called pseudo uinimolecular reaction. The acetic acid formed during the reaction is titrated against NaOH solution.

The rate constant of a first order reaction is given by the following expression:

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

In a volumetric method a and (a-x) are replaced by ($V_\alpha - V_o$) and ($V_\alpha - V_t$) respectively. ($V_\alpha - V_o$) corresponds to the initial concentration of the ester and ($V_\alpha - V_t$) corresponds to (a-x), the concentration of the ester at time, t.

16.3.3 Procedure

1. Prepare 0.05 N NaOH and 0.5 N hydrochloric acid.
2. Transfer 100 cm^3 of 0.5 N hydrochloric acid in a 250 cm^3 bottle. Keep this bottle in a thermostatically controlled water bath.
3. Standardise sodium hydroxide solution with 0.05 oxalic acid.
4. Pipette out 50 cm^3 of ester(mthyl acetate) into a 250 cm^3 bottle and place it in the same thermostatically maintained water bath. Note the temperature of the waterbath.
5. Pipette out 10 cm^3 of 0.2 N methyll acetate into the bottle containing 100 cm^3 of 0.5 N hydrochloric acid and shake well. Immediately pipette out 5 cm^3 of this reaction mixture into a conical flask containing a few ice pieces and two drops of phenolphthalein indicator. The ice pause the reaction. Start a stop watch.
6. Titrate against standard 0.05 N sodium hydroxide solution from burette. The end point is the appearance of pale pink colour. Note the burette reading as given in Table 1. The volume of sodium hydroxide solution consumed is the value, V_o , corresponding to time, $t = 0$.
7. Pipette out 5 cm^3 of reaction mixture into a conical flask containing ice and phenolphthalein at regular time intervals of 10, 10, 15, 15,and 20 minutes. Titrate each with standard sodium hydroxide as before. Note the volume of sodium hydroxide consumed each time. This gives the values for V_t.
8. Pipette out 15 cm^3 of the reaction mixture and warm the bottle in a water bath at 80^oC for 20 minutes. This procedure brings the reaction to completion. Pipette out 5 cm^3 of this solution in a conical flask containing ice pieces and phenolphthalein indicator. Titrate this mixture with sodium hydroxide solution in the burette. The titre values give V_α.
9. A plot of log $(V_\alpha - V_t)$ against t would yield a straight line , Figure 1, with slope equal to -2.303/k from which k can be calculated.

Table 1. Titration of reaction mixture against standrized NaOH solution

S.N	Time (sec)	Burette reading (cm^3)		Volume of sodium hydroxide (cm^3)	$(V_\alpha - V_t)$	log $[(V_\alpha - V_o)/(V_\alpha - V_t)]$	Rate constant, k (s^{-1})
		Initial Reading	Final Reading				

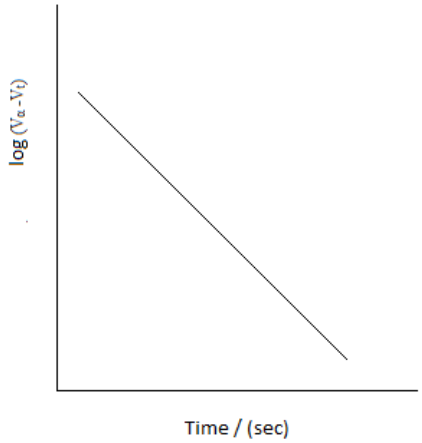


Fig. 1 A plot of log (V_α -V_t) against t

16.3.4 Calculations

The reaction is a pseudo first order reaction. The rate constant is given by

$$k = \frac{2.303}{t} \log [(V_\alpha - V_o)/(V_\alpha - V_t)]$$

(V_α -V_o) corresponds to the initial concentration of the ester, a.

(V_α -V_t) corresponds to (a-x), the concentration of the ester at time, t.

16.3.5 Result

The rate constant of the acid catalysed hydrolysis of the ester at …..^oC

a. By calculation, k = ……s^{-1}.
b. From graph, k = ……s^{-1}.

16.4 TO DETERMINE ALKALINE HYDROLYSIS OF ETHYL ACETATE BY CONDUCTOMETRY

16.4.1 Chemicals and apparatus required

0.01 N NaOH, 0.2 N ethyl acetate, 0.01N sodium acetate and conductivity water,conductivity cell, Conductivity bridge, beakers, pipettes, stop watch and a thermostat.

16.4.2 Principle

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

The progress of the reaction is measured by change in conductance of the reaction solution at different time intervals.

16.4.3 Procedure

1. Prepare 0.01 N NaOH, 0.01 N sodium acetate and 0.2 N ethyl acetate solution with conductivity water.
2. Measure the conductance of a 0.01 N sodium acetate solution taken in a beaker.
3. Pipette out 20 cm^3 of 0.01 N NaOH into a 250 cm^3 beaker (labeled A) containing 50 cm^3 of conductivity water and keep it in a thermostatically maintained water bath.
4. Pipette out 10 cm^3 of 0.2 N ethyl acetate into another beaker (labeled B) containing 50 cm^3 of conductivity water and keep this beaker also in a thermostatically maintained water bath.
5. After thermal equilibrium is attained pipette out 30 cm^3 of the solution containing the ester from beaker B into the beaker A containing the sodium hydroxide and start a stop watch.
6. Record the conductance of the solution at regular time intervals until the reaction reaches completion as given in Table 2.

$k_2 = \{ (C_o-C_t) /(C_t-C_a)\}/\{0.01 \times t\}$

$k_2 (0.01 \times t) = (C_o-C_t) /(C_t-C_a)$

$t = \{(C_o-C_t) /(C_t-C_a)\} / k_2 \times 0.01$

where:-

C_o and C_a are the conductance of 0.01N NaOH solution and 0.001 N sodium acetate solution

Plot a graph of t against $(C_o-C_t)/(C_t-C_a)$. Find the value of the rate constant from the slope of the straight line.

Table 2: Conductance at various time intervals

S.N.	Time (min)	Conductance (mhos)	$k_2=\{(C_o-C_t)/(C_t-C_a)\}/\{0.01xt\}$

16.4.4 Result

The calculated rate constant, k_2 = …….$dm^3\ mol^{-1}\ s^{-1}$

The rate constant obtained from the graph, k_2 = ……. $dm^3\ mol^{-1}\ s^{-1}$

16.5 CLOCK REACTION

16.5.1 AIM: To study (a) the effect of concentration of iodide ion solution on the rate of iodide ion oxidation by persulphate ions using iodine clock reaction, (b) to determine the Activation energy of the reaction by studying the effect of temperature on the rate constant and (c)to study the effect of ionic strength on the rate constant of the reaction.

16.5.2 Principle

In a clock reaction two clear solutions of potassium iodide, KI and sodium persulphate,

$Na_2S_2O_8$ are added together with a delaying agent (sodium thiosulphate) and starch so that a blue-black colour is observed. The appearance of blue black colour is instantaneous. The reaction is called a clock reaction because the amount of time that elapses before the solution turns blue depends on the concentrations of the starting chemicals. Sodium thiosulphate is added to the solution to delay the appearance of blue black colour. The colour appears only when all thiosulphate is exhausted and iodine is free to form a blue black coloured complex with starch.

The rate of this reaction reaction is first order with respect to the concentration of persulphate ion

$[S_2O_8^{-2}]$ and second order with respect to the concentration of iodide ion $[I^-]$.

$\text{Rate} = k [S_2O_8^{-2}] [I^-]^2$

The reactions that forms the basis for the iodine clock reaction is shown below.

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ (1)

The rate of reaction may be measured by adding a small, known quantity of thiosulphate. The iodine produced in this reaction (1) is, as it is formed, reduces back to iodide by the thiosulphate:

$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$ (2)

thiosulphate tetrathionate

This continues until all the thiosulphate has been consumed. Further iodine formed in reaction (1) has nothing to react with and begins to appear in the solution. To make the measurement more precise, the colour of the iodine is enhanced by the addition of starch solution. So by determining when iodine first becomes visible, it is possible to measure the speed of reaction (1). In Part 1 of the experiment you will investigate the effect of reactant concentration on the rate of reaction, and thereby obtain the rate equation. The effect of temperature is studied in Part 2, and the results used to find the activation energy for the reaction. Finally, in Part 3 the effect of the ionic strength of the solution on the rate is measured, from which a possible structure of the reaction intermediate may be deduced.

At constant temperature and ionic strength, the rate equation for reaction (1) is

$\text{Rate (1)} = - d[S_2O_8^{2-}]/ dt = k [S_2O_8^{2-}]^m [I^-]^n$

In this experiment you will use the initial rate method to find the orders m and n. The stoichiometric equation (1) tells us that the rate of consumption of persulphate equals the rate of iodine production.

In each experiment, the time, Δt, taken to consume a known amount of thiosulphate (at which point the solution turns blue) is noted. Provided the amount of thiosulphate added is much less than the initial amount of persulphate, we can make the approximation

$-\{d[S_2O_8^{2-}]/dt\}_{init} = \{d[I_2]/dt\}_{init} = \Delta[I_2]/\Delta t$

Since $\Delta[I_2]$ is the same for each experiment, it follows that the initial rate is inversely proportional to Δt, i.e.

$-\{d[S_2O_8^{2-}]/dt\}_{init} = constant/\Delta$ *(3)*

(

$\ln 1/\Delta t = \ln k + m \ln [S_2O_8^{2-}] + n \ln [I^-] + c$; where c is the integration constant (4)

Thus a plot of $-\ln \Delta t$ against $\ln[S_2O_8^{2-}]$ at constant $[I^-]$ should yield a straight line of slope m, and a graph of $-\ln \Delta t$ against $\ln [I^-]$ at constant $[S_2O_8^{2-}]$ will give n.

According to the stoichiometry of reaction 2, 1 mole of I_2 reacts with 2 moles of $S_2O_3^{2-}$

Therefore at the time (t) when deep blue black colour appears,

$[I_2]_{formed} = [S_2O_8^{2-}]_{initial}/2$

Knowing the molar concentration of I_2 at An exact time gives the rate of formation of I_2.This helps in calculating the rate of reaction 1 for any combination of reaction conditions as long as the amount of $2S_2O_3^{2-}$ is kept constant.

The difference between the initial and final concentration of iodine divided by the amount of time needed for this change gives the rate of the reaction.

Rate= $\Delta [I_2]/\Delta t$ or

Rate = $[S_2O_8^{2-}]_{initial}/(2 \Delta t)$

The time of the colour change t_{colour} is also the time passed during the reaction Δt.

Therefore

Rate = $[S_2O_8^{2-}]_{initial}/(2 t_{colour})$

16.5.1 Effect of reactant concentration on the rate of reaction

16.5.1.1 Chemicals and apparatus required

Potassium iodide, sodium persulphate, sodium thiosulphate, starch and distilled water, Beakers (50 cm^3), standard volumetric flasks and thermometer.

16.5.1.2 Procedure

1. Prepare 1000 cm^3 of 1 M KI solution by weighing 166 g of KI and dissolving it in 1000 cm^3 distilled water. From this stock solution, 0.8, 0.4, 0.2 and 0.1 M KI solutions were prepared. Prepare 0.04 M sodium persulphate solution (2.7 g of $Na_2S_2O_8$ was weighed and dissolved in distilled water in a 250 cm^3 volumetric flask). Prepare 250 cm^3 of 0.05 M of sodium thiosulphate by weighing 1.977 g of $Na_2S_2O_3$ and transferring it into a 250 cm^3 standard flask and making up the solution with distilled water.
2. Label the three solutions 1.0 M KI, sodium thiosulphate and sodium persulphate solution A, B and C, respectively.
3. Prepare a reaction mixtures by pipetting out 10 cm^3 of 1.0 M KI (solution A) and 10 cm^3 of sodium persulphate (solution C) and transfer into conical flask for set 1.
4. Then, add 1 cm^3 of starch solution. At last add 5 cm^3 sodium thiosulphate solution (solution B) and time taken for the first appearance of blue black colour recorded after this addition is noted by a stop watch.
5. Repeat the procedure for set 2, set 3 set 4 and set 5 (different concentrations of potassium iodide solution but constant concentration of sodium thiosulphate and sodium peroxodisulphate). Table 3 shows the total mixture compositions for the experiment.
6. Construct tables of time for appearance of blue- black solution for concentrations of KI at constant concentration of sodium persulphate $S_2O_8^{2-}$, Table 4 and concentration of $S_2O_8^{2-}$ at constant iodide concentration, Table 5.
7. Calculate the rate of the reaction, k =1/t
8. Plot two graphs. One for -ln Δt against ln$[S_2O_8^{2-}]$ at constant $[I^-]$ and the second for -ln Δt against ln $[I^-]$ at constant $[S_2O_8^{2-}]$. Plot of -ln Δt against ln$[S_2O_8^{2-}]$ at constant $[I^-]$

should yield a straight line of slope m, and a graph of -ln Δt against ln [I^-] at constant [$S_2O_8^{2-}$] will give n .

9. The rate constant, k, can be calculated from one of the experiments after we have determined m and n. Put the concentrations of $S_2O_8^{-2}$ and I^- used in that particular experiment.

16.5.1.3 Observations

Table 3. Total mixture compositions

Set	Volume of $S_2O_8^{2-}$ (cm^3)	Volume of $S_2O_3^{2-}$ (cm^3)	Volume of I^- (cm^3)	Starch (cm^3)	Deionised water (cm^3)
1	10	5	10	1	4
2	10	5	8	1	6
3	10	5	6	1	8
4	10	5	4	1	10
5	10	5	2	1	12
6	11	5	10	1	3
7	12	5	10	1	2
8	13	5	10	1	1
9	14	5	10	1	0

Table 4. Table for rate of the reaction: Concentrations of KI at constant concentration of sodium persulphate $S_2O_8^{2-}$ and time for appearance of blue- black solution

Set	Volume of KI (cm^3)	Concentration of KI (M)	Time taken for first appearance of blue-black colour t_{colour} (s)	Rate=$[S_2O_8^{2-}]_{initial}/(2\ t_{colour})$ (mol l^{-1} s^{-1})
1	10	1		
2	8	0.8		
3	6	0.6		

4	4	0.4		
5	2	0.2		

Table 5. Table for rate of the reaction: Concentration of $S_2O_8^{2-}$ at constant iodide concentration and time for appearance of blue-black solution

Set	Volume of $S_2O_8^{2-}$ (cm^3)	Time taken for first appearance of blue-black colour, t_{colour} (s)	$[S_2O_8^{2-}]_{initial}/(2\ t_{colour})$ (mol l^{-1} s^{-1})
5	10		
6	11		
7	12		
8	13		
9	14		

16.5.2 Effect of temperature

The rate coefficients k of many simple reactions are found to vary with temperature T according to the Arrhenius equation

$k = A \exp^{(-Ea/RT)}$

in which A is the pre-exponential factor and E the activation energy of the reaction. We may interpret A as a measure of the collision frequency between reactants in solution and exp-E/RT as the Boltzmann factor which gives the fraction of the molecules with sufficient energy, E, to react.

$\ln k = \ln A - E_a /R\ T$

(6)

provided that E_a is independent of temperature, which is usually a good approximation over a small temperature range. Thus both A and E_a may be obtained from a graph of ln k against 1/ T .

16.5.2.1 Procedure

1. Make up a mixture of 10 cm^3 of solution persulphate (C) with a few drops of starch solution, and a second solution containing 10 cm^3 of thiosulphate (B) and 10 cm^3 of KI (A).
2. Place the persulphate/starch and iodine/thiosulphate solutions in a thermostat bath for 10 minutes, and then record the temperature of the solutions.
3. Mix and note the time for the appearance of the blue colour.
4. Repeat the procedure at 5 temperatures up to 50^oC.
5. Prepare tables as in the previous section to calculate k.
6. Plot a graph of log k vs 1/T. The slope of the straight line is equal to - E_a/(2.303 R) from which the value of activation energy, E_a, can be determined. The intercept of the straight line is equal to log A, where A is the Arrhenius constant or pre-exponential factor.

16.5.2.2 Calculations

Calculate values of the activation energy and pre-exponential factor

ln k = ln A - E_a /R T

2.303 log k = 2.303 log A – E_a/RT, where R is the ideal gas equation (8.314 J mol^{-1} K^{-1})

log k = log A - E_a /(2.303 RT)

Find the value of the rate constant at 298 K.

16.5.2.3 Result

The activation energy E_a for the reaction is …….J mol^{-1}

16.5.3. Effect of ionic strength

The ionic strength of the solution affects the rate constant of an ionic reaction. This is effect is termed “primary kinetic salt effect”. It results due to interactions between the reactants and activated complex and the ionic atmospheres of oppositely charged ions which surround them in solution. Three conditions are possible

(a) If the charges on the reactants have the same sign, increasing the ionic strength of the solution will increase the rate constant by lowering the effective activation energy.

(b) If the charges on the reactants have different signs, the rate constant will decrease with ionic strength.

(c) If one of the reactants is uncharged, there will be no change in the rate constant with ionic strength.

1. Prepare 250 cm^3 of 0.1M $(NH_4)_2S_2O_8$; solutions (A).
2. Prepare 500 cm^3 of 0.1M $(NH_4)_2SO_4$;solutions (B).
3. Prepare 250 cm^3 of 0.01M $Na_2S_2O_3$; solution (C).
4. Fill burettes with solutions (A) and (B).
5. Make up a solution (D) in a 500 cm^3 volumetric flask with 333 cm^3 of solution (B), and dissolving in it 8.30 g (0.050moles) of solid KI, and making up to 500 cm^3 with deionized water. Check that the total ionic strength of solution (D) is the same as that of solution (A) and of solution (B); the formula for ionic strength is

$$I = \frac{1}{2}\sum c_i z_i^2$$

where c_i is the concentration (in molality) of each ionic species, and z_i the charge of each species. The summation must include all ionic species present in the solution.

6. Transfer 10 cm^3 of solution A (0.1M $(NH_4)_2S_2O_8$) and a drop of starch solution in a 100 cm^3 conical flask. Add 10 cm^3 of 0.1 M KI solution (D) and 5 cm^3 solution C (0.01M $Na_2S_2O_3$).
7. Mix, start the stopwatch, and record the time to the appearance of the blue colour. Repeat with different volumes of the $S_2O_8^{2-}$ and I^- solutions as indicated in Table 6 below, keeping the ionic strength constant in each case by making up the volume with the ammonium sulphate solution.

Table 6. Table for ionic strength

Set	Volume of $S_2O_8^{2-}$ (cm^3)	Volume of $(NH_4)_2SO_4$ (cm^3)	Volume of $S_2O_3^{2-}$ (cm^3)	Volume of I^- (cm^3)	Time of appearance of blue-black colour, t_{colour}	Rate
1	10	0	5	10		

2	10	2	5	8		
3	10	4	5	6		
4	10	6	5	4		
5	10	2	5	10		
6	10	4	5	10		
7	10	6	5	10		

For determining the effect of ionic strength on the rate of the reaction, compare the initial rates at room temperature for the following two reaction mixtures as an example. You can construct a table as in Table 7 for similar comparisons.

10 cm^3 $S_2O_8^{2-}$, 5 cm^3 $S_2O_3^{2-}$, 10 cm^3 I^- and 10 cm^3 0.1M $(NH_4)_2SO_4$ solution.

10 cm^3 $S_2O_8^{2-}$, 5 cm^3 $S_2O_3^{2-}$, 10 cm^3 I^- and 10 cm^3 deionised water.

Table 7. Table for effect of ionic strength on the rate of the reaction

Volume of $S_2O_8^{2-}$ cm^3	*Volume of* $S_2O_3^{2}$ cm^3	*Volume of 0.1M* $(NH_4)_2SO_4$ cm^3	*Volume of* I^- cm^3	*Volume of deionised water* cm^3	Time of appearance of blue colour	Rate
10	5					
10	5					

16.5.3.1 Result

The effect of reduction in ionic strength on the rate of reaction is ……

16.6 IODINATION OF ACETONE BY COLORIMETRY

16.6.1 Chemicals required and apparatus required

0.005 M Iodine solution, 0.5 M hydrochloric acid, 0.5 M acetone,s tandard volumetric flasks, spectrophotometer, cells, pipettes, paper wipes.

16.6.2 Principle

In this experiment, the progress of a reaction is followed spectrophotometrically. An aqueous iodine solution is yellow. Hence it absorbs at visible region of the spectrum. When an aqueous iodine solution is added to acetone in the presence of an acid, the yellow color fades as the iodine is consumed to give the iodinated product, iodoacetone. As the reaction progresses to completion the absorbance monitored at 400 nm keeps reducing.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} (CH_2I)\,COCH_3 + HI$$

The rate law for this reaction can be written as:

rate = $k\,[I_2]^a\,[H^+]^b\,[(CH_3)_2C{=}O]^c$, where a, b, c are the order with respect to iodine, acid and acetone. In this experiment you will use the method of initial rates to determine the value of the rate constant, k, and the orders of the reaction with respect to I_2 (the value of a), H^+ (the value of b), and CH_3COCH_3 (the value of c).

The rate of this reaction will be followed by watching the solutions' yellow color fade over time.

rate = $-\,\Delta\,[I_2]/\Delta t$

You will perform six runs using different concentrations of reactants. For each run, you will produce an Absorbance vs. Time plot. The slope of each plot can be used to find the initial rate of the reaction for that particular run. Since the iodine concentration is proportional to absorbance (A), you must also calculate the constant *b* relating absorbance to iodine concentration for your spectrometer using the following equation.

$A = b\,[I_2]$

rate = $-\,\Delta\,[I_2]/\Delta t$

Because you are following the rate of the reaction by measuring the change in absorbance of the solution, you will need to divide the change in absorbance vs. time by the constant b.

rate = = $\Delta A/ (b \Delta t)$

In this manner, the Absorbance vs. time plot can be used to obtain the initial rate of the reaction in concentration per unit time.

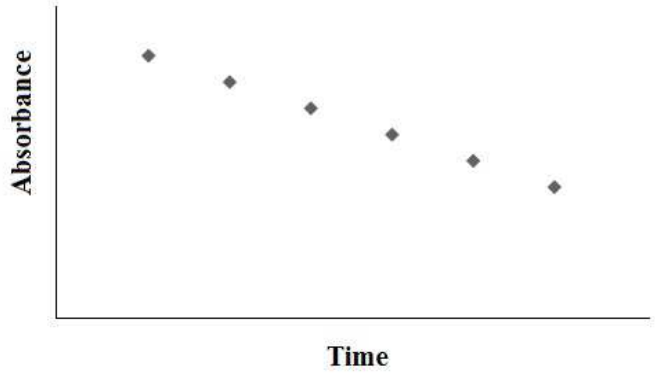


Fig.2. A plot of Absorbance vs. Time

16.6.3 Procedure

1. Prepare and label clean dry test tubes so that there is a test tube for each set as given in Table 1. Add the components, except iodine, for each experiment into the corresponding test tube. (For example: Set 1 would have 1 cm^3 of acetone, 5 cm^3 of hydrochloric acid and 3 cm^3 of deionized water.)
2. Add the corresponding volume of iodine solution into the test tubes labeled Set 1, Set 2 etc. when you are ready to put the solution in a cuvette for measurements.
3. Rinse and fill one of the cuvettes (¾ full) with deionised water (the blank). Hold the cuvette from the opaque sides of the cuvette. Wipe the sides of the cuvette.
4. Place the cuvette containing the blank in the spectrometer. Calibrate the spectrophotometer.
5. Then place the cuvette with the sample.
6. Determine the wavelength of maximum absorbance which is at 400 nm.
7. Record the absorbance at 400 nm as a function of time at 2 minutes interval as given in Table 7. The solution will start losing color as soon as reactants are mixed together and the absorbance value will decrease.

16.6.4 OBSERVATIONS

Table 7. Absorbance at 450 nm with time

Set 1		Set 2		Set3		Set4		Set 5		Set 6	
T	Abs.	T	Abs	T	Abs	T	Abs	T	Abs	T	Abs
0 2 4 6 8 10 12											

T= time in min, Abs.= absorbance

7. Plot absorbance as a function of time for each of the sets. Calculate the rates.

rate= k $[I_2]^a$ $[H^+]^b$ $[acetone]^c$

The value of rates obtained for set 1 and 2 leads to the expression

Rate1/rate2 = k $[I_2]_1^a$ / k$[I_2]_2^a$

The concentrations of acetone and H^+ are the same for these two reaction mixtures and since the concentration of iodine is in the ratio of 2:1, the above equation can be rearranged as

$rate_2 / rate_1 = 2^a$

or, log $[rate_2/ rate_1]$ = a log 2

a = log $[rate_2/ rate_1]$ / log 2

Similarly, we can find the rate ratio for reaction mixtures or sets where the concentrations of acid and acetone are different and the values of b and c can be calculated, respectively.

16.6.5 Result

i. The order of the reaction with respect to Iodine, a, is …….
ii. The order of the reaction with respect to Hydrochloric acid, b, is……
iii. The order of the reaction with respect to Acetone, c, is ……

16.7 SUMMARY

In this chapter we learned about the kinetics of reaction, mechanism of hydrolysis of ethyl acetate. We get knowledge about order of reaction and its determination by volumetric analysis.The experiments also provided an idea about rate constant and determination of energy of activation. Colorimetric estimation of iodine gives an idea about spectroscopic technique used for characterization of molecules.

16.8 TERMINAL QUESTIONS

1. Define rate of a reaction
2. Define order of a reaction
3. What are the factors which determine the rate of a reaction?
4. Which equation gives the temperature dependence of rate constant?
5. What happens to the ratio of rate constants of a reaction if the reaction is carried out at two temperatures T_1 and T_2 with a difference of 10 ^oC?
6. What is the order of acid-catalyzed hydrolysis of methyl acetate?
7. What is the purpose of adding sodium thiosulphate to a solution of potassium iodide, KI and sodium persulphate, $Na_2S_2O_8$ in a I_2 clock reaction?
8. What is the principle behind alkaline hydrolysis of ethyl acetate by conductometry?
9. Give Beer-Lambert's law.
10. What was the absorbance wavelength monitored for aqueous iodine solution in iodination of acetone?

16.9 ANSWERS

1. Rate of a reaction is the amount of substance reacted or produced per unit time.
2. The order of a reaction is the sum of all the exponents to which concentration terms are raised in a rate law.

3. The factors that affect the rate of a reaction are initial concentration of reactants, temperature and catalyst.
4. Temperature dependence of rate constant is given by Arrehenius equation,
   $k = A\, e^{(-Ea/RT)}$
5. The ratio of rate constants doubles and in some cases triples.
6. It is a pseudo first order reaction.
7. The purpose of adding sodium thiosulphate to a solution of potassium iodide, KI and sodium persulphate, $Na_2S_2O_8$ in a I_2 clock reaction is to delay the appearance of blue colour of the I_2 starch complex. It converts iodine back to iodide ions.
8. The principle behind alkaline hydrolysis of ethyl acetate by conductometry is to monitor the progress of a base catalysed reaction by conductivity measurements which depend on the mobility of ions produced or replaced in the reaction solution.
9. $A=\varepsilon cl$, where
   A is the absorbance, ε is the molar absorbtion coefficient, c is the comcentration expressed in mol L^{-1} and l is the path length of the cuvette (1 cm).
10. Aqueous iodines absorbtion was monitored at 400 nm.