EXPERIMENT-1

Basic laboratory Techniques

OBJECTIVES

After studying this unit, you should be able to:

- Cut and bend glass rods/tubes;
- Bore rubber cork;
- Seal the glass apparatus for leakage;
- Measure the volume, mass and density of a given substance;
- Perform simple laboratory operations such as filtration, crystallisation and distillation;
- Use burner properly in the laboratory.

1.1 TO CUT A GLASS TUBE OF DESIRED LENGTH

Materials Required: Glass tube / rod, ruler, small triangular file, gas burner/ spirit lamp.

1.1.1 How to perform the experiment?

Take the given glass tube and measure the required length with the help of a ruler/ measuring tape and put a mark on it with an ink pen or glass marking pencil. Hold it with one hand near the point where the cutting is to be done. Make a single straight scratch with the help of a triangular file, see Fig. (i). Do not apply too much pressure on the tube otherwise the glass tube will break. Hold with a piece of cloth and press the tube gently outward. The tube will break into two pieces, Fig.(ii).

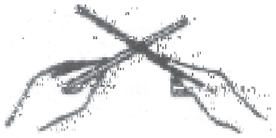


Fig. (i): *Making a scratch on the glass tube*

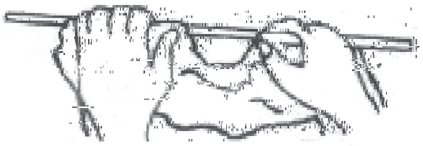


Fig. (ii): *Holding & Breaking a glass tube*

Notes

If the tube does not break, put the scratch again at the same point and try to break it by the same method.

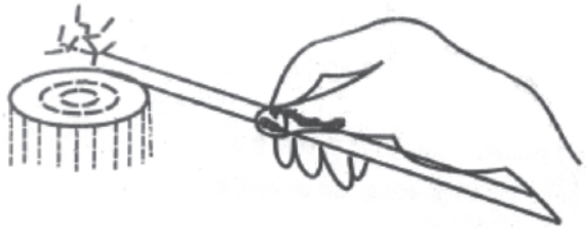


Fig. (iii): *Rounding off the edges of the broken*

Normally, the freshly cut ends are sharp and may cause injury to the hands. Therefore, round off the ends by rotating the tube in the blue zone of the flame for a short time as shown in the Fig. (iii). Keep your fingers at a safe distance from the flame.

1.1.2 Precautions

1. The file should be moved always in backward down direction.
2. If difficulty is experienced in breaking the glass tube or rod, put another scratch on the point.

Note: To a cut glass rod same procedure should be used as done for the glass tube.

1.2 BENDING OF A GLASS TUBE

Material Required: Glass tube, burner, file, and asbestos sheet.

1.2.1 How to perform the experiment

Hold the glass tube horizontally with the portion of the glass tube to be bent on the blue flame of the burner. Heat this portion of the glass tube with simultaneous rotation, in the blue flame of the burner, as shown in the Fig. (iv). Allow the tube to bend under its own weight (Fig. v).

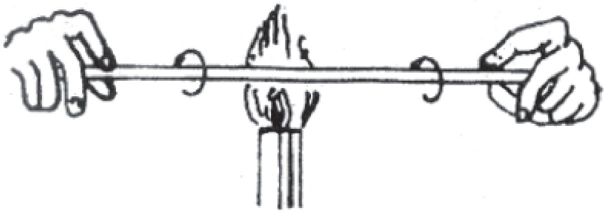


Fig. (iv): *Heating the glass tube*

When the tube becomes soft, bend the glass tube from its ends to the desired angle. Do not bend the tube abruptly. Maintain the desired angle by holding the glass tube ends with both hands. Press the bent limbs to make them coplanar by putting it on the asbestos sheet as shown in Fig. (vi).

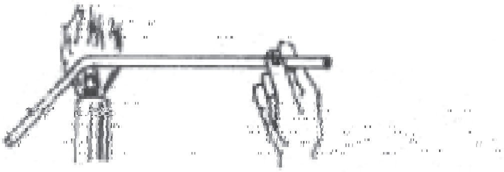


Fig (v): *Bending of glass tube under*

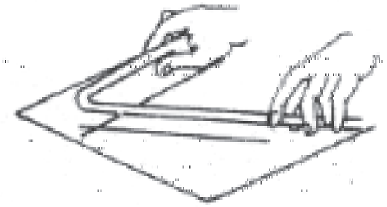


Fig. (vi): *Making the bent limbs of the glass tube coplanar*

1.2.2 Precautions

Do not touch the bent portion of the tube with fingers until it is cooled.

1.3 TO BORE A CORK AND FIT A GLASS TUBE IN IT

Materials Required: A cork, cork borer set, glass tube.

1.3.1 How to perform the experiment

Take a cork free from cracks. Check that it fits tightly in the mouth of apparatus for which it is needed. Wet the cork with water and soften it with the help of a cork press. If it is not available, you may do it by rolling under your shoe as shown in Fig. (vii). Select a cork borer, whose diameter is slightly less than that of the glass tube or rod, for which the hole is needed. Place the cork on the table with its narrow ends upward and hold it with one hand. Make a round hole in its centre by pressing the borer gently inward with the other hand as shown in the Fig. (viii).

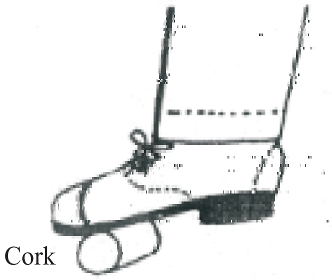


Fig. (vii): *Pressing the cork with shoe*

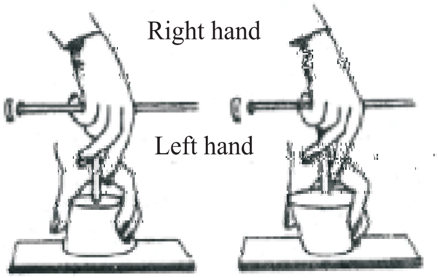


Fig. (viii): *Boring of cark*

1.3.2 Precautions

1. While boring the cork, make sure that the hole is made in straight line.
2. While inserting the glass tube into the hole, the tube should be pushed gently with a rotatory motion.
3. The tube should be lubricated with water or soap solution to avoid accidental breakage.

1.4 FILTRATION

In filtration, insoluble small solid particles/dust/ impurities etc. are separated from liquids by passing the mixture through filter paper which is affixed inside the funnel The filter papers have small pores through which only the liquid (or only particular particle size) can pass through.

Materials Required: Funnel, glass rod, beaker, filter paper, sugar solution with small amount of sand.

1.4.1 How to perform the experiment?

Filtration involves two steps Fig. (ix). In first step, the filter paper is folded and fitted into the funnel. For this, take a clean filter paper and cut it in a circle of required diameter with scissors. Fold it in half (semi circle) and then in quarters. Open one section of folded filter-paper so that a cone is formed. Place the filter paper into a clean funnel. Wet the filter paper with distilled water/ liquid which is part of the mixture. Place clean beaker/ conical flask below the funnel to collect filtrate. Transfer the mixture to the funnel slowly by using a glass rod as shown in the Fig. (ix).

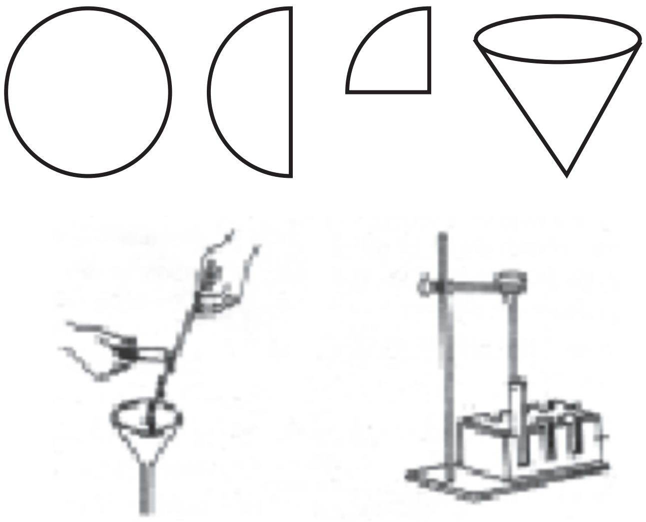


Fig. (ix): *Filtration*

Hold the glass rod at an angle over the funnel, the lower end of the glass rod should not touch the filter paper but should be just above it. Pour the mixture down the rod. The level of the mixture to be filtered should be not more than 3/4th the height the filter paper. Collect the filtrate in a beaker or test-tube or conical flask. For easy and quick filtration, first transfer the clear supernatent liquid of the mixture on to the filter paper and then the remaining portion.

1.4.2 Precautions

(i) Do not transfer all the mixture to the filter funnel at one time,

(ii) The filter paper should be smaller in size than funnel.

(iii) The mixture level should never be above 3/4th of the height of the filter paper,

(iv) The lower end of the funnel should just touch the inside wall of the beaker.

1.5 DISTILLATION

Distillation is used to purify liquids such as water and organic solvents, and/or recycling used solvents. Distillation is the process in which the impure liquid is heated to its boiling point in a closed vessel. The vapour thus formed are cooled by passing through an air or a water condenser. As a result, the pure liquid is obtained.

Materials Required:

(a) **Apparatus:** Conical flask / round bottomed flask, condenser, thermometer, beaker, heating mantle and oil bath.

(b) **Chemicals:** Impure solvents and tap water.

1.5.1 How to perform the experiment ?

Take the impure solvent in the round bottomed (RB) flask. Fill the flask to about half of its capacity. Add a few piece of pumice stone. Fit a cork with a hole

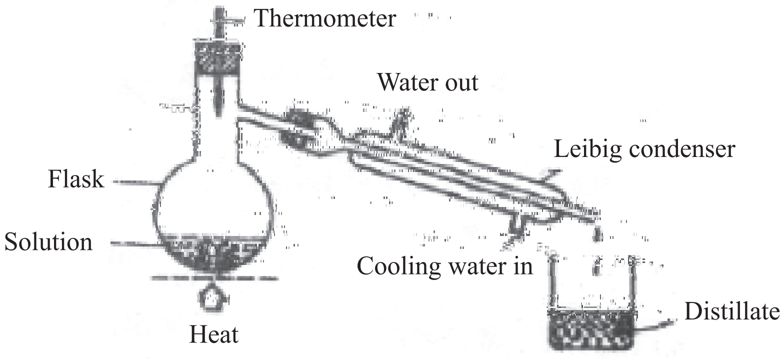


Fig. (x): *Distillation*

in the mouth of the round bottom flask. In the hole, fit a thermometer as shown in Fig. (x). Fit a liebig condenser as shown in Fig. (x). Place the round bottom flask on the heating bath.

Heat the contents of the flask. At the boiling point of the liquid, it starts boiling and the emanating vapours pass through the condenser and get condensed into liquid. Collect the liquid at the end of the condenser. Collect the pure liquid at constant boiling point. Always leave some liquid in the round bottom flask.

1.5.2 Precautions

(i) Slowly increase heating rate.

(ii) Do not open the round bottom flask during heating.

(iii) Stop distillation when a small amount of liquid is still left in the flask. Do not evaporate to dryness.

(iv) Punice stones should be added in the beginning itself.

(v) In case of organic solvents, you have to watch the thermometer's temperature throught the experiment to avoid overheating.

1.6 CRYSTALLIZATION

Crystallization is a process of obtaining crystals of a pure substance from a solution which may contain some impurities.

A hot saturated solution of impure substance is prepared in a suitable solvent. This is filtered to remove insoluble impurities and then allowed to cool slowly to room temperature. During the cooling period, the solution should not be disturbed. Crystals of pure substance are gradually formed. Then filter the crystals.

1.7 MEASUREMENT OF VOLUME, MASS AND DENSITY

The volume of liquids can be measured with the help of measuring cylinders, graduated beaker, pipette, burette and syringe. These measuring vessels can be chosen according to the need of accuracy of the experiment. Except syringe, measuring vessels are directly calibrated in cubic centimeter c.c. (or milliliters i.e. mL). These measuring vessels sometime may be wrongly graduated. Therefore, it is desirable to check the measuring vessel before using it.

Before you actually perform measurements for any liquid, you should take following precautions:

- Clean the measuring vessels with soap and water and dry them in air.

- Check the nature of the liquid. If it is an acid or some poisonous liquid, take care that your fingers do not get wet with it while handling the liquid.
- If the liquid is hot, then allow it to cool to room temperature.

(i) Now, find out the least count (i.e. the least measurable volume) of each given measuring vessel. This is the value of the volume between two successive marks on the measuring vessel.

(ii) Take the small measuring vessel and transfer the given liquid into it slowly. The rim of vessel containing liquid should be slightly inside the rim of the measuring vessel. Keep the measuring vessel slightly tilted from vertical as shown in the Fig (xi), so that the liquid falls down the wall smoothly. If it is not tilted, then the liquid falling from a height strikes the surface with splash and some of the liquid drops may sprinkle out of the measuring vessel.

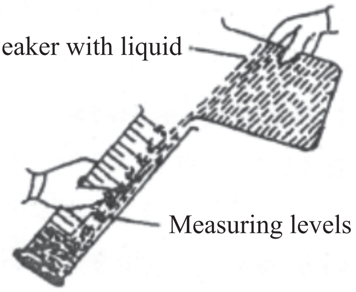


Fig. (xi): *Transferring liquid into the measuring vessel*

(iii) If the given liquid is less in volume than the total capacity of the measuring vessel, then after transferring the whole liquid, put the measuring vessel on the table. Allow its level to become steady. Now take the reading of the level of the liquid in the vessel which gives the volume of the given liquid.

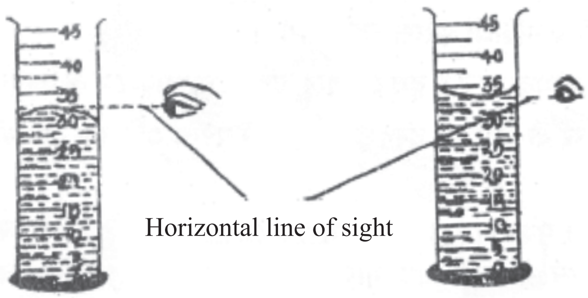
(iv) If the quantity of the given liquid is more than the capacity of the measuring vessel, then fill the vessel to its capacity. Method to fill the vessel to capacity is as follows:

As the measuring vessel is being filled, it should also be moved to make it vertical, when it gets filled close to the uppermost mark corresponding to the capacity marked on the vessel. Use the dropper for transferring liquid drop by drop to fill the vessel exactly upto the uppermost mark. Transfer this liquid into an empty container. Again fill the measuring vessel with the remaining liquid and repeat the procedure.

The total volume (V) of the given liquid is now given by

$$\begin{array}{l}\text{Number of times the}\\ \text{measuring vessel is}\\ \text{filled to its capacity}\end{array} \times \begin{array}{l}\text{capacity of}\\ \text{the vessel}\end{array} + \begin{array}{l}\text{level reading in the}\\ \text{last transfer}\end{array}$$

(v) If, however, the liquid is highly viscous like glycerine, then it would stick to the walls of the vessel. In such cases, in each transfer from the measuring vessel to the extra container, you have to wait till whole of the viscous liquid is transferred slowly to the container and the measuring vessel becomes empty. But it may take too much time and you may use only the measuring vessel of capacity larger than the given liquid.



(b) (a)

Fig. (xii): *Taking reading of the (a) concave surface and (b) convex surface of liquid in vessel*

(vi) The liquid meniscus in the measuring vessel is curved (concave or convex), therefore take the reading of the mark tangential to the lowest point of the curved surface in case of concave meniscus and uppermost point of the curved surface in case of convex mensiscus, as shown in the Fig. (xii).

(vii) If the liquid is transparent, then it should be properly illuminated by side light while taking the reading of its concave or convex surface.

(viii) Take the readings of the level of liquid in the measuring vessel by keeping your eye in horizontal plane with the level, keeping the vessel on the table only, otherwise it may cause error due to parallax.

In case the vessel containing the given liquid does not have a rim like that of a beaker, then you can take help of a glass rod to transfer the liquid. For example, suppose the liquid is milk contained in a glass. Hold the glass rod in your left hand and lower it into the measuring vessel as shown in the Fig. (xiii). Now transfer the milk from the glass into the measuring vessel by touching the rim of the glass to the rod. The milk easily flows down the glass rod to the measuring

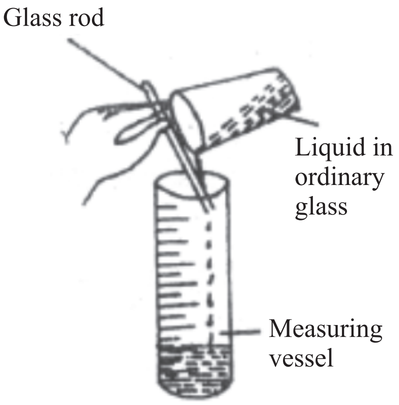


Fig. (xiii): *Transfering liquid into a vessel*

vessel, without flowing down along the surface of tilted glass outside the measuring vessel. A given volume of a liquid can be measured using either a graduated cyclinder, a pipette, or a syringe, depending upon the quantity and accuracy required. Burettes and volumetric flasks are also used to measure liquid volumes accurately.

1.8 GRADUATED CYLINDERS

Graduated cylinders are not highly accurate, but they are adequate for measuring specified quantities of solvents and wash liquids as well as liquid reactants that are present in excess. The level of the liquid should always be read from the bottom of the liquid meniscus.

1.9 PIPETTES

Graduated or volumetric pipettes can be used to measure accurately relatively small quantities of a liquid. Suction is required to draw the liquid into a pipette. However, suction by mouth is unwise because of the danger of drawing toxic or corrosive liquids into the mouth. An adaptor should be used to pipette out harmful/corrosive liquids. It is used as follows:

1. Insert the adaptor into the top end of the pipette.
2. Dip the pipette tip in the liquid.
3. Press the adaptor to force the air out and then release to suck the liquid into the pipette.
4. Fill the pipette to just above the calibration mark.
5. Adjust the liquid upto the calibration mark and pipette out the liquid.
6. Remove the adaptor from the pipette.

Most volumetric pipettes are calibrated “to deliver” a given volume, meaning that the measured liquid is allowed to drain out by gravity, leaving a small amount of liquid in the bottom of the pipette. This liquid is not removed, since it is accounted for in the calibration. Graduated pipettes are generally filled to the top (zero) calibration mark and then drained into a separate container until the calibration mark for the desired volume is reached. The remaining liquid is either discarded or returned to its original container. The maximum indicated capacity of some graduated pipettes is delivered by draining to a given calibration mark and of others by draining completely. It is important not to confuse the two, since draining the first type completely will deliver a greater volume than the indicated capacity of the pipette.

1.10 SYRINGES

Syringes are most often used for the precise measurement and delivery of very small volumes of liquid, as in gas-chromatographic analysis. A syringe is filled by placing the needle in the liquid and slowly pulling out the plunger until the barrel contains a little more than the required volume of liquid. Then the syringe is held with the needle pointed up and the plunger is pushed into eject the excess sample. Excess liquid is wiped off the needle with a tissue.

Syringes should be cleaned immediately after use by rinsing them several times with a volatile solvent, then reused.

1.11 MASS

In chemical laboratory, mass of chemicals can be determined by single pan balance or rough balance.or a chemical balance . To make solutions for general purposes, one can use an ordinary balance, but when chemicals are needed to perform reactions, one should weigh them by the use of chemical balance. Therefore the mass of chemicals is very accurately needed. You can use chemical balance to measure mass of chemicals. The details of using chemical balance are given in experiment 15.

1.12 DENSITY OF A LIQUID

For determining the density of a liquid, the mass of the substances is divided by its volume. The densities of few liquids are shown in the table given below:

Table: Densities of some liquids

Liquid	Volume in milliliters (ml)	Mass (g)	Density (g cm^{-3})
Water	100	100	1.00
Cooking oil	100	92	0.92
Glycerine	100	125	1.25
Whole milk	100	103	1.03

Precautions:

1. Don't use water to cool hot tube, beaker
2. Keep your hand dry and clean while performing the work
3. Always follow precaution given in each section.

1.13 CHECK YOUR UNDERSTANDING

1. Why, while cutting a glass tube, one should not make multiple scratches?

   ....

2. What is the right choice of a cork borer?

   ....

3. Why is the cork moistened and softened before boring?

   ....

4. How can you round off the edges of a freshly cut glass tube?

   ....

1.14 NOTE FOR THE TEACHER

The Laboratory techniques such as cutting a glass tube, bending a glass tube are little difficult for the students. The teacher should help the students and should watch them throughout their practice.

1.15 CHECK YOUR ANSWERS

1. Multiple scratches, if made on the glass tube will cause a rough and irregular cut.
2. The outer diameter of the borer should be slightly less than that of the glass tube or rod, for which the hole is needed.
3. To avoid cracking of the cork and to get a smoother bore, it is moistened with water and pressed in a cork presser.
4. The edges should be heated gently by rotating on a flame.

EXPERIMENT-2

To determine the melting point of a solid substance having low melting point

OBJECTIVES

After performing this experiment, you should be able to:

- set up an apparatus to determine the melting point;
- determine the melting point of a given solid substance; and
- relate the melting point of a substance with its purity;

2.1 WHAT YOU SHOULD KNOW

The melting point of a solid is that constant temperature at which the solid and liquid phases of the substance are in equilibrium with each other.

This is an important physical constant used for establishing the identity and determining the purity of a solid substance. A sharp melting point is usually indicative of high purity of a substance. The presence of impurities lower down the melting point. Thus, an impure solid substance has a lower melting point than that of its pure form.

2.2 MATERIALS REQUIRED

(1) Apparatus	**(2) Chemicals**
Beaker (100 mL). Thermometer, Glass capillary tube (5-6 cm long), Burner, Iron stand, Clamp and boss, Tripod-stand, Wire gauze, Stirrer, Spatula. Glass tube (25-30 cm), Watch glass, Cork with one bore,	Liquid paraffin (~60 mL), Naphthalene, Urea, Oxalic acid, Benzoic acid.

Notes

2.3 HOW TO PERFORM THE EXPERIMENT

(1) Take a glass capillary tube of about 5-6 cm in length and seal one end of it. This is done by heating the tip of tube with the side of the flame of the Bunsen burner. The end of the capillary tube melts and seals itself. It is indicated by the formation of a small glass bead at the tip. Fig 2.1.

(2) Take a small quantity of a solid (about 50 mg) in watch glass, powder it by crushing it with the help of a spatula.

(3) Fill the powdered substance in the capillary tube upto about 1 cm height. This is done by pushing the open-end of the capillary tube into the heap of powdered substance kept in a watch glass. Now drop the capillary tube with the sealed end down through a glass-tube (25-30 cm length) kept vertically on a plane surface so that the powder reaches the closed end of the capillary.

(4) Take a beaker of 100mL capacity. Fill it nearly half with paraffin oil. Place this beaker (paraffin bath) over a wire gauze kept on a tripod stand.

(5) Take a thermometer and dip it in the paraffin bath so as to wet its lower end. Bring the capillary tube near to the wet end and spread a thin film of paraffin oil on one side of capillary tube. Bring the wet side of the capillary tube in contact with the thermometer. The capillary tube sticks to the thermometer due to the surface tension of paraffin. (Fig. 2.2). Now hang it on a clamp such that its bulb dips completely in the liquid paraffin but the open end of capillary is above it.

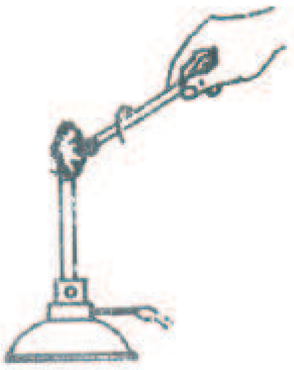


Fig. 2.1: *Sealing of Capillary tube*

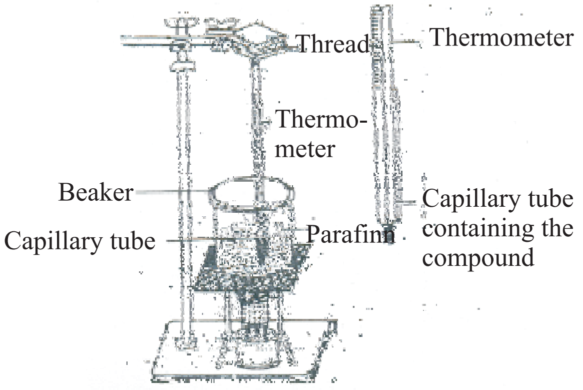


Fig. 2.2: *Determination of melting point*

(6) Heat the paraffin bath slowly with a burner and keep stirring the oil so as to maintain a uniform temperature.

(7) Continue heating till the substance melts. Note down the temperature (t_1) at which the substance begins to melt. Observe carefully whether the

substance melts at a fixed temperature or it melts over a range of temperature. A melting point is said to be sharp when the compound melts at a fixed temperature.

(8) Remove the burner and allow the temperature to come down. Note the temperature (t_2) at which the solid just reappears.

(9) The average of the readings ($t_1 + t_2$) is the correct melting point.

2.4 PRECAUTIONS

1. The substance whose melting point is to be determined should be completely dry.
2. The thermometer and the capillary should not touch the bottom or the sides of the beaker.
3 . The heating of bath should be very slow with the help of a low flame so that the change in the state of the substance (solid to liquid) is clear.
4. The bath should be stirred gently to maintain a uniform temperature.

2.5 OBSERVATIONS

Temperature at which the substance begins to melt (t_1) = ... °C

Temperature at which the substance resolidifies (t_2) = ... °C

Melting point (T_1) = ... °C

Note: In case of pure substance values t_1 and t_2 are almost the same or the difference between t_1 and t_2 is very small. In case of impure substance, t_1 and t_2 are different and the difference between t_1 and t_2 depends upon the amount of impurity.

2.6 CONCLUSION

i) The melting point of the given substance is ..... °C.

ii) The melting point of the substance is sharp / not sharp. Hence the substance is of a pure / impure quality.

2.7 CHECK YOUR UNDERSTANDING

1. Define the melting point of a substance.

....

2. What will be the effect of impurity on melting point of a substance?

   ....

3. How can you keep the temperature of the bath uniform while heating?

   ....

4. What is the usefulness of determination of melting point?

   ....

5. What is meant by sharp melting point?

   ....

6. What will be the effect on melting point of the substance if the oil in the bath is not stirred regularly.

   ....

2.8 NOTE FOR THE TEACHER

Following substances may be given to the students for determination of melting point:

	Compound	**M.P. (^{o}C)**
1.	Nephathalcnc	80
2.	Citric Acid	100
3.	Oxalic Acid	101
4.	Benzoic Acid	121
5.	Urea	132

2.9 CHECK YOUR ANSWERS

1. Melting point of a substance is the temperature at which the solid and liquid phase of the substance are in equilibrium.
2. The presence of impurity lowers the melting point of a substance.
3. By stirring the paraffin oil gently.
4. To establish the identity and determining the purity of a solid substance.
5. The temperature at which a solid melts almost completely.
6. The lower part of the oil will have higher temperature than upper part and thus observed melting point will differ from the actual value.

EXPERIMENT-3

To prepare dilute solutions of given concentrations of hydrochloric acid, sulphuric acid and nitric acid from their stock solution.

OBJECTIVES

After performing this experiment, you should be able to:

- explain the meaning of the terms saturated solution, standard solution and dilution.;
- use proper glassware to prepare solutions of different dilutions; and
- prepare solutions of given concentrations by dilution.

3.1 WHAT YOU SHOULD KNOW

The most commonly used acids in laboratories are hydrochloric, sulphuric and nitric acids. The concentration of these commercially available acids are 12M, 18M and 16M respectively. But except a few cases, we need these acids in lower concentrations. The acids in their lower concentrations can be obtained by dilution of concentrated acids.

To make a solution of required concentration, we use the standard relation

$$M_1 V_1 = M_2 V_2$$

Where, M = molarity of concentrated acid, and V_1 = Volume of concentrated acid. M_1 = Molarity of acid required, V_2 = Volume of acid required.

3.2 MATERIALS REQUIRED

(1) Apparatus	**(2) Chemicals**
Standard flask (100mL), Funnel, Glass rod. Wash bottle, Pipette and burette	Hydrochloric acid (12M), Sulphuric acid (18M), Nitric acid (16M) and Distilled water.

3.3 HOW TO PERFORM THE EXPERIMENT

You are required to prepare

1. 100 mL of 1 molar solution of hydrochloric acid;
2. 100 mL of 0.5 molar solution of sulphuric acid and
3. 100 mL of 2 molar solution of nitric acid from the commercially available acids.

For preparing 100 mL of 1 molar hydrochloric acid we use the equation, $M_1V_1 = M_2V_2$. We first calculate the volume of concentrated acid and water required.

M_1 = molarity of concentrated acid = 12M

V_1 = Volume of concentrated acid = ?

M_2 = Molarity of acid required = 1M

V_2 = Volume of acid required = 100mL

$$V_1 = \frac{M_2V_2}{M_1} = \frac{1\text{x}100}{12} = 8.33\text{ ml} \approx 8.3\text{mL}$$

Take about 50 mL of distilled water in a 100 mL standard flask. Transfer 8.3 mL of concentrated acid from a burette to the standard flask. Shake the mixture gently. Add water to make up the volume of acid in the standard flask upto the mark. Close the flask with glass-stopper. Mix the solution by tilting the flask upside down.

For the preparation of dilute solution of sulphuric and nitric acids, follow the same procedure as given above.

3.4 PRECAUTIONS

(i) The acids should be used with utmost care.

(ii) All the three acids are corrosive to skin.

(iii) Add concentrated acids slowly to water with constant stirring.

3.5 OBSERVATIONS

(i) Volume of 12 M HCl taken for preparing 1 M HCl, (100mL solution = 8.3 mL)

(ii) Volume of 18M H_2SO, taken for preparing 0.5 M, H_2SO_4 (100 mL solution) = ...

(iii) Volume of 16 M HNO_3 taken for preparing 2M HNO_3 (100 mL solution) = ...

3.6 CONCLUSION

The solution of required concentrations may be prepared from their concentrated solution by the dilution method.

3.7 CHECK YOUR UNDERSTANDING

1. What are the components of a solution?

   ....

2. What do you understand by dilution?

   ....

3. What is molarity?

   ....

4. Calculate the volume of 8M HCl required to prepare 250 ml of 2M hydrochloric acid.

   ....

3.8 NOTE FOR THE TEACHER

All the three concentrated acids are highly corrosive. One should be careful while handling these acids

The students need help in transferring acids from the commercial bottles into reagent bottles. The students should not be allowed to take acids from the commercial bottles.

3.9 CHECK YOUR ANSWERS

1. There are two components in a solution (a) the solvent, and (b) solute.
2. Dilution is a physical process involving addition of a solvent to the concentrated solution.
3. Molarity is the number of moles of solute present in 1 litre of the solution.
4. $M_1 V_1 = M_2V_2$

$$V_1 = \frac{M_2V_2}{M_1}$$

$$V_1 = \frac{2 \times 250}{8} = 62.5 \text{ mL}$$

EXPERIMENT-4

(a) To determine the pH of the following substances by using a universal indicator solution or pH paper.

(i) Salt solutions

(ii) Acids and bases of different dilutions

(iii) Vegetables and fruit juices

(b) To study the pH change by common ion effect in case of weak acids and weak bases using universal indicator solution or pH paper.

OBJECTIVES

After performing this experiment, you should be able to:

- find the pH of solutions of different substances by using universal indicator solution or pH paper;
- classify various substances as neutral, acidic or alkaline;
- explain the nature of substances on the basis of their pH values;
- observe changes in pH of a weak acid when a compound containing common anion with the weak acid is added to it;
- observe change in pH of weak base when a compound containing common cation with the weak base is added to it; and
- explain the significance of buffer solution.

4.1 WHAT YOU SHOULD KNOW

Solutions of weak acids and bases in water have hydronium ions [H_3O^+] and hydroxyl ions [OH^-] in different ‘Concentrations. Acidic solutions have [H_3O^+] ions greater than 10^{-7} mol L^{-1} and alkaline solutions have [OH^-] ions greater than 10^{-7} mol L^{-1} at 25°C. A neutral solution, or pure water has $[H_3O^+] = [OH^-]$. For expressing the concentration of H_3O^+ in a solution, the negative powers of 10 are involved. This inconvenient use of figures involving negative powers of 10 can be avoided by using a concept of pH scale. The pH of a solution is defined as the negative logarithm to the base 10 of the hydronium ion concentration.

$$pH = -\log_{10} [H_3O^+]$$

The pH of acidic solutions is less than 7, that of basic solution, is greater than 7 and the neutral solutions have pH = 7.

pH of a basic solution can be calculated by using the relation,

$$pH = 14 - \log_{10} [OH]$$

pH is accurately measured by a pH meter, but a reasonably good estimate can be made with the help of universal indicator solution or pH paper. These have characteristic colours depending upon the pH of the solution.

Now you would like to see the pH change of a solution of weak acid or weak base, when their salt is added to the solution. Weak acids and bases do not dissociate completely. An equilibrium exists between the dissociated and undissociated molecules. For example, for a weak acid HA, you can write the equilibrium as follows,

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$NaA \longrightarrow Na^+ + A^-$$

This equilibrium is characterised by a constant, K_a. Addition of a salt containing a common ion, say NaA to its solution causes the equilibrium to shift to the left (Le Chatelier's principle). As a consequence, the concentration of hydrogen ions gets reduced and the pH gets increased. You would study this phenomenon (common ion effect) by using acetic acid as the weak acid and sodium acetate as its salt. Similar arguments hold true for the ionization of weak base (e.g. NH_4OH). You can check this by adding NH_4Cl to NH_4OH solution (a weak base and its salt). Such mixtures of weak acid or weak bases with their respective salts are called as Buffer Solution. pH of an acidic buffer can be calculated by using the following equation

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

K_a is the acid dissociation constant and pK_a is the negative logarithm of K_a.

pH for a basic buffer (a weak base and its salt) can be calculated by using the following equation:

$$pH = 14 - pK_b - \log \frac{[Salt]}{[Base]}$$

K_b is the base dissociation constant and pK_b is the negative logarithm of K_b.

pK_a for acetic acid at 25°C = 4.76

pK_b for ammonium hydroxide at 25° C = 4.75

4.2 MATERIALS REQUIRED

(1) Apparatus	**(2) Chemicals**
Test tubes - 6, Test tube stand, Spatula, Measuring cylinder (25mL) and a Dropper.	Dilute acid and base solutions, Neutral solution (NaCl), Solution of hydrolysable salts like $CuSO_4$, NH_4C1, CH_3COONa, fruit and vegetable juices, pH paper or universal indicator solution with colour chart, Acetic acid (0.1M), and Sodium acetate

4.3 HOW TO PERFORM THE EXPERIMENT

(a) For determining the pH of a given solution proceed as follows:

Take six test tubes and label them 1 to 6. If you are using universal indicator solution, then take 3 - 4 mL each of the test solution (about one fourth of test tube) into separate labelled test tubes. To all the test tubes, add 4 to 5 drops of the universal indicator solution and observe the appearance of colour, if any. If you are using pH paper, add 1-2 drop each of the test solutions with the help of a dropper on a pH paper strip. (Alternatively, you may dip the pH paper strips into each of the test solution). Observe the colour. Compare the colour of the solution in the test tubes or on the pH papers with the standard colour chart as provided to you to find the pH. Record your observations in Table 4.1 given in section 4.6. Classify the solutions as neutral, acidic or alkaline.

(b) To study the pH change due to common ion effect proceed as follows :

Take 5 labelled test tubes and place them in a test tube stand. Take 5 mL of given acetic acid solution in each of the labelled test tubes. Add 0.5 g, 1.0 g, 1.5 g and 2.0 g of sodium acetate to test tube No. 2,3,4 and 5 respectively and dissolve to get clear solutions. Add 4-5 drops of the universal indicator solution to each of the test tubes. In case of pH paper, add 1 -2 drops of the solutions to pH papers separately with the help of separate dropper. (Alternatively, you may dip the pH paper strips into each of the test solution). Compare the colours in test solution or on pH paper developed with the colour chart and record the corresponding pH values, in Table 4.2 of section 4.6. Calculate the pH of each buffer solution you have prepared using the appropriate equation and list these in the Table 4.2.

You may try the same procedure given above at (b) to study the pH in case of basic buffer using ammonium hydroxide as a base and ammonium chloride as its salt.

4.4 PRECAUTIONS

1. Compare the colour which appears on pH paper with the standard colour chart carefully.
2. Don't add too much of the indicator solution. You may follow the instruction given on the label of the indicator bottle.

4.5 OBSERVATIONS

Table 4.1: pH values of different test solutions

S. No.	Solution	pH value
1.		
2.		
3.		
4.		
5.		
6.		

Table 4.2: pH values of different combinations of CH_3COOH and CH_3COONa

S.No.	Vol. of acetic acid (mL)	Amount of sodium acetate (g)	pH Observed	Calculated pH
1.	5.0	0.0		
2.	5.0	0.5		
3.	5.0	1.0		
4.	5.0	1.5		
5.	5.0	2.0		

4.6 CONCLUSIONS

(a) pH of solution 1 is......................and therefore, it is acidic/basic/neutral

pH of solution 2 is......................and therefore, it is acidic/basic/neutral

pH of solution 3 is......................and therefore, it is acidic/basic/neutral pH of solution 4 is.......................and therefore, it is acidic/basic/neutral

pH of solution 5 is.......................and therefore it is acidic /basic / neutral

pH of solution 6 is.......................and therefore, it is acidic/basic/neutral

(b) pH of acetic acid solution increases / decreases / remains unchanged on adding increasing amounts of sodium acetate to it.

4.7 CHECK YOUR UNDERSTANDING

1. Calculate the pH of 10^{-2} M HCl solution and 10^{-2} M NaOH solution'?

   ....

2. The pH of an aqueous sodium chloride solution is 7. Explain, what does it mean?

   ....

3. Why does copper sulphate solution (a salt solution) has a pH other than 7?

   ....

4.8 NOTE FOR THE TEACHERS

For acetic acid- sodium acetate experiment, dilute 3 mL of glacial acetic acid with water to get 100 mL solution in a measuring cylinder.

4.9 CHECK YOUR ANSWERS

1. pH = 2 for 10^{-2} M HCl

   pH= 12 for 10^{-2} M NaOH

2. NaCl is a salt of strong acid (HCl) and a strong base (NaOH). In solution it dissociates completely to give sodium and diloride ions which do not hydrolyse. In aqueous solutions the hydrogen ions come only from water and have a concentration of 10^{-7} M hence the pH = 7.

3. $CuSO_4$ solution will have a pH which is less than 7, because in water solution, $CuSO_4$ will hydrolyse to give strong acid (H_2SO_4) which makes the solution acidic in nature.

EXPERIMENT-5

To prepare a sol of

(a) Starch

(b) Ferric hydroxide

(c) Aluminimum hydroxide

OBJECTIVES

After performing this experiment, you should be able to:

- prepare a sol of starch;
- prepare a sol of ferric hydroxide;
- prepare a sol of aluminimum hydroxide; and
- explain the properties of sol of aluminium hydroxide, Starch and ferric hydroxide.

5.1 WHAT YOU SHOULD KNOW

Like gum and egg albumin, starch forms a stable hydrophilic sol. However, the preparation is carried out with boiling water for better and quicker dispersionn of starch into water.

Ferric hydroxide forms a hydrophobic sol. Hence it is prepared indirectly by the hydrolysis of ferric chloride with boiling water. The reaction takes place as follows:

$$FeCl_3 + 3H_2O \xrightarrow{\text{Boil}} Fe(OH)_3 + 3HCl$$

The ferric ions (Fe^{+3}) produced from $FeCl_3$ solution are absorbed on the surface of the particles of $Fe(OH)_3$. As a result, the colloidal particles of $Fe(OH)_3$ acquire a positive charge. Hence because of similar charge on the colloidal particles, they keep on repelling each other and cannot come together or aggregate together to form bigger particles. This prevents their coagulation and is responsible for the stability of the sol. How-ever the HCl formed simultaneously with Fe(OH), destabilizes the sol. Hence HCl, being an electrolyte is removed from the collidal sol by dialysis. Another important point in the preparation of this sol is that as the presence of ions destabilizes the sol, the flask in which the hydrolysis is to carried out must be free frorrm all types of ions.

The method of preparation of the colloidal sol of $AI(OH)_3$ is exactly similar to that of $Fe(OH)_3$ sol except that instead of $FeCl_3$, 2% $AlCl_3$ solution is used. The hydrolysis takes place as follows

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

The HCl produced is removed by dialysis. The sol formed in this case is colourless.

5.2 MATERIALS REQUIRED

Apparatus Required

Tripad stand, Burner, Beaker, Glass rod, a round bottomed flask, funnel, 250 ml. conical flask, glass tubing, rubber stoppers, clamp stand, burner, wire gauge, tripod stand, a boiling tube.

Chemical Required

Strach (about 1 g) , Ferric chloride, 2% AlCl3 solution and distilled water.

5.3 HOW TO PERFORM THE EXPERIMENT

(a) To prepare a sol of starch

(i) Grind the strarch in the mor-tar with the help of pestle. Add a little distilled water to make a thin paste of the starch.

(ii) Take about 100 mL of distilled water in a 250 mL beaker and heat it to boiling.

(iii) Add the paste of the starch into the boiling water along a glass rod and keep on stirring constantly with the glass rod.

(iv) When the addition of the paste is complete, boil the contents of the beaker for further 5 minutes.

(v) Allow the beaker to cool down to room temperature and then filter. The filtrate is the required sol of starch.

(b) To prepare a sol of ferric hydroxide.

The procedure consists of the following three steps

(i) *Cleaning of the conical flask.* The apparatus is set up as shown in the Fig. 5.1. Distilled water is taken in a round bottomed flask fitted with a funnel in its mouth. A glass tubing passes through the funnel and is held within the funnel with loose rubber stopper. Water in the flask is heated to produce steam. The conical flask is held in an inverted position ever the top of the glass tubing. As the steam hits the inside of the flask, it condenses and dissolves away any ions sticking to the inside of the flask.

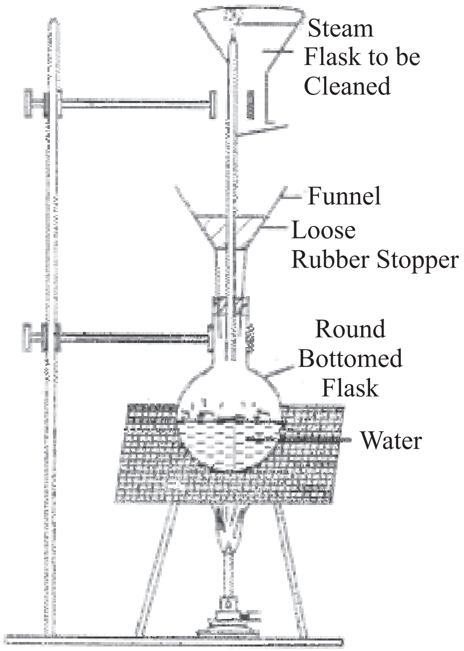


Fig. 5.1: *Cleaning of the conical flask by steaming out process.*

(ii) *Preparation of ferric hydroxide sol.* Prepare about 20 nil of 2% $FeCl_3$ solution in a boiling tube (by dissolving about 0.4 g in about 20 ml of distilled water). Filter if necessary. Take about 10 ml. of distilled water in the cleaned conical flask. Heat it to boiling. To the boiling water, add $FeCl_3$ solution dropwise with constant stirring till a deep wine red colour is obtained which is the colloidal sol of $Fe(OH)_3$.

(iii) *Purification of the ferric hydroxide sol.* Ferric hydroxide sol obtained above contains HCl as impurity. This is removed by the process of dialysis.

(c) To prepare a colloidal sol of aluminimum hydroxide

The method of preparation of the colloidal sol of $AI(OH)_3$ is exactly similar to that of $Fe(OH)_3$ sol except that instead of $FeCl_3$, 2% $AlCl_3$ solution is used.

5.4 PRECAUTIONS

(i) The starch powder should not be added directly to boiling water. Instead a thin paste should be prepared and added.

(ii) The contents of the beaker should be cooled down to room temperature before filtration.

(iii) The apparatus must be cleaned before use.

(iv) The separation of HCl (dialysis) must be carried out immediately after the preparation of the colloidal sol.

(vi) $FeCl_3$ solution should be added dropwise into the boiling water.

(vii) After the addition is complete, stir the mixture for at least five minutes more,

(viii) Allow the solution in the beaker to cool 'down to room temperature and then filter, The filtrate is the sol of gum.

(ix) Test the sol by throwing beam of light from a torch or an electric bulb with a slit placed in front of it. The path of the beam of light is visible.

5.5 OBSERVATIONS

1. Colloidal sol of starch is ....
2. Colloidal sol of ferric hydroxide is ....
3. Colloidal sol of aluminimum hydroxide is ....

5.6 CONCLUSION

Starch forms a stable hydrophilic sol. Ferric hydroxide and aluminium hydroxide forms a hydrophobic sol.

5.7 CHECK YOUR UNDERSTANDING

1. Name two colloids that can be prepared by chemical methods.

   ....

2. Differentiate between Lyophilic and Lyophobic sol.

   ....

3. How does colloidal solution differ from true solution?

   ....

5.8 NOTE FOR THE TEACHER

All the three sol preparation requires heating. One should be careful while heating the solutions at required temperature.$AlCl_3$ is corrosive in nature and it should be handled carefully.

$FeCl_3$ solution should be added dropwise into the boiling water.

5.9 CHECK YOUR ANSWERS

1. $Al(OH)_3$, $Fe(OH)_3$

2. **Lyophilic sol :**

   1. easy to prepare
   2. affinity between dispersed phase and dispersion medium.
   3. Reversible

   Lyophobic

   1. special method used for preparation
   2. No affinity between the two phases.
   3. Not reversible

3.

True solution	Colloidal solution
1. Size of solute in less than 1 nm.	1. Particle size (1–100) nm.
2. Form transparent solution and allows light to pass through them.	2. Path of light becomes visible.

EXPERIMENT-6

To study the variation of cell potential in Zn | Zn^{2+} || Cu^{2+} | Cu with change in concentration of electrolytes (CuSO4 or $ZnSO_4$) at room temperature.

OBJECTIVES

After performing this experiment, you should be able to:

- prepare solutions of copper sulphate;
- prepare solutions of zinc sulphate;
- prepare salt bridges;
- set up simple electrochemical cells and measurement of its EMF; and
- explain the importance of electrochemical cells.

6.1 WHAT YOU SHOULD KNOW

The EMF of a cell varies with the concentration of the two electrolyte solutions according to the following Nernst equation

$$E = E^\circ - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

where E = the electromotive force of the cell E° = the standard electromotive force of the cell

In the case of the Daniel, cell

$$E = E^\circ - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

6.2 MATERIALS REQUIRED

Apparatus

100 ml beakers 6, 250 ml beaker 1, measuring flasks 6, 100 ml measuring cylinder 1, connecting lead, voltmeter 1, U tubes 5, cotton.

Chemicals

Copper strip, zinc strip, copper sttlhhate, zinc sulphate, potassium chloride.

6.3 HOW TO PERFORM THE EXPERIMENT

(a) Preparation of solutions copper sulphate

1. Weigh 29.9698 of copper sulphate on a watch glass. Transfer it to a 250 ml beaker and dissolve it in water (sufficiently less than 10U ml) transfer the solution into 100 ml measuring flask and make its volume to 100 nil. It is 1.00 M CuSO4 solution and store it ‘Mark it A.
2. Prepare 1.00 ml copper sulphate solution each of 0.5 M, 0.25 M, 0-125 M and 0.0625 M strength by dilution as follows.

   To prepare 0.5 M $CuSO_4$ solution, take 50 ml of 1.0 M $CuSO_4$ solution prepared above in step 1 in another measuring flask with the help of measuring cylinder bpd make its volume to 1.00 ml. Mark it as B.

Similarly you prepare the solution of 0.25M, 0.125M and 0.0625M

(b) Preparation of zinc sulphate solution

Prepare 100 ml 1.0 M zinc sulphate solution by dissolving 28.756 g zinc sulphate in water.

(c) Preparation of salt bridges

(i) Take a U tube of glass of about 10 cm length.

(ii) Dissolve about 2 ° 0 g of agar agar completely in about 25 ml of water taken in a borosil beaker by heating it at a low flame.

(iii) Dissolve about 12 *g* of solid potassium chloride, KCI completely in the agar agar solution in water by stirring.

(iv) Fill the U tube with it and allow it to remain in an upright position till it tools and agar agar gets set.

(d) Setting up of simple electrochemical cells and measuring its EMF

Assemble the following electrochemical cells with different combinations of concentra-tions as depicted in the table.

$$Zn\ (s)\ |\ Zn^{2+}\ (aq)\ \|\ Cu^{2+}\ (aq)\ |\ Cu\ (s)$$

use separate salt bridges for different readings

(i) Take 30 ml of 1.0 M copper sulphate solution (from flask A) in a 100 ml beaker and 30 ml of 1, 0 M zinc sulphate solution in another 100 A beaker.

Notes

(ii) Immerse the metal strips in solutions containing the same metal ions.

(iii) Connect both the metal strips to each other through a voltmeter with the help of con-necting lead.

(iv) Connect both the solutions through salt bridge as shown in Fig. 6.1.

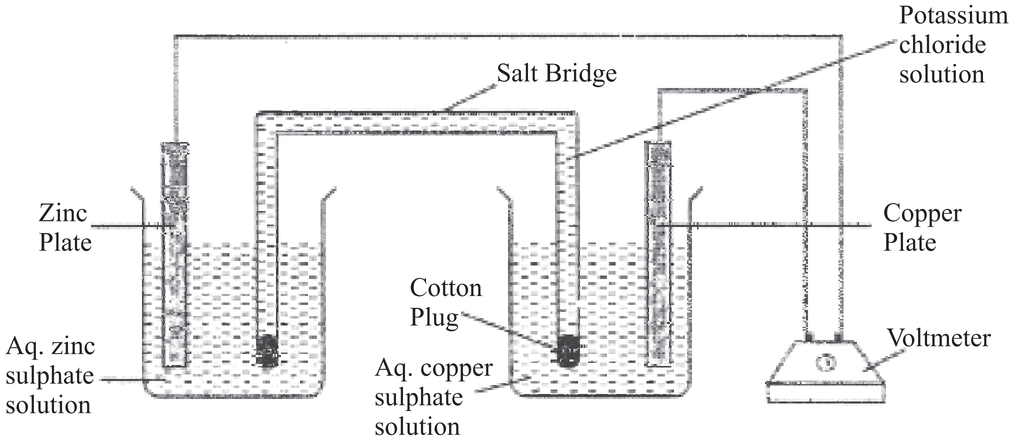


Fig 6.1: *Arrangement of the electrochemical cell* $Zn\ (s)\ |\ Zn^{2+}\ (aq)\ ||\ Cu^{2+}\ (aq)\ |\ Cu\ (s)$.

(v) Note the voltmeter reading that gives the E.M,F of the cell.

(vi) Repeat the same procedure with copper sulphate solutions of different concentrations using 0.1 M solution of zinc sulphate.

6.4 PRECAUTIONS

(i) Electrodes should be cleaned by sand paper.

(ii) There should be no air bubble in the salt bridge.

(iii) Use separate salt bridge for every cell.

(iv) Each voltmeter reading should be taken after stirring the solution.

6.5 OBSERVATIONS

S.No.	Molarity of $ZnSO_4$ (M)	Volume of $ZnSO_4$/(ml)	Molarity of $CuSO_4$ (M)	Volume of $CuSO_4$ (ml)	E* calcu lated (U)	Cell potential measured (U)
A	1	30	1•0	30	1.0	
B	1	30	0.5	30	1.09	
C	1	30	0.25	30	1.08	
D	1	30	0.185	30	1.07	
E	1	30	0.0625	30	1.06	

6.6 CALCULATION

$$*E = -\frac{0.059}{2}\log\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

Graph. Using Nernst equation, the graph of E_{cell} vs $\log\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$ should be straight line.

Plot the graph of E_{cell} measured vs $\log\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$. It should also come out to a straight line.

6.7 CONCLUSION

Cell potential decreases with decrease in concentration of copper Sulphate at room temperature.

6.8 CHECK YOUR UNDERSTANDING

1. What is a galvanic cell or a voltaic cell?

   ....

2. What is a Daniel cell?

   ....

3. Define electrode potential.

   ....

4. What is standard electrode potential?

   ....

5. When is electrode potential called reduction potential?

   ....

6. What is a redox reaction?

   ....

7. What is a salt bridge?

   ....

8. What is e.m.f, of a cell?

    ....

9. Represent a Daniel cell.

    ....

10. Name the salt in the salt bridge.

    ....

11. Name the electrode of the Daniell cell where oxidation occurs.

    ....

12. Name the electrode of the Daniel cell where reduction takes place.

    ....

13. What is the difference between the electrochemical cell and an electrolytic cell?

    ....

14. What is the function of the porous pot?

    ....

6.9 NOTE FOR THE TEACHER

Each voltmeter reading should be taken after stirring the solution. Use separate salt bridge for every cell.

6.10 CHECK YOUR ANSWERS

1. It is a device which is used to convert chemical energy into electrical energy.
2. It is a galvanic cell based on the following redox reaction

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu.$$

3. The electrode potential of an electrode is defined as its tendency to gain or lose electrons
4. The electrode potential of an electrode is called standard electrode potential if the activity of the ions is unity (or concentration is I N) and the temperature is 298 K. If the gas is involved, it should be one atmospheric pressure.
5. The electrode potential is called reduction potential if reduction takes place on the electrode with respect to normal hydrogen electrode (NHE).
6. It is a reaction in which gain and loss of electrons takes place simultaneously.

7. It is a U tube made of glass which connects the two solutions in a galvanic toll. It is filled with a solution of electrolyte such as KCl or KNO_3 to which agar agar has been added to make it a semi solid.

8. It is the difference of potentials between the electrodes of a galvanic cell.

9. $Zn \mid ZnSO_4$ (0.1 M) $\|$ $CuSO_4$ ().1M) $\mid Cu$

10. KCl or KNO_3

11. Zinc electrode.

12. Copper electrode.

13. An electrochemical cell is a device in which chemical energy is converted into electrical energy whereas electrolytic cell is a device in which electrical energy is converted into chemical energy.

14. The porous pot helps in the flow of ions and prevents the mixing of the two solutions.

EXPERIMENT-7

To estimate the enthalpy of neutralization of hydrochloric acid and sodium hydroxide.

OBJECTIVES

After performing this experiment, you should be able to:

- Define enthalpy of neutralization;
- classify various acids and bases as strong or weak acids and bases;
- observe changes in temperature during neutralization of an acid with an base;
- explain the significance of enthalpy of neutralization.

7.1 WHAT YOU SHOULD KNOW

Heat is evolved during neutralization of an acid with an alkali. Known quantities of the standard solutions of an acid and alkali arc mixed and the change in temperature is noted and from this, the enthalpy of neutralization is calculated. Enthalpy of neutralization is the heat evolved when one gram equivalent of the acid is completely neutralized by one gram equivalent of a base in dilute solutions. Neutralization involves bond formation between $H^+(aq)$ and $OH^-(aq)$ to form water molecule. For example in the neutralization of HCl and NaOH

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l),\ \Delta H = -57KJ$$

7.2 MATERIALS REQUIRED

Apparatus

Polythene bottle (250 ml.) with mouth, Rubber cork (with two holes) to fit in the mouth of polythene bottle, thermometer (1/10th degree), stirrer, with a cork and a handle, magnifying glass and 100 ml graduated cylinder.

Chemical Required

dil HCl, dil NaOH

7.3 HOW TO PERFORM THE EXPERIMENT

(a) Determination of water equivalent of the bottle.

(b) Determination of the enthalpy of neutralization.

(i) Take polythene bottle fitted with a thermometer (1/10th degree) and stirrer.

(ii) Remove the cork and by means of a graduated cylinder add 100 ml. of the 0.5 N acid solution into the bottle and cork the bottle,

(iii) Fix the thermometer in the cork in such a way that its bulb is just near the bottom of the bottle.

(iv) Place 100 ml. of 0.5 N sodium hydroxide solution in a polythene beaker.

(v) Note the temperature of each of the two solutions after every one minute till solutions attain same temperature. If the temperature of bottle the solutions is not the same, make it so by stirring the solution with lower temperature with a .tube containing hot water.

(vi) Note this temperature. Let it be t_1°C.

(vii) When both the solutions acquire the same temperature (t°C), transfer 100 ml. of 0.NaOH solution from the polythene beaker into the acid solution in the polythene bottle quickly without any loss of time. Ensure that there is no splashing.

(viii) Immediately fit the cork having the thermometer and the stirrer in the mouth of the polythene bottle and stir well gently.

(ix) Note the temperature after every one minute till it becomes constant.

Note down the maximum temperature (t_0 0.1°) attained (t_2°C)

7.4 PRECAUTIONS

(i) Temperature should be no ed very carefully. Greater the accuracy with which the temperatures are measured, smaller will be the percentage error.

(ii) The final temperature should be noted after stirring the mixture well.

7.5 OBSERVATIONS

Record observation for water equivalent. Suppose it comes out to be W.

Volume of 0.5 N HCl = 100 ml.

Volume of 0.5 N NaOH = 100 ml

Total volume of the mixture = 200 ml

Initial temperature of HCl and NaOH solution = t_1°C

Final temperature after mixing = t_2°C

Rise in temperature = $(t_2 - t_1)$°C

Heat capacity of water = 4.18 J

Calculations

Heat evolved during neutralization

$$= (200\ W)\ (t_2 - t_1) \times 4.2 \text{ Joules}$$

$$= x \text{ Joule (say)}$$

Thus x Joules of heat is evolved by the neutralization of 100 ml. of 0.5 N HCl

∴ Enthalpy of neutralization for 1000 ml. of 1 N HCl (i.e., one gram equivalent)

$$= \frac{x}{100} \times 1000 \times \frac{1}{0.5} = 20x \text{ Joule}$$

$$= \frac{20x}{1000} \text{ kJ} = \frac{x}{50} \text{ kJ}$$

7.6 CONCLUSION

The heat of neutralisation of sodium hydroxide and HCl is .... kJ.
[This value is 57.3 kJ per gram, equivalent for all strong acids and bases),
Percentage error involved = ...

7.7 CHECK YOUR UNDERSTANDING

1. Define enthalpy of neutralization?

   ....

2. Heat of formation of water from H+ and OH- is same as enthalpy of neutralization of a strong acid and a strong base. Why?

   ....

3. Why enthalpy of neutralization of acetic acid is less than the hydrochloric acid?

   ....

7.8 NOTE FOR THE TEACHER

Temperature should be noted very carefully. Greater the accuracy with which the temperatures are measured, smaller will be the percentage error.

7.9 CHECK YOUR ANSWERS

1. It is defined as the enthalpy cahnge when one gram equivalent of the acid is completely neutralized by one gram equivalent of a base in dilute solutions.
2. This is due to common reaction taking place in these two reactions

   $H^+(aq) + OH^- (aq) \longrightarrow H_2O(l),\ \Delta H = -57KJ$
3. Acetic acid is a weak Acid. It does not completely ionizes in water. Fraction of hydration energy is used in the ionization of acetic acid. Hence , less heat is produced as compared to hydrochloric acid.

EXPERIMENT-8

To study the shift in equilibrium between ferric ions and thiocyanate ions by increasing/ decreasing the concentration of these ions.

OBJECTIVES

After performing this experiment, you should be able to:

- perform dilution of the solutions using measuring cylinder;
- compare the intensity of colours in two solutions visually;
- predict the direction in which the equilibrium will shift if the concentration of any reactant is increased or decreased;
- predict the direction in which the equilibrium will shift, if the concentration of any product is increased or decreased.

8.1 WHAT YOU SHOULD KNOW

A reversible reaction never reaches the completion stage but results in an equilibrium state in which concentrations of all the reactants and products become constant. This equilibrium is dynamic in nature and it is the result of two opposite reactions occurring simultaneously and at the same rate. However, no 'net' change occurs in the system.

According to Le Chatelier's Principle "*when any system at equilibrium is disturbed by changing concentrations, temperature or pressure, the equilibrium shifts either in forward or backward direction and a 'net' change occurs in it so as to decrease the effect of the disturbing factor*" .

Considerthe following equilibrium

$$A + B \rightleftharpoons C + D$$

The equilibrium constant for it is given by

$$K = \frac{[C][D]}{[A][B]}$$

When concentration of A or B is increased, the equilibrium will shift in forward direction, so that some quantity of A and B is consumed and corresponding quantities of products C and D are formed. When concentration of A or B is decreased, (he quilibrium will shift in backward direction. Now same quantity of C and D is consumed and corresponding quantities of reactants A and B are produced. Similarly when concentration of products C or D is increased, the equilibrium will shift in the backward direction and when it is decreased it will shift in the forward direction.

Ferric ions react with thiocyanate ions to form a blood red coloured complex, $[Fe(CNS)]^{2+}$, and the following equilibrium is established.

$$Fe(aq)^{3+} + CNS^{-}(aq) \rightleftharpoons [Fe(CNS)]^{2+}(aq)$$

pale yellow colourless   deep blood red

The effect of change in concentration of Fe^{3+} or CNS^{-} ions on this equilibrium can be studied easily. If this equilibrium shifts in forward direction, more quantity of the complex will be formed and the colour of the solution will become more intense. Similarly, when the equilibrium shifts in backward direction, some quantity of the complex will break and the colour of the solution will become light.

8.2 MATERIALS REQUIRED

(1) Apparatus	(2) Chemicals
Test tube stand	0.02 M KCNS Solution
Test tubes - 5	0.02 M $Fe(NO_3)_3$ Solution
Measuring cylinder - 10 mL	
Measuring cylinder - 50 mL	
Wash bottle	
White glazed tile or a sheet of plain white paper.	

8.3 HOW TO PERFORM THE EXPERIMENT

1. Take five clean and dry test tubes, number them from 1 to 5 and keep them in a test tube stand. Mark the test tube number 3 as "Reference Tube".
2. Take 10 mL Fe $(NO_3)_3$ solution (0.02 M) in a clean and dry 50 mL measuring cylinder. Fill it up with distilled water upto 40 mL mark and stir to mix. Take 5 mL of this diluted (0.005 M) Fe $(NO_3)_3$ solution in each of the five test tubes.

3. In a clean and dry 10 mL measuring cylinder take 10 mL KCNS solution (0.02 M). Out of it, add 5 mL solution to test tube, number 1 .
4. The measuring cylinder now contains 5 mL of 0.02 M KCNS solution. Add distilled water to make the volume upto 10 mL mark in the measuring cylinder with a wash bottle and stir to mix. You get KCNS solution of 0.01 M concentration. Pour 5mL of 0.01 M KCNS solution into test tube number 2.
5. Add distilled water in the remaining solution to make the volume upto 10 mL which will give a solution 0.005 M and transfer 5 ml of this solution to test tube number 3.
6. Again add distilled water in the remaining solution in the measuring cylinder to obtain a 10 mL solution of 0.0025 M KCNS and transfer 5 mL of this solution to test tube number 4.
7. Similarly, get 10 ML of 0.00125M solution by adding distilled water to the measuring cylinder containing 0.0025M KCNS solution. Transfer 5 mL of this solution to the fifth test tube.
8. Shake all the five test tubes to mix the solutions and keep them back on test tube stand.
9. Compare the intensity of red colour in test tube number 1 with that in'Reference Tube' (Number 3). For this purpose, hold the two tubes against white background of a glazed tile or a plain white paper. Find out whether the colour intensity is more or less than the Reference tube and record it in Table 8.1 given in section 8.6.
10. Similarly, compare the intensity of red colour in the remaining test tubes numbered 2,4 and 5 and record the observations in Table 7.1.
11. Similarly, we can study the effect of [Fe^{3+}] on the equilibrium by performing another experiment where we vary the concentration of Fe^{+++} while keeping the concentration of [CNS^-] constant. For this, use KCNS solution in step 2 and $Fe(NO_3)_3$ solution in steps 3 to 8. Record your observations in Table 7.2 given in section 7.6.

8.4 PRECAUTIONS

(1) All glass apparatus (test tubes and measuring cylinders) should be thoroughly clean, otherwise the solutions will stick to their sides and not mix properly.

(2) Volumes of solutions and distilled water should be measured carefully so that the solution of desired concentration can be obtained.

(3) Mixing of solution and water or of two solutions should be done by gentle shaking and avoiding their splashing.

8.5 OBSERVATIONS

Table 8.1: Effect of concentration of CNS^- ion on the equilibrium

Test tube No.	**Conc. of $Fe(NO_3)_3$ soln. used (mol^{-1})**	**Conc. of KCNS soln. used (mol^{-1})**	**Intensity of red colour as compared to the reference tube (more/less)**	**Shift in equilibrium (forward/ backward)**
1	0.005	0.02	....	....
2	0.005	0.01	....	....
3	0.005	0.005	Reference	....
4	0.005	0.0025	....	....
5	0.005	0.00125	....	....

Table 8.2: Effect of concentration of Fe^{3+} ions on the equilibrium

Test tube No.	**Conc. of $Fe(NO_3)_3$ soln. used (mol^{-1})**	**Conc. of KCNS soln. used (mol^{-1})**	**Intensity of red colour as compared to the reference tube (more/less)**	**Shift in equilibrium (forward/ backward)**
1	0.02	0.005	....	....
2	0.01	0.005	....	....
3	0.005	0.005	Reference	....
4	0.0025	0.005	....	....
5	0.00125	0.005	....	....

8.6 CONCLUSIONS

1. When any reactant concentration is increased, the equilibrium shifts in ________ direction.
2. When any reactant concentration is decreased, the equilibrium shifts in —— —— direction.

8.7 CHECK YOUR UNDERSTANDING

1. State Le Chalelier's Principle.

   ....

2. Why is the equilibrium reached by a reversible reaction called dynamic equilibrium?

   ....

3. What will happen to the equilibrium reached by mixing $Fe(NO)_3$ and KCNS solutions, if a few drops of $FeCl_3$ solution are added to it.

   ....

4. What will happen if some $[Fe(SCN)]^{2+}$ ions are removed from the above equilibrium?

   ....

5. What will be the effect of addition of a few drops of dilute NH_4OH solution to the above equilibrium? Give reasons.

   ....

8.8 NOTE FOR THE TEACHER

1. The teacher should help the students while doing the experiments.
2. Chemicals should be supplied in pure state.

8.9 CHECK YOUR ANSWERS

1. Le Chatelier's Principle states, when any system at equilibrium is disturbed by changing concentrations, temperature or pressure, the equilibrium shifts in a direction so as to nullify or reduce the effect of that change.
2. It is because even after equilibrium is established, two opposite reactions continue to occur but at the same rate.
3. The equilibrium will shift in forward direction as the concentration of reactant Fe^{3+}ion will increase on addition of $FeCl_3$
4. As $[Fe(SCN)]^{2+}$ ions (product) are removed the equilibrium will shift in forward direction.
5. The equilibrium will shift in backward direction. It is because OH^- ions from NH_4OH will combine with some Fe^{3+} ions and form brown precipitate of $Fe(OH)_3$. Thus reactant (Fe^{3+} ions) concentration will decrease and the equilibrium will shift in backward direction.

EXPERIMENT-9

(a) To study the effect of concentration on the rate of reaction between sodium thiosulphate and hydrochloric acid.

(b) To study the effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid.

OBJECTIVES

After performing this experiment, you should be able to:

- observe the effect of concentration of reactants on rates of reactions;
- predict the effect of concentration of reactants on rates of reactions;
- observe the effect of temperature on rates of reactions;
- predict the effect of temperature on rates of reactions.

9.1 WHAT YOU SHOULD KNOW

Concentration and temperature are two important factors which affect the rate of a reaction. Effect of concentration on rate of a reaction is given by its rate law.

For a general reaction

$$aA + bB \longrightarrow \text{Products}$$

The rate law may be written as, rate = $= k[A]^a[B]^b$

Here, a and b are the orders of the reaction with respect to reactants A and B respectively. The overall order, n, is given by

$$n = a + b$$

And k is the rate constant of the reaction.

Generally, a and b are positive integers. However, in some cases they may be fractions or zero, Thus generally speaking, on increasing the concentration of a reactant, the rate of reaction increases. The rate of reaction also depends upon the temperature. Arrhenius equation gives the relationship between the two

$$k = A.e^{-Ea/RT}$$

where, *k* is the rate constant of the reaction at temperature *T*. *A* and *Ea* are constants for a given reaction. While *A* is known as Arrhenius factor and *Ea* as activation energy. Activation energy is the minimum energy which the reactant molecules must possess over and above of their average energy in order to undergo chemical change. On raising the temperature, more reactant molecules possess sufficient energy required for reaction. Hence, the rate of the reaction increases.

The reaction between sodium thiosulphate and hydrochloric acid occurs according to the following equation,

$$Na_2S_2O_3(aq) + 2HCl(aq) \longrightarrow 2\,NaCl(aq) + H_2O(l) + SO_2(g) + S(s)$$

As the reaction proceeds, the amount of precipitated sulphur increases, the solution becomes increasingly turbid and at a certain stage it becomes opaque. This stage can be fairly judged accurately by a simple method. The flask containing the reaction mixture is kept on a sheet of white paper on which a cross is marked in ink and when the reaction mixture becomes opaque, the cross is no longer visible. Rate of the reaction is inversely proportional to the time interval between the start of the reaction and the disappearance of the cross mark.

Effect of concentration of each reactant can be studied by changing the concentration of one reactant while keeping that of the other constant. The time for disappearance of cross mark (X) is noted in each case. The inverse values of the time intervals are compared. Effect of temperature can be studied by starting the reaction with the same concentrations of both the reactants at different temperatures. The inverse values of the time intervals for the cross mark to disappear are compared.

9.2 MATERIALS REQUIRED

(1) Apparatus	**(2) Chemicals**
four 150 mL conical flasks, 50 mL measuring cylinder, Thermometer, - 10 to 110°C Stop watch Bunsen burner Tripod stand Wire gauze Sheet of plain white paper	Dilute HCl - 1 M Sodium thiosulphate solution- 0.1M

9.3 HOW TO PERFORM THE EXPERIMENT

(a) Effect of Concentration

Take three clean and dry conical flasks and mark them 1, 2 and 3. If necessary, clean the flasks with dilute nitric acid and then wash with water thoroughly before using them. With the help of measuring cylinder, take 30 mL distilled water in the conical flask 1 and 20 mL-each in flask 2 and flask 3. Rinse the measuring cylinder with the solution of sodium thiosulphate and add 10 mL of it each in flask 1 and flask 2 and 20mL-in the flask 3. Using ball point pen, mark a cross on a sheet of plain white paper, lay it on the table and keep the flask 1 on it, so that it covers the cross - mark. Make sure that the flask is absolutely dry from outside and base, before keeping it on paper. If necessary, wipe it dry with a piece of filter paper. Wash the measuring cylinder with water and rinse it with hydrochloric acid. Now add 10 mL of hydrochloric acid to the flask 1 , swirl it to mix the solutions and simultaneously start the stop watch. Keep the flask back on the white paper. Observe the cross mark through the solution and stop the watch as soon as it disappears. Record the time interval and its inverse in the Table 9. 1 (given in section 9.5) and reset the zero of the stop watch for next reading. Repeat the procedure, first, using flask 2 and adding 20 mL hydrochloric acid to it and then with flask 3 and adding 10 mL hydrochloric acid. Record the readings in Table 9.1.

(b) Effect of Temperature

Take three clean and dry conical flasks and mark them 1, 2 and 3. If necessary, before using, clean them with dilute nitric acid and wash with water thoroughly. Using a clean measuring cylinder take 30 mL distilled water in each flask. Rinse the measuring cylinder with sodium thiosulphate solution and add 10 mL of it in each of these three conical flasks. Using a ball-point pen, make a crossmark on a plain white sheet of paper and lay it on table. Wash the measuring cylinder with water and rinse with hydrochloric acid. Take another conical flask (other than the three marked flasks) and take 10 mL hydrochloric acid in it using the measuring cylinder.

Heat both the flasks (flask No. 1 containing $Na_2S_2O_3$ and the other containing HC1) to a temperature of about 40° C separately on two tripod stands with wire gauze on them. Place the flask 1 on the sheet of white paper covering the cross-mark. Quickly pour the hot HC1 solution into the flask 1 . Mix the solutions by swirlling and start the stop watch simultaneously. Keep it back on the white sheet of paper. Measure the temperature of the mixture solution and record in table 9.2 (given in section 9.5). Observe the cross mark through the solution and stop the watch as soon as it disappears. Record the time interval and its inverse in Table 9.2. Reset the zero of the stop watch for next reading. Repeat this procedure two more times. First time use the flask 2, and heat the solutions to about 50°C. Second time use flask 3 and heat the solutions to about 60°C. Record the observations in table 9.2.

9.4 PRECAUTIONS

1. All conical flasks should be of same capacity and total volume of reaction mixture should be same for each observation.
2. Same sheet of white paper with cross marked on it should be used in all the observations.
3. Start the stop watch as soon as the solutions are mixed. Stop the stop watch as soon as the cross -mark just disappears.
4. While placing on white paper, the base and outer surface of the conical flask should be absolutely dry, else, the white paper or the cross marked on it would be spoiled.
5. Wash the conical flasks immediately after taking the reading with the help of dilute HNO_3 first and then with water. If not washed immediately, the sulphur starts depositing on the walls of the flask and makes the cleaning more difficult.

9.5 OBSERVATIONS

Table 9.1: Effect of concentration on rate of reaction between HCl and $Na_2S_2O_3$

S.No.	Volume of				Initial Conc. of		Time	Time
	Water 0.1	M$Na_2S_2O_3$	1MHCl	Total	$Na_2S_2O_3$	HCl		inverse
	mL	mL	mL	mL	mol^{-1}	mol^{-1}	s	s^{-1}
1.	30	10	10	50	....	....	....	....
2.	20	10	20	50	....	....	....	....
3.	20	20	10	50	....	....	....	....

Table 9.2: Effect of temperature on rate of reaction between HCl and $Na_2S_2O_3$

S.No	Volume of				Temperature	Time	Time
	0.1M$Na_2S_20_3$	Water	1MHCl	Total			inverse
	mL	mL	mL	mL	°C	s	s^{-1}
1.	10	30	10	50	......	......	......
2.	10	30	10	50	......	......	......
3.	10	30	10	50	......	......	......

9.6 CONCLUSION

1. The rate of reaction increases/decreases/remains unchanged when concentration of either sodium thiosulphate or HC1 is increased while keeping the other constant.

2. The rate of the reaction increases/decreases/remains unchanged when it is carried out at higher temperature while keeping all other factors like concentration constant.

9.7 CHECK YOUR UNDERSTANDING

1. What are the initial concentrations of sodium thiosulphate and HCl in a solution obtained by mixing 10 mL of 0.1 M$Na_2S_2O_3$, 20 mL of M HCl and 20 mL water. Assume that no reaction has started as yet.

   ....

2. While studying the effect of temperature on the rate of reaction, same volumes of sodium thiosulphate and HCl solutions are used in each experiment. Why it is so?

   ....

3. Why does increase in temperature generally increases the rate of a reaction?

   ....

4. What will be the effect of decrease in temperature on rates of reactions which occur in biological processes? Give one example where it is used.

   ....

5. Sometimes the solution of sodium thiosulphate starts becoming turbid even before adding HCl to it. What can be its reason?

   ....

9.8 NOTE FOR THE TEACHER

Emphasize the importance of proper cleaning of conical flasks, specially after the flask has been used once. The students may be told that sulphur precipitated in the reaction sticks to the walls of the flask and is not easily removable. Therefore, washing should be done immediately after taking the reading. If simple washing by water does not remove the sulphur coating, washing may first be done with very dilute HNO_3 and then with water. Washing with water must be thorough so that HC1 (used in the experiment) or HNO_3 (used for washing) are completely washed away. Otherwise, these will start the reaction in the next reading even before HCI is added.

9.9 CHECK YOUR ANSWERS

1. Final concentrations can be calculated by using the relation $M_1 V_1 = M_2 V_2$ where M_1 and V_1 are the molarity and volume of the initial solution and

M_2 and V_2 are the molarity and volume of the final solution obtained after dilution.

(a) Molarity of $Na_2S_2O_3$

$M_1 = 0.1M$ $\qquad V_2 = 10 + 20 + 20 = 50$ mL

$V_1 = \mathbf{10}$ mL $\qquad M_2 = ?$

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.1 \text{ x } 10}{50} = 0.02M$$

(b) Molarity of HCl

$M_1 = 1M$ $\qquad V_2 = 10 + 20 + 20 = 50$ mL

$V_1 = 20$ mL $\qquad M_2 = ?$

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.1 \text{ x } 20}{50} = 0.4 \text{ M}$$

2. If different volumes of sodium thiosulphate or HCl solutions are used besides temperature, their concentrations would also be different in different observations. Now the rate of the reaction would be affected by both the factors, and not only by temperature alone which is the aim of the study.

3. On raising the temperature, more reactant molecules possess the sufficiently high energy to overcome the activation energy barrier of the reaction. This increases the rate of the reaction.

4. It will decrease the rate of reactions occurring in biological proceses. It is used in refrigeration or cold storage of food articles to increase their shelf life (or to keep them fresh for longer period of time) by slowing down the bacterial decay which occurs in them.

5. It can be due to improper washing of conical flask with some HCl (from the previous reading) or HNO_3 used for washing of the flask) still remaining in it. The acid left in conical flask reacts with sodium thiosulphate and the solution becomes turbid due to the formation of sulphur.

EXPERIMENT-10

To prepare crystals of

(a) Ferrous ammonium sulphate (Mohr salt), $FeSO_4.(NH_4)2SO_4.6H_2O$.

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

(c) Potassium ferric oxalate $K_3[Fe(C_2O_4)_3].3H_2O$.

OBJECTIVES

After performing this experiment, you should be able to:

- set up an apparatus for preparation of these crystals;
- prepare crystals of Ferrous ammonium sulphate (Mohr salt);
- prepare crystals of Potash alum;
- prepare crystals of Potassium ferric oxalate;
- explain the principle involved in the preperation of these salt.

10.1 WHAT YOU SHOULD KNOW

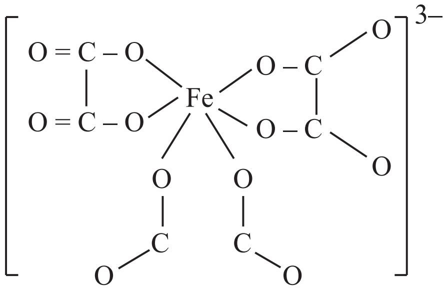
Mohr salt is a double salt containing ferrous sulphate and ammonium sulphate in equimolar amounts. Hence when these two salts are mixed in the ratio of their molecular masses and then a hot saturated solution prepared, filtered and the hot filtrate cooled, light blue or green crystals of Mohr salt (octahedral in shape) are obtained.

$$\underset{278}{FeSO_4.7H_2O} + \underset{132}{(NH_4)_2.SO_4} \longrightarrow \underset{\text{Mohr salt}}{FeSO_4(NH_4)2SO_4.6H_2O} + H_2O$$

Potash alum is a double salt of assium sulphate and aluminium sulphate, Hence it is prepared by taking the amount of K_2SO_4 and $Al_2(SO_4)_3.18H_2O$ in the ratio of their molecular masses, preparing their concentrated solutions separately followed by mixing the con-centrated solutions and heating the resulting solution to the crystallization point when white crystals of 1 otash alum (octahedral in shape) are obtained. The rea ction may be represented as follows

$$\underset{174}{K_2SO_4} + \underset{666}{Al_2(SO_4)_3.18H_2O} + 6H_2O \longrightarrow \underset{\text{Potash alum}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

Potassium ferric oxalate is an inorganic complex which dissociates in a suitable solvent to give simple potassium (K^+) and the complex ferric oxalate, $[Fe(C_2O_4)_3]^{3-}$ ions. In the complex ferricoxalate ion, ferric (Fe^{3+}) ion is linked to three oxalate groups $(C_2O_4)^{2-}$ through six covalent bonds as shown below



Three molecules of water of hydration are present in potassium ferric oxalate.

It is prepared by heating solid ferrous oxalate with saturated solution of potassium oxalate at 40°C by adding required amount of 3% hydrogen peroxide slowly in two lots under stiring. Finally the solution is heated to boiling. Then requisite amount of 1 M oxalic acid is added dropwise to the boiling solution till solt.:ion becomes green. It is cooled to get crystalline salt.

10.2 MATERIALS REQUIRED

Apparatus

Two 250 ml beakers, 250 ml conical flask, glass rod, funnel, filter paper, wire gauze, tripod stand. Bunsen burner.

Chemicals required

Ferrous ammonium salt (Mohr's salt)	5-5g
$FeSO_4(NH_4)_2SO_46H_2O$	
Sulphuric acid (4 M)	5 ml
Oxalic acid	3 g
Oxalic acid (1 M)	30 ml
Potassium oxalate	5 g
Hydrogen peroxide	Small amount
Ethyl alcohol	small amount

Potassium sulphate, K_2SO_4	3 g approx.
Aluminium sulphate, $Al_2(SO_4)_3.18H_2O$	12 g approx.
Dilute sulphuric acid	1 ml approx.
Ferrous sulphate crystals ($FeSO_4.7H_2O$)	10 g approx.
Ammonium sulphate crystals, $(NH_4)_2SO_4$	5 g approx.
Dilute sulphuric acid	2-3 ml
Ethyl alcohol	2-3 ml

10.3 HOW TO PERFORM THE EXPERIMENT

(a) Preparation of crystals of Ferrous ammonium sulphate (Mohr salt), $FeSO_4.(NH_4)_2SO_4.\ 6H_2O$.

(i) Weigh 10 g of ferrous sul-p Tiate crystals and 5 g of ammonium sulphate crys-tals on two separate pieces of paper on a rough balances

(ii) Transfer the amounts thus weighed into a 250 **ml** beaker.

(iii) Boil about 20-30 ml of distilled water in the second beaker for about 5 minutes to remove the dissolved air (as otherwise, it may oxidize fer-rous sulphate to ferric sulphate in presence of sulphuric acid),

(iv) Add the boiling water to the contents of the first beaker, Immediately add 2-3 **ml** of dilo $HASO_4$ (to check the hydrolysis of ferrous sulphate by the boiling water).

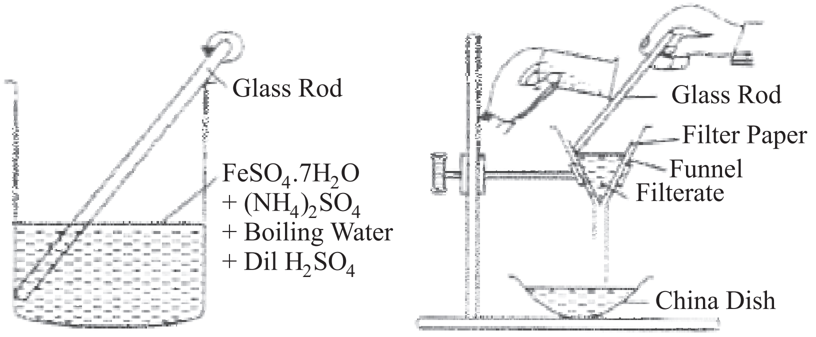
(v) Stir the contents of the above beaker till the salts dissolve,

(vi) Filter the above solution directly into a china dish to remove the suspended or the undissolved impurities.

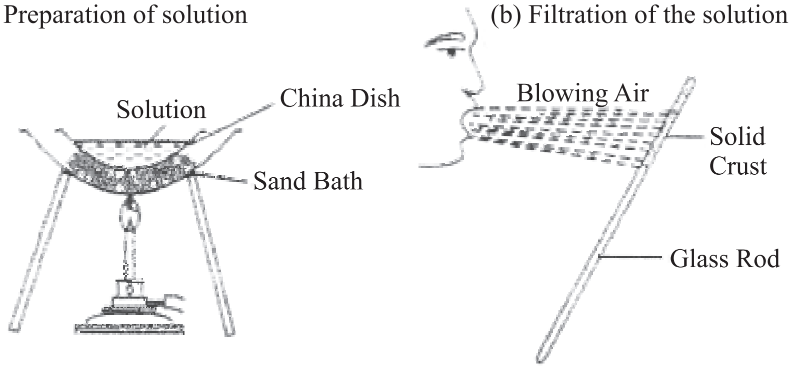
(vii) Heat the china dish containing the solution on a wire gauge or a sand bath to concentrate it till the crystallization point is reached. This is tested by dipping an end of a glass rod into the hot solution and then blowing air over it from the mouth to cool it. If a solid crust is formed on the rod, the crystallization point is reached.

(viii) Allow the china dish to cool either directly in the air (for slow cooling to get big sized crystals) or by placing it over the mouth of a beaker filled with water (for fast cooling if samll sized crystals are re-quired). In the latter case,’ the water of the beaker has to be replaced 2-3 times. However in either case, the china dish must be kept undis-turbed during cooling. Light green or blue coloured crystals will be obtained.

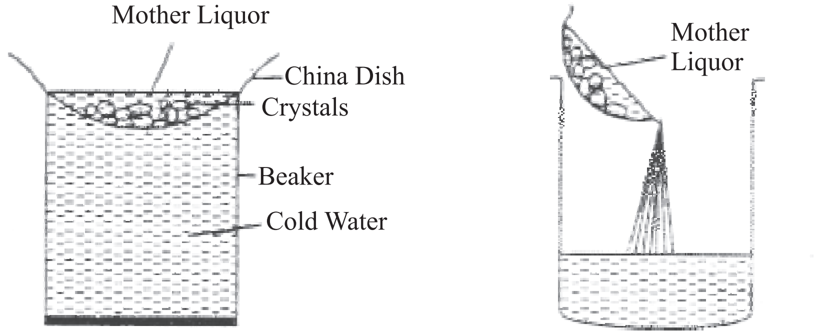
(ix) Separate the crystals from the mother liquor by decantation (as shown in Fig. 10.1.



(a) Preparation of solution (b) Filtration of the solution



(c) Concentration of the solution (d) Testing the crystallization point.



(e) Cooling in the hot concentrated solution (f) Separation of crystals from another liquor by dacantation.

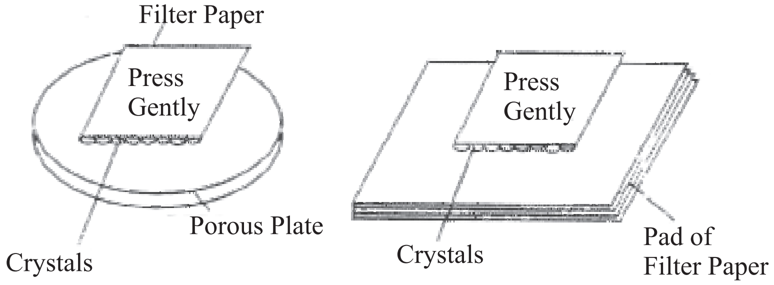


Fig. 10.1 *Various steps in the preparation of Mohr salt*

(x) Wash the crystals with a little alcohol to remove the sulphuric acid sticking to the surface of the crystals.

(xi) Transfer the crystals on a pad of fil-ter papers or a clean porous plate and dry them by pressing them gently with filter papers to avoid cracks in crystals.

(xii) Weigh the crystals obtained on the rough balance. Compare it with the theoretically calculated value.

(b) Preparation of crystals of Potash alum K_2SO_4. $Al_2(SO_4)_3.24H_2O$

(i) Take about 3 g of potassium sulphate crystals in a 250 ml beaker. Add about 25 ml of distilled water. Stir with a glass rod to dis-solve the salt. Heat if necessary.

(ii) Take about 12 g of aluminium sulphate crystals in another beaker. Add about 25 ml of distilled water and a few drops of dil. sulphuric acid (to prevent the hydrolysis of aluminium sulphate). Stir with a glass rod to dissolve the salt. Heat if necesary. Filter if the solution is not clear.

(iii) Mix the two solutions by transferring them into a china dish. Heat the china dish gently on a water bath to conceiarate the solution upto the crystallization point (Test as in Expt. 6.1).

(iv) Allow the solution in the china dish to cool undistrubed either in the air overnight or by placing it over the mouth of a beaker filled with cold water for some time. White octahedral crys-tals of potash alum are obtained.

(v) Separate the crystals by decanting off the mother liquor.

(vi) Wash the crystals with a smalll amount of ice cold water.

(vii) Finally dry the crystals either by placing them between folds of filter paper.

(c) Preparation of crystals of Potassium ferric oxalate $K_3[Fe(C_2O_4)_3].3H_2O$.

Preparation of ferrous oxalate, $Fe(C_2O_4).2H_2O$.

(i) Dissolve 5.5 g of Mohr's salt (ferrous ammonium sulphate), $Fe(NH_4)_2(SO_4)_26H_2O$, in 17 ml of warm water in 250 ml.

(ii) Add a few drops of (4 M) sulphuric acid to the solution necessary for complete dissolution of Mohr's salt to avoid hydrolysis of ferrous ion in water.

(iii) In another 250 ml beaker dissolve about 3g of oxalic acid in 30 ml of water to prepare 30 ml of oxalic acid solution.

(iv) Add 30 ml of oxalic acid solution to the ferrous sulphate solution.

(v) Heat the mixed solution to boiling with ion continuous stirring.

(vi) Remove the beaker from the flame and allow the precipitate of ferrous oxalate $Fe(C_2O_4)$ $2H_2O$ to settle.

(vii) Decant the supernatant liquid and leave the precipitate in the beaker.

(viii) Wash the precipitate. This is done by heating the precipitate with 30 ml of distilled water to 50°C, allowing the precipitant to settle down and decanting off the supernatant liquid. Better repeat this waslupg procedure once again.

Preparation of potassium ferric oxalate $K_3[Fe(C_2O_4)_3]3H_2O$.

(i) Prepare a saturated solution of potassium oxalate solution.

(ii) Take the ferrous oxalate precipitate on a 250 ml beaker and add to it 11 ml of saturated solution of potassium oxalate.

(iii) Heat the mixture to 40°C and add 3np. 20 ml of 3% hydrogen peroxide (H_2O_2) slowly with stirring.

(iv) Add another 20 ml of 3% H_2O_2 and heat the mixture to boiling.

(v) Add 10 ml of 1 M oxalic acid (the first 5 ml at once and the last 5 ml dropwise) to the boiling solution continue heating until the colour of the solution becomes green.

If the required colour is not obtained, repeat the whole procedure.

Crystailisation of potassium ferric oxalate

(i) Filter the hot green Coloured solution into a conical flask.

(ii) Add to the filtrate about 20 ml of ethyl alcohol and heat the mixture to 70°C. Add some more alcohol dropwise until the solution just term cloudy.

(iii) Cool the solution and let the crystals of the complex settle down.

If the crystals are obtained, suspend a short piece of thread into the liquid and gently cork the flask. Keep the flask in the cupboard. After a few days good crystals of potassium ferric oxalate will be formed.

(iv) Filter, dry (by pressing between the sheets of filter paper) and weigh the potassium ferric oxalate.

10.4 PRECAUTIONS

(i) To avoid oxidation of fer-n sulphate boiled water (containing no dis-solved air) should be used to make the solution.

(ii) Dilute sulphuric acid must be added immediately after adding water into the mixture of the salts. Sulphuric acid prevents hydrolysis of $FeSO_4$.

(iii) The solution should not be heated beyond the crystallization point otherwise a solid mass will be formed.

(iv) The solution should not be distrubed while being cooled for crystallization. A slight dis-turbance may curie change in the shape and yield of the crystals.

(v) Cover the china dish while cooling the concentrated solution.

(vi) Concentrated solutions of K_2SO_4 and $Al_2(SO_4)_3$ should be taken.

(vii) Dil. H_2SO_4 must be added to $Al_2(SO_4)_3$ solution to prevent its hydrolysis.

(viii) The solution should be kept undisturbed for crystallization.

(ix) The solution should not be concentrated beyond the crystallization point.

10.5 OBSERVATIONS

Yield .... g

Theoretical value .... g

10.6 CONCLUSION

Crystals of Ferrous ammonium sulphate (Mohr salt), $FeSO_4.(NH_4)2SO_4.6H_2O$ ....

Crystals of Potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$ ....

Crystals of Potassium ferric oxalate ....

10.7 CHECK YOUR UNDERSTANDING

1. Name the two types of solids.

   ....

2. Rubber or glass is a solid. NaC1 is also a solid. What is the difference between the two ?

   ....

3. What is the difference between an amorphous substance and a crystalline substance ?

   ....

4. Why is crystallization done?

   ....

5. What is a double salt ? Give one example.

   ....

6. What are alums ?

   ....

7. What is the formula of potash alum ?

   ....

8. What is the common name of potash alum?

   ....

9. In the preparation of a double salt, in what ratio are the salts mixed ?

   ....

10. What is the liquid present along with the crystals called ?

    ....

11. In the preparation of Mohr salt, water is boiled before using it for making solutions ?

    ....

10.8 NOTE FOR THE TEACHER

Fresh light green coloured sample of ferrous sulphate should be used. Old samples are yellow brown coloured due to its oxidation by atmospheric oxygen into ferric sulphate.

If crystals of potash alum do not appear after cooling for a long time, a crystal of potash alum may be added. This process is called seeding

Better results are obtained if a 20 ml solution containing 5.5 g of ferrous ammonium sulphate is provided instead of solid ferrous ammonium sulphate.

10.9 CHECK YOUR ANSWERS

1. Amorphous and crystalline.
2. Rubber or glass is an amporphous solid whereas NaCl is a crystalline solid.
3. In a crystalline substance, the atoms, ions or molecules of which the solid is made up are arranged in a definite geometric pattern while this is not so for amorphous substances.
4. Crystallization is done for two purposes:
   (i) For purification of solids
   (ii) For preparation of double salts.
5. A double salt is a salt containing equimolar amounts of two different salts having different cations but same anions alongwith some definite number of molecules of water of crystallization. An example is – Mohr salt i.e., $FeSO_4(NH_4)2SO_4.6H_2O$.
6. Alums are double salts having the general formula $X_2SO_4.Y_2(SO_4)_3.24H_2O$ where X is a monovalent metal whereas Y is a trivalent metal.

7. $K_2SO_4.Al_2(SO_4)_3.24H_2O$.
8. Fitkari.
9. The salts are mixed in the ratio of their molecular masses.
10. Mother liquor.
11. Water is boiled to remove the dissolved air as otherwise it may oxidize ferrous sulphate to ferric sulphate.

EXPERIMENT-11

Preparations of

(a) Iodoform

(b) Acetanilide

OBJECTIVES

After performing this experiment, you should be able to:

- Prepare iodoform;
- Prepare acetanilide;
- explain the various synthetic steps involved in the preparation of iodoform and acetanilide;
- observe the chemical changes during the preparation of iodoform and acetanilide; and
- explain the synthetic importance and properties of iodoform and acetanilide.

11.1 WHAT YOU SHOULD KNOW

Preparation of organic compounds the laboratory is an integral part of organic chemistry. Without it the study of organic chemistry is incomplete. The synthesis of organic compounds in the laboratory is an art which can be learnt only through experience and rigorous training in the laboratory. The criteria of a good organic preparation are isolation of the product in excellent yield with high degree of purity. In this unit, we shall discuss the preparation of some important organic compounds such as iodoform and acetanilide.

Preparation of Iodoform

Iodoform is the iodine analogue of chloroform. It is a pale yellow crystalline solid (m.p. 119°C), having a characteristic odour. It is used as a mild antiseptic and disinfectant. It is also used in the preparation of many medicinal oint-ments used as pain-relievers.

Iodoform can be prepared by treating any organic compound containing $CH_3CH(OH)$ - group (e.g., ethanol, 2-propanol, 2-butanol etc.) or CH_3CO^-

group (e.g., propanone, 2-butanone, etc.) with iodine in presence of sodium hydroxide. In the laboratory, it is usually prepared from either ethanol or propanone. The chemical reactions involved are:

(a) With ethanol

$$2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$$

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + NaOI \longrightarrow CH_3CHO + NaI + H_2O$$

$$CH_3CHO + 3NaOI \longrightarrow I_3CCHO + 3NaOH$$

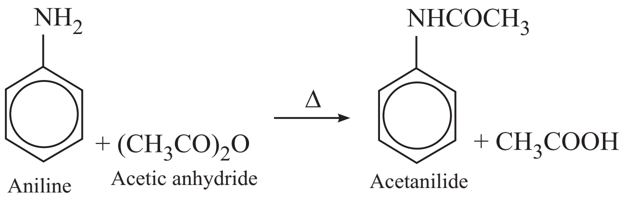
$$I_3CCHO + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod. formats}}{HCOONa}$$

(b) With Propane

$$\underset{\text{propane}}{CH_3COCH} + 3NaOI \longrightarrow \underset{\text{Tri-iodoacetone}}{CH_3COCI_3\ 3NaOH}$$

$$CH_3COCI_3 + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod acetate}}{CH_3COONa}$$

Acetanilide is the acetyl derivative of aniline. It is widely used in industry for the preparation of a number of important organic compounds. It is usually prepared by acetylation of aniline with acetic anhydride and glacial acetic acid. The reaction involved is



MATERIALS REQUIRED

Apparatus required

100 ml round bottomed flask, conical flasks, water condenser, water bath, measuring cylinder, filter paper, Buchner funnel, suction pump, balance, weight box etc.

Chemicals required:

(i) Propanol or ethanol ....5 ml

(ii)	Iodine	.... 5 g
(iii)	Sodium hydroxide	.... 5% solution
(iv)	Rectified spirit	.... 15-20 ml *(for crystallization)*
(v)	Aniline	....5 ml
(vi)	Acetic anhydride	....5 ml
(vii)	Glacial acetic acid	....5 ml
(viii)	Zinc dust	....:0.1 g
(ix)	Alcohol	2-3 ml

HOW TO PERFORM THE EXPERIMENT

(a) Preparation of iodoform

(i) Dissolve 5 g of iodine in 5 ml propane or ethanol in a 100 nil conical flask or round bottomed (R.B.) flask.

(ii) Add 5% NaOH solution in small portions while continously shaking the flask. Cool the flask from time to time under tap water. The addition of NaOH solution is further continued till the brown colour of iodine just disappears.

(iii) Allow the flask to stand for 5-10 minutes.

(iv) Decant off the clear supernatant liquid.

(v) Filter the iodoform, wash with little cold water and then dry on a filter paper.

Crystallization of iodoform

(i) Place the crude iodoform in a 100 ml conical flask.

(ii) Add small amount of rectified spirit and heat it on a water bath.

(iii) Add more rectified spirit slowly till the iodoform dissolves.

(iv) Filter the solution quickly through a fluted filter paper into a beaker.

(v) Cool the solution in ice. The iodoform will crystallize rapidly.

(vi) Filter the crystals on a Buchner funnel dry the crystals between the ibids of the filter paper

(b) Preparation of acetanilide

(i) Take a 100 ml clean and dry R.B. flask and pour 5 ml of aniline into it followed by 5 ml of acetic anhydride and 5 ml of glacial acetic acid. Also add about 0.1 g of zinc dust and a few boiling chips.

(ii) Attach a reflux condenser to the flask and heat the reaction mixture gently on a sand bath for about. 30 minutes as shown in Fig. 11.2

(iii) Remove the flask and pour the hot liquid in a thin stream into 125 ml of cold water with continuous stirring.

(iv) Cool the flask in ice and filter the crude acetanilide at the suction pump using a Buchner funnel.

(v) Wash the crude solid with little cold water and dry upon filter paper in the air.

Crystallization

Place the crude acetanilide in a 250 ml beaker and add gradually 100-125 ml of boiling water. Add 2-3 ml of alcohol to help the dissolution of acetanilide. Heat the contents of the beaker to boiling to get a clear solution. Now keep the beaker undisturbed for slow cooling. White crystals of acetanilide will soon separate out. Filter off the crystals at the pump, wash with little cold water and dry.

PRECAUTIONS

(i) Handle acetic anhydride carefully as it cause irritation to the eyes.

(ii) If aniline sample is too much coloured, distill it before carrying out the experiment, because yield is lowered with impure aniline.

(iii) Use perfectly dry apparatus

(iv) Wash the solid 2-3 times with cold water till the filtrate is neutral to litmus.

OBSERVATIONS

Yield of Iodoform ... g

Yield of acetanilide ... g

CONCLUSION

.... coloured .... g crystals of iodoform is prepared.

.... coloured .... g crystals of acetanilide is prepared.

CHECK YOUR UNDERSTANDING

1. What is the criteria of a good preparation?
2. What is the formula of iodoform? Give its IUPAC name.
3. What other compounds besides ethyl alcohol and acetone can give iodoform test?
4. What other acetylating agent other than acetic anhydride can be used?
5. Give IUPAC name of acetanilide?

NOTE FOR THE TEACHER

A small amount of zinc dust is added during refluxing. Zinc reduces the coloured impurities of aniline and also prevent its oxidation during the reaction.

CHECK YOUR ANSWERS

1. The criteria of good preparation is its good yield, and the product should be pure and crystalline.

   ....

2. CHI_3, IUPAC Name - Triiodomethane

   ....

3. Organic compound containing -$COCH_3$ group or $CH_3CH(OH)$ - group.

   ....

4. Acetyl Chloride CH_3COCl.

   ....

5. N-phenylethanamide.

   ....

EXPERIMENT-12

Separation of the coloured components of the following by paper chromatography and comparison of their R_f values.

(a) Black ink or a mixture of red and blue inks

(b) Juice of a flower or grass

OBJECTIVES

After performing this experiment, you should be able to:

- separate the various constituents of inks, juice of a flower and / or grass, and
- calculate the R_f values of the various components of a mixture.

12.1 WHAT YOU SHOULD KNOW

Chromatography is a technique by which a mixture of various substances can be (a) separated, (b) purified, and (c) identified.

The term chromatography is applied to separation processes based on the principle of distribution of a sample between two phases namely:

(i) a stationary phase or a fixed phase; and

(ii) a moving phase.

There are two variations in the types namely,

(i) solid-liquid chromatography

(ii) liquid - liquid chromatography.

In solid- liquid chromatography, the solid surface adsorbs the substance which is loaded (charged) on the surface and the compounds are separated on the solid surface. It can also be classified as (i) adsorption chromatography, (ii) partition chromatography, (iii) and ion-exchange chromatography. Adsorption chromatography is based on selective adsorption of substances on the surface of an adsorbent. Column chromatography, thin layer chromatography, etc. are based on the adsorption phenomenon. In column chromatography, the stationary phase is an adsorbent and the mobile phase is a solvent.

Liquid-liquid chromatography involves the distribution of a substance between two immiscible solvents to different extents. Paper chromatography is an example of liquid-liquid chromatography. The stationary phase is supported by sheet of filter paper. The filter paper, known as chromatography paper, holds water which acts as a stationary phase. The mobile phase is another liquid which carries the substance on the paper along with it.

Every substance has a characteristic R_f value at a given temperature and for a given solvent.

R_f stands for 'Ratio of Fronts' or the retention factor. It is the ratio of the distance travelled by the component to the distance travelled by the solvent, from the orign (Fig 12.1).

$$R_f = \frac{\text{distance travelled by the substance from the initial line}}{\text{distance travelled by the solvent from initial line}}$$

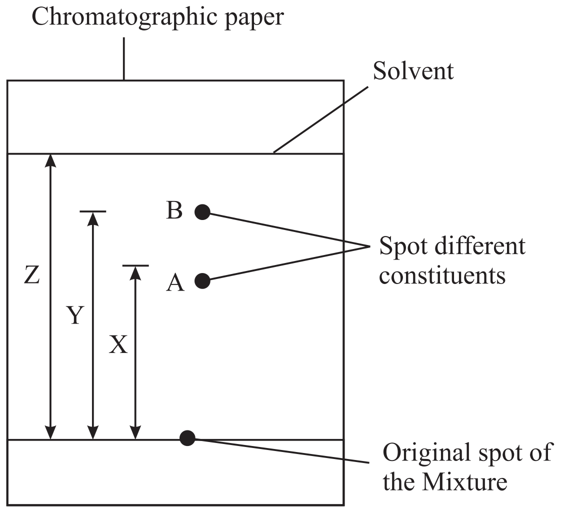


Fig. 12.1: *Measurement of R_f values*

R_f of component $A = \frac{X}{Z}$ and R_f of component $B = \frac{Y}{Z}$

12.2 MATERIALS REQUIRED

(1) Apparatus	**(2) Chemicals**
Gas jar, Gas jar cover, Glass rod, Filter paper strip (Whatmann No. 1), Fine capillary tube, Hook or clip for hanging the paper, Cork.	A mixture of red and blue inks, Alcohol,

12.3 HOW TO PERFORM THE EXPERIMENT

(a) To separate the components of a mixture of red and blue inks and find out their R_f values.

Take the Whatmann filter paper strip (25 × 2 cm). Draw a line with a pencil about 4 cm above the lower end as shown in Fig. 12.2.

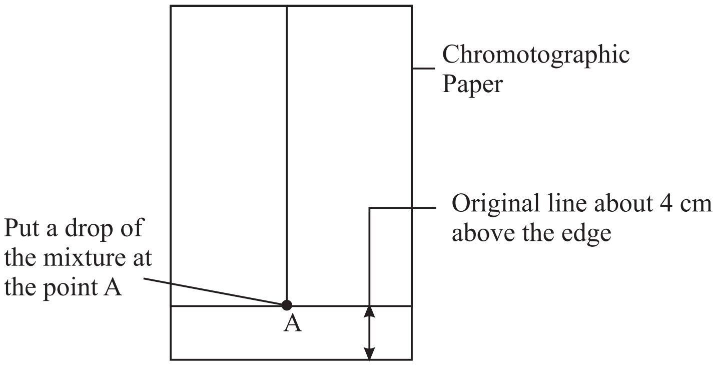


Fig. 12.2: *Spotting the chromatographic paper*

Spotting: With the help of a fine capillary tube, put a drop of the mixture of red and blue inks at point A (Fig. 12.2) on the filter paper strip. Let the spot dry in air. Put another drop on the same spot and dry again. Repeat the process 2-3 times to make the spot rich in the mixture. Suspend the filter paper vertically in the gas jar containing the solvent mixture (50% alcohol). Hang the paper from the glass rod with the help of clips or hook in such a way that the spot remains about 2 cm above the solvent level. Alternatively cork with hook may be used.

Cover the jar with a glass cover and keep it undisturbed. Notice the rise of the solvent as it ascends the paper. After the solvent has risen about 20 cm, you will see two different spots of red and blue colours on the filter paper. Take the filter paper out of the jar and mark the level of the solvent with a pencil. Dry the paper. Mark the centres of the blue and the red spots. Measure the distance of the two spots and that of the solvent from the initial line. Fig 12.2. Record your observations in Table 12.1 and calculate the R_f values of the red and blue spots.

(b) To separate the coloured components present in grass / flower juice by paper chromatography and find the R_f values of the components separated out.

Material Required

(1) Apparatus	(2) Chemicals
Same as in experiment 9 (a)	Flower or grass juice as the sample. Solvent mixture (17 mL of petroleum ether + 3 mL of acetone),

Note: The flower or grass juice is extracted by crushing the flowers or grass in a mortar with the help of a pestle and then extracting the juice by adding a little amount of acetone.

Perform the experiment in the same way as in experiment 12(a)

12.4 PRECAUTIONS

1. Use very fine capillary tube for spotting. Otherwise the spot will become too big.
2. Allow the spot to dry before putting another drop. A good spot is small and does not contain too much of the mixture.
3. Do not press the capillary tube very hard, otherwise it may pierce the paper or break. If you make a hole in the paper then the compound will not rise.
4. Do not allow the paper to curl at the ends. It should hang straight, without touching the sides of the jar.
5. Keep the jar covered. Do not disturb the jar after hanging the filter paper till the solvent has risen up to the desired level,
6. The spot should not dip in the solvent. Otherwise the compounds will dissolve in it.
7. Use distilled water for making the solvent mixture to be taken in the jar.

Precaution for 12(b)

Same as in Experiment 12(a)

12.5 OBSERVATIONS

Observation for Experiment 12(a)

- Record your observations and R_f in Table 12.1

Table 12.1

S.No.	Colour of the spot	Distance travelled by the spot from the initial line/cm	Distance travelled by the solvent from the initial line/cm	R_f
1.	Red	....	....	....
2.	Blue	....	....	....

Observation for Experiment 12(b)

Table 12.2

S.No.	Colour of the spot	Distance travelled by the spot from the initial line/cm	Distance travelled by the solvent from the initial line/cm	R_f
1.	Green (Chlorophyll)	....	....	....
2.	Yellow (Xanthophyll)	....	....	....
3.	Red (Carotene)	....	....	....

12.6 CONCLUSIONS

The R_f of red ink = ...

The R_f of blue ink = ...

R_f of the green component (chlorophyll) = ...

R_f of the yellow component (xanthophyll}= ....

R_f of the red component (carotene) = ...

12.7 CHECK YOUR UNDERSTANDING

1. What is chromatography?

   ....

2. What is the basic principle of chromatography?

   ....

3. What is paper chromatography?

   ....

4. What is meant by R_f value?

   ....

5. What is a chromatogram?

   ....

6. How are colourless compounds detected on a chromatogram?

   ....

7. What will happen if the paper strip is not vertical or it touches the side of the jar?

   ....

8. While spotting, if a hole is created on the paper, how will it affect the separation?

   ....

12.8 NOTE FOR THE TEACHER

(i) An exercise can be given to separate a mixture of Ni^{2+}, Co^{2+} and Zn^{2+} by paper chromatography using the solvent mixture (85 mL acetone + 5 mL water + 10 mL conc. HCl).

(ii) When students extract fruit juice or grass juice, the teacher should explain the method of extraction.

(iii) Even high moisture content in the atmosphere will interfer in the solvent extraction. Therefore, the teacher should advise the students to perform in dry condition.

(iv) The teacher should help students to use proper ratio of solvents, so that the required polarity can be maintained.

12.9 CHECK YOUR ANSWERS

1. Chromatography is a technique by which mixtures of various substances can be (a) separated (b) purified, and (c) identified.

2. Chromatography is based on the principle of distribution of a sample between two phases, namely a stationary phase and a moving phase.

3. Paper chromatography is a type of liquid - liquid chromatography. Here the water held on the cellulose of the paper acts as the stationary phase and the moving solvent acts as the moving phase.

4. R_f value is the ratio of distance travelled by the component from the original spot to the distance travelled by the solvent from the original spot. R_f is a constant for a given substance at a particular temperature and for a given solvent.

5. The colour spots appear on the paper at different levels after the chromatographic separation is over. This is called a chromatogram.

6. The colourless compounds can be made visible by spraying a reagent on the paper. The separated component on the paper react with the reagent and produces a coloured compounds which become visible.

7. If the paper strip is not vertical or it touches the sides of the jar then solvent flow will not be uniform or separation will not be proper.

8. If a hole is created in the paper then the constituents of the mixture will not rise at all, but spread near the original point.

EXPERIMENT-13

To detect the presence of extra elements (nitrogen, sulphur and halogens) in an organic compound.

OBJECTIVES

After performing this experiment, you should be able to

- detect the presence of nitrogen, sulphur and halogens (extra elements) present in a given organic compound;
- explain the reason for the necessity of fusing an organic compound with sodium metal in the detection of extra elements; and
- write chemical equations of various reactions taking place in this experiment.

13.1 WHAT YOU SHOULD KNOW

The determination of structure of an unknown organic compound requires the detection of the elements present in it. Generally all organic compounds contain carbon and hydrogen. In addition to these elements, they may also contain oxygen, nitrogen, sulphur and halogens. The elements nitrogen, sulphur and halogens are known as extra elements.

For detecting the presence of elements in a compound, these have to be converted into ionic forms. This is done by fusing the compound with sodium metal. The elements, nitrogen, sulphur and halogens present in the compound are converted into soluble sodium salts according to the following equations.

$$\mathrm{Na + C + N \rightarrow NaCN}$$

$$\mathrm{2Na + S \rightarrow Na_2S}$$

$$\mathrm{Na + X \rightarrow NaX}$$

(where X is Cl, Br or I)

If a compound contains both nitrogen and sulphur, sodium thiocyanate is formed on fusing with sodium. The soluble sodium salts are extracted with water. The extract is usually known as sodium fusion extract.

13.1.1 Test for Nitrogen

Nitrogen is present as sodium cyanide in sodium fusion extract. Sodium cyanide is converted to sodium ferrocyanide on treating with ferrous sulphate. On further treating it with ferric chloride, a Prussian blue complex, ferricferrocyanide is formed.

$$6NaCN + Fe\,SO_4 \rightarrow Na_4\,[Fe(CN)_6] + Na_2\,SO_4$$

$$Na_4\,[Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4\,[Fe(CN)_6)]_3 + 12NaCl$$

Ferricferrocyanide
(Prussian blue)

13.1.2 Test for Sulphur

(i) Sulphur is present in sodium extract as sodium sulphide. It gives a purple colour with sodium nitroprusside due to the formation of sodium thionitroprusside.

$$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4\,[Fe(CN)_5NOS]$$

Sodium nitroprusside   Sodium thionitroprusside
(Purple)

(ii) A sulphide reacts with lead acetate to yield lead sulphide as a black precipitate.

$$Na_2S + Pb\,(CH_3OO)_2 \rightarrow PbS + 2CH_3COONa$$

Lead sulphide
(black)

(iii) A sulphide reacts with silver nitrate to yield silver sulphide which is black in colour.

$$Na_2S + 2AgNO_3 \rightarrow Ag_2S + 2\,NaNO_3$$

Silver Sulphide (black)

13.1.3 Test for Nitrogen and Sulphur when present together

When both nitrogen and sulphur are present together in an organic compound, sodium thiocyanate is produced during sodium fusion. Sodium thiocyanate gives blood red colour with ferric chloride.

$$NaCNS + FeCl_3 \rightarrow [Fe(CNS)]^{2+} + Na^+ + 3Cl^-$$

(Blood red)

13.1.4 Test for Halogens

Halogens, present as halides in sodium extract, are tested as follows:

(i) **Silver Nitrate test:** Chlorides give white precipitate of silver chloride with silver nitrate. The precipitate is soluble in ammonium hydroxide.

$$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$$
$$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]\,Cl + 2H_2O$$

Bromides yield yellow precipitate, sparingly soluble in ammonium hydroxide. Iodides yield dark yellow precipitate, insoluble in ammonium hydroxide.

(ii) When a solution containing bromide or iodide is treated with chlorine water, the bromide and iodide are oxidised to the corresponding halogens. Being covalent, these halogens get dissolved in carbon tetrachloride $CC1_4$. Bromine imparts yellow to brown colour and iodine imparts purple colour in $CC1_4$ layer.

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$
$$2Nal + Cl_2 \rightarrow 2NaCl + l_2$$

Chlorine being more electronegative, displaces bromides and iodides from solution.

13.2 MATERIALS REQUIRED

(1) Apparatus	(2) Chemicals
Test tubes - 6, Test-tube stand,	Sodium metal, Ferrous sulphate,
Test tube holder,	Ferric chloride, Silver nitrate,
Ignition tubes - 3, Spatula, Watch-glass,	Ammonium hydroxide, Chlorine water,
Filter paper, Pair of tongs, Porcelain dish,	Carbon tetrachloride,
Funnel, Glass rod, Dropper, Wire gauze.	Nitric acid

13.4 HOW TO PERFORM THE EXPERIMENT

The experiment consists of two stages, (i) preparation of sodium fusion extract and (ii) to test for individual elements.

(1) Preparation of Sodium Fusion Extract

Take out a small piece of sodium metal from a petri dish with the help of pair of forceps. Dry the sodium piece between the folds of filter papers. Put a small piece of sodium metal into a clean and dry ignition tube. Hold the tube with a pair of tongs and heat it gently over the flame so that sodium melts and makes a stirring ball. Remove the ignition tube away from the flame and immediately add a small amount of solid organic compound into it. Heat the tube to red hot. Again add a little of the compound into the tube and heat it again to red hot. Plunge the red hot ignition tube in about 10 mL of distilled water taken in a porcelain dish. Immediately cover the porcelain dish with a wire gauze to avoid bumping of any unreacted sodium piece. Repeat the process of sodium fusion using two more ignition tubes. Break the tubes into small pieces with a clean glass rod. Boil the mixture for about 2-3 minutes and filter.

(In case of liquid compounds, cover the molten sodium with solid sodium carbonate and then add the compound with a dropper).

Now proceed systematically and perform the following tests with the given sample (s), of organic compounds and identify the extra elements present in them. Record your observations and inferences in the table 13.1 in the following manner.

Table 13.1

S. No.	Experiment	Observations	Inference
1.	**Test for nitrogen** Take about 1 mL of sodium fusion extract in a test tube and add a pinch of ferrous sulphate. Shake the contents and acidify with dilute hydrochloric acid, Boil the contents and add a few drops of ferric chloride solution.	Prussian blue or green precipitate or colour	Nitrogen present
2.	**Test for suiphur** (i) Take 1 mL of sodium fusion extract in a test tube and add a few drops of sodium nitroprusside to it and shake.	Purple colour	Sulphur present
	(ii) Take 1 mL of sodium fusion extract in a test tube and acidify it with acetic acid. Add a few drops (4-5) of lead acetate solution to it	Black precipitate	Sulphur present
3.	**Nitrogen and Sulphur present together** Take about 1 mL of sodium fusion extract in a test tube and acidify it with dilute hydrochloric acid. Add a few drops of ferric chloride solution.	Blood red Colour present	Nitrogen and Sulphur

4. **Test for Halogens** (i) Take about 1 mL of sodium fusion extract in a test tube and acidify it with dilute nitric acid. Add to it about 2 mL of silver nitrate solution.Observe the appearance of any precipitate and its colour.	(a) A curdy white precipitate soluble in NH_4OH	Chlorine present
Add 2-3 mL of ammonium hydroxide to the precipitate and shake the contents. Observe the solubility of precipitate	(b) A light yellow precipitate partially soluble in NH_4OH	Bromine present
	(c) A pale yellow precipitate insoluble in NH_4OH	Iodine present
(ii) If chloride is absent, perform the following test for bromide and iodide. Take 2 mL of sodium fusion extract in a test tube and acidify it with dilute hydrochloric acid. Add 1 mL of carbon tetrachloride. Being denser, $CC1_4$ forms the lower layer. Add excess of chlorine water and shake the mixture vigrously. Observe the appearance of any colour in CCl_4 layer.	(a) Orange Colour (b) Violet Colour	Bromine presence Iodine presence

13.5 PRECAUTIONS

1. Sodium metal is highly reactive. When exposed to air, it reacts even with the moisture present in the atmosphere. It also reacts with the sweat of hands. Hence, do not hold it with hands. Always use forceps handling sodium.
2. Before using sodium metal, press it within the folds of filter paper to remove oil.
3. Use dry ignition tubes for sodium fusion. Sodium reacts with water violently.
4. Put the unused sodium piece back in bottle. Do not throw it in to the sink.
5. Repeat the process of sodium fusion with three ignition rubes. This is to ensure that the fusion has taken place.

6 After immersing the red hot ignition tube in water, break it with a glass rod gently. Boil the contents for 2-3 minutes so as to extract the soluble sodium salts in water.

Notes

13.5 OBSERVATIONS

Table 13.1

S.No.	Experiment	Observations	Inference

The given sample responded positively to ...., ... and .... tests. Therefore, the extra elements present in the sample is ....

10.6 CONCLUSION

The given organic compound contains .... as extra elements.

10.7 CHECK YOUR UNDERSTANDING

1. Why is only freshly cut sodium metal used for fusion of an organic compound?

   ....

2. Why is it necessary to carry out the fusion of an organic compound with sodium, more than once using different ignition tubes?

   ....

3. While testing for nitrogen why is it necessary to neutralize the sodium extract completely with an acid?

   ....

4. Why is it necessary to fuse an organic compound with sodium for carrying out the tests for extra elements present in it?

   ....

5. Why are bromide and iodide displaced from their salts in solution by chlorine water?

   ....

6. What will happen if sodium extract is not completely neutralized before performing silver nitrate test for halogens?

   ....

7. Why is it essential to use distilled water in the preparation of sodium extract?

....

13.8 NOTE FOR TEACHER

Sodium metal is highly reactive. Ensure that students handle it carefully and take all precautions.

In preparing sodium fusion extract, the low concentrations of ions in solution give only a faint colour or precipitate. It is advisable to use 2-3 ignition tubes during sodium fusion. In case of liquid compounds, the molten sodium metal is first covered with sodium carbonate. The liquid compound is added over it so that it is absorbed in sodium carbonate. The low boiling liquids tend to escape without undergoing reaction with sodium.

After the students have performed the tests of all the extra elements, they may be asked to identify the extra elements in given compounds and write full details in the experiment sheet.

13.9 CHECK YOUR ANSWERS

1. Sodium is a highly reactive metal. Its surface gets a coating of its oxide due to its reaction with atmospheric oxygen. By taking a freshly cut sodium, the exposed surface is free from Oxide.
2. A majority of organic compounds are low boiling and volatile. They tend to escape out of the ignition tube during heating. To ensure an adequate concentration of ions containing extra elements in test solution, it is preferable to carry out the sodium fusion 2-3 times.
3. On adding ferrous sulphate to sodium extract, ferrous hydroxide forms a dirty green precipitate. To avoid this, the test solution is neutralized completely.
4. The extra elements are present as covalently bonded atoms in organic compounds. To test them in solution, these are converted into ionic form by fusing the compound with sodium.
5. Chlorine, being more electronegative displaces bromide and iodide in solution.
6. A grey black precipitate of silver oxide is formed. It becomes difficult to identify the colour of silver halides.
7. Ordinary water contains chloride ions. These interefere with the halide ions formed from halogen of the organic compound.

EXPERIMENT-14

Study of simple reactions of carbohydrates, fats and proteins and detection of their presence in given foodstuffs.

OBJECTIVES

After performing this experiment, you should be able to:

- test the presence of carbohydrates, proteins and fats in the given food samples;
- establish whether the given carbohydrate is reducing or non reducing.
- distinguish between saturated and unsaturated fats.

14.1 WHAT YOU SHOULD KNOW

14.1.1 Carbohydrates

Carbohydrates are polyhydroxy aldehydes or ketones and the substances which yield these on hydrolysis. Carbohydrates are classified as :

i) Monosaccharides - glucose, fructose- ($C_6H_{12}O_6$)

ii) Disaccharides - sucrose, maltose- ($C_{12}H_{22}O_{11}$)

iii) Polysaccharides - starch, cellulose, glycogen.

All the carbohydrates, except cellulose, are hydrolysed in our body to glucose which on slow oxidation, in presence of oxygen, liberates large amount of energy. The oxidation of glucose can be represented as:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2 \xrightarrow{\text{Respiration}} 6CO_2 + 6H_2O + \text{Energy}$$

Thus carbohydrates (sugars and starch) are the main source of energy in our body. The cellulose acts as a roughage. The carbohydrates which reduce Fehling's solution and Tollen's reagent are called reducing sugars. All the Monosaccharides and most of the disaccharides are reducing sugars. Sucrose (cane-sugar) is a non-reducing sugar and hence does not reduce Fehling's solution.

Test for Carbohydrates

1. **Molisch's Test** (for all carbohydrates): When an aqueous solution or suspension of a sample containing a carbohydrate is treated with α- naphthol (Molish's reagent), followed by the addition of few drops of conc, sulphuric acid along the sides of the test tube a red-violet ring appears at the junction of two layers. This happens because concentrated sulphuric acid converts carbohydrates to furfural or its derivatives which reacts with α-naphthol to give a coloured (red-violet) product.

2. **Tollen's Test** (for reducing sugars); Any aldose or ketose having a free carbonyl groups reduces Tollen's reagent to metallic silver. This test is commonly known as silver mirror test as a kind of mirror is obtained on the walls of the test tube.

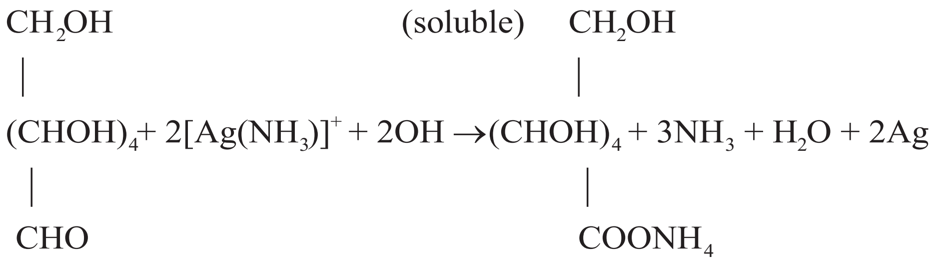
   The reactions involved in this test are as follows

   $$\mathrm{AgNO_3 + NH_4OH \rightarrow NH_4NO_3 + AgOH}$$

   $$\mathrm{2AgOH \rightarrow AgO_2 + HO_2}$$

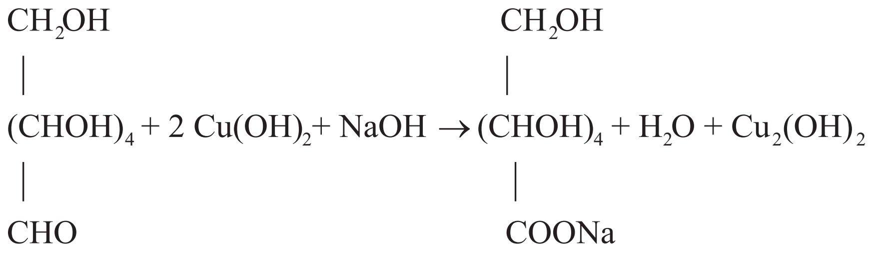
   $$\mathrm{Ag_2O + 2NH_4\,OH \rightarrow [Ag(NH_3)]_2^+\ OH^- + H_2O}$$

   (soluble)



$$\underset{\mathrm{CHO}}{\overset{\mathrm{CH_2OH}}{\underset{|}{\overset{|}{(\mathrm{CHOH})_4}}}} + 2[\mathrm{Ag(NH_3)}]^+ + 2\mathrm{OH} \rightarrow \underset{\mathrm{COONH_4}}{\overset{\mathrm{CH_2OH}}{\underset{|}{\overset{|}{(\mathrm{CHOH})_4}}}} + 3\mathrm{NH_3} + \mathrm{H_2O} + 2\mathrm{Ag}$$

3. **Fehling's Test** (for reducing sugars): When equal quantities of Fehling's solution A and B are mixed with an aqueous solution of a reducing sugar and the mixture is heated on a boiling water bath, a reddish precipitate of cuprous oxide is formed. The following reactions are involved in the test.



$$\underset{\mathrm{CHO}}{\overset{\mathrm{CH_2OH}}{\underset{|}{\overset{|}{(\mathrm{CHOH})_4}}}} + 2\,\mathrm{Cu(OH)_2} + \mathrm{NaOH} \rightarrow \underset{\mathrm{COONa}}{\overset{\mathrm{CH_2OH}}{\underset{|}{\overset{|}{(\mathrm{CHOH})_4}}}} + \mathrm{H_2O} + \mathrm{Cu_2(OH)_2}$$

$$\mathrm{Cu_2(OH)_2 \rightarrow Cu_2O + H_2O}$$

4. **Iodine Test for starch:** Starch gives a purple-blue colour when treated with iodine. It is due to the adsorption of iodine on the surface of starch. The colour gets discharged on heating and reappears on cooling.

Notes

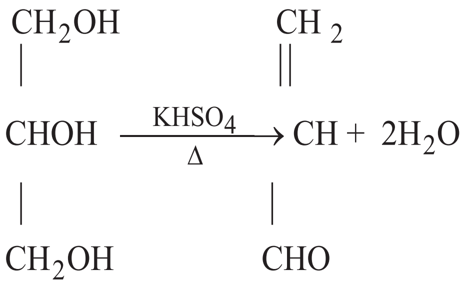
14.1.2 Fats

Fats are triesters of long chain fatty acids and glycerol. One of the function of fats in the body is to provide energy. Fats provide twice as much energy as that provided by the same amount of carbohydrates. Fats are insoluble in water. During the process of digestion, fats are hydrolysed into simple substances, like fatty acids and glycerol which further break down into still simpler substances. Sources of fats in our food are butter, ghee, cheese, milk, egg-yolk, meat, nuts, groundnut and soyabean etc.

Tests for Fats

1. **Spot Test:** When a sample containing fats is pressed or rubbed on a clean white sheet of paper, a greasy spot (translucent spot) appears.
2. **Solubility Test:** This test is based on the fact that fats are soluble in organic solvents like chloroform, alcohol etc but are insoluble in water. A small amount of the sample is mixed with a few drops of water, chloroform and alcohol in different test tubes and inferences are drawn on the basis of the miscibility and immiscibility of the sample with the water or organic solvents.
3. **Acrolein Test:** When a sample containing fat is heated with solid potassium bisulphate ($KHSO_4$) in a test tube, a pungent irritating odour of acrolein is produced according to the following chemical reaction;

$$\text{Oil or fat} \xrightarrow{\text{Respiration}} \text{Glycerol + fatty acid}$$

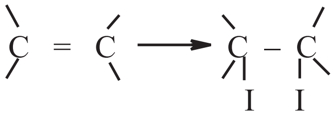


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\Delta]{KHSO_4} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \end{array} + 2H_2O$$

Glycerol Acrolein

4. **Huble's Test (for determination of unsaturation in fats):** This test is based on the fact that greater the amount of unsturation in a fat or an oil, greater is the amount of Huble's solution required to produce a permanent violet colour.

For this equal amount of saturated fat (cotton seed oil) and unsaturated fat or oil (linseed oil) are taken in two different test tubes and Huble's solution is added to each test tube dropwise. The number of drops of Huble's solution required for getting a permanent colour are counted in each case. More the number of drops of Huble's solution, greater is the unsaturation in an organic compound. Iodine from Huble's solution adds up across the unsaturation sites of oil or fat giving a colourless product and a little more of iodine gives a permanent violet colour to the solution.



14.1.3 Proteins

Proteins are complex nitrogenous organic compounds of high molecular mass. These help in the growth and maintenance of living body and in transmission of genetic information. Proteins are made up of -amino acids as the basic building blocks. In all, there are 20 different amino acids required by the body. Some of these are called essential amino acids as they cannot be synthesized by the organisms. These must form a part of our food.

Tests for Proteins

1. **Biuret Test:** When a sample of protein is treated with a solution of copper sulphate in alkaline medium, a violet colour appears. The intensity of the colour also indicates the relative amount of protein present in different samples.
2. **Ninhydrin Test:** When a few drops of a 0.1% alcoholic solution of ninhydrin, are added to a very dilute solution /suspension of protein and the contents are boiled for 1 -2 minute, a red-purple colour appears.
3. **Xanthoprotein Test:** When an aqueous solution of protein is treated with a few drops of nitric acid and contents are allowed to stand; a deep yellow colour appears.
4. **Million's Test:** A few drops of milk are warmed with mercuric nitrate in presence of dil. sulphuric acid and cooled. One drop of sodium nitrate solution is added and the mixture is again warmed. A red colour appears showing the presence of proteins in milk.

14.2 MATERIAL REQUIRED

(1) Apparatus	(2) Chemicals
Test tubes with stand, Burner	Fehling's solutions - A and B, Molisch reagent (α-Naphthol), Silver nitrate, Ammonium hydroxide, Iodine solution, Ethyl alcohol, Huble's solution, Potassium bisulphate, dilute sulphuric acid, Mercuric nitrate, Sodium nitrate, Nitric acid, Ninhydrin solution (0.1% in alcohol), Sodium hydroxide, Copper sulphate, and some food samples like: milk, sucrose, glucose, wheat flour, vegetable oil, ghee, butter, cheese potato pieces, lemon, grapes, banana, eggs etc. 5% solution of egg white protein.

14.3 HOW TO PERFORM THE EXPERIMENT

14.3.1 Worksheet No. 1: Test for Carbohydrates

Experiment	Observation	Inferences
For Carbohydrates **(i) Molisch's test:** Take 2-3 mL of aqueous solution or suspension of the sample. Add a few drops of Molisch's reagent and shake it. Then add 5-6 drops of conc. H_2SO_4 slowly along the side of the test tube.		
ii) Tollen's test: Take a test tube and clean it thoroughly with NaOH solution. Then wash the tube with excess of water to remove NaOH. Take 2-3 mL of aqueous solution of carbohydrate in the test tube and add 2-3 mL of freshly prepared Tollen's reagent to it. Keep the test tube in a boiling water bath for about 10 minutes.		
iii) Fehling's Test: Take a small amount of crushed food items (1g) or 2-3 mL of aqueous solution ofthe sample (nearly 5%) . Add 2 mL each of Fehling's solution A and Fehling's solution B. Keep the test tube in a boiling water bath.		
iv) Iodine Test for Starch: Take a small amount (l-2g) of the food sample in a test tube and add a few drops of dilute iodine solution.		

14.3.2 Worksheet No. 2: Test for Fats

Experiment	**Observation**	**Inferences**
For Fats **i) Spot Test:** Take a food item to be tested and press or rub it on a clean white sheet of paper and hold it against light.		
ii) Solubility test: Take a small amount (50 mg) of the given sample in a test tube. Add 2-3 mL water in it and shake. Observe if it has dissolved in it. Similarly check the solubility of the compound in alcohol, and $CC1_4$ separately.		
iii) Acrolein Test: Heat a small amount (2-3g) of sample with same amount (2-3g) of solid $KHSO_4$ in a test tube. Bring the mouth of the test tube near the nose and smell the gas evolved, if any, only superficially.		
iv) Ruble's test for unsaturation: Take two test tubes labelled as 'A' and 'B'. Add about 3-4 mL of chloroform to each test tube. Put some samples (2-3g) of unsaturated fat (linseed oil) in test tube 'A' and saturated fat (cottonseed oil) in test tube 'B'. Add Ruble's solution to each test tube dropwise and keep on adding while counting the drops, until a permanent violet colour appears in each test tube.		

14.3.3 Worksheet = 3: Test for Proteins

Experiment	**Observation**	**Inferences**
For Proteins **i) Biuret Test:** Take one mL of milk or any other protein containing sample in a test tube. Make it alkaline by adding a few drops (4-5) of NaOH solution Then add 4-5 drops of dil solution of $CuSO_4$.		
ii) Ninhydrin Test: Take about 1 mL of 5% solution of egg white in a test tube. Add to it 4-5 drops of 0.1% ninhydrin solution. Boil the contents for about one minute and cool it		
iii) Xanthoprotein Test: Take 2-3 grams of gjutenin of wheat in a test tube. Add 2-3 mL of cone. HNO_3, to it. Shake the contents and keep aside.		
iv) Milton's Test: Take about 1 mL of milk in a test tube. Add 1-2 drops of mercuric nitrate solution and one drop of di H,SO_4. Boil and cool the contents and then add 1 drop of $NaNO_3$ olution. Warm the mixture again and cool it.		

14.4 PRECAUTIONS

1. Smell the gases coming out of reactions carefully.
2. Some compounds are highly corrosive. For example, phenol can cause blisters and burn your skin when it falls on it. Immediatly resort to first aid.
3. Use a water bath for warning the contents. Do not heat organic the compounds on a direct flame, these can catch fire easily.

4. Neutral ferric chloride must be prepared fresh (procedure is given in appendix.)

5. Tollen's reagent must be freshly prepared (Procedure is given in the appendix)

6. Fehling's solution should be prepared by mixing equal amounts for Fehling's solution A and Fehling's solution B required for the test.

14.5 OBSERVATION

Record your observations in the blank worksheet in the following manner:

1 .... Are found in the given food stuffs.

Table 14.1

Test	Glucose	Sucrose	Starch
1. Solubility in water	Soluble	Soluble	Insoluble
2. Fehling's test			
3. Tollen's test			
4. Molisch's test			
5. Benedict's test			
6. Iodine test			

Table 14.2

Sl. No.	Test	Fat (Saturated)		Fat (Unsaturated)
		Animal	Vegetable	
1.	Spot test			
2.	Solubility test (in org. solvent)			
3.	Acrolein test			
4.	Ruble's test			

14.6 CONCLUSIONS

Following conclusions are drawn based on test For Carbohydrates:

i) The given sample / does not / contain carbohydrates.

ii) The given sample contains reducing / non-reducing sugar.

For Fats:

i) The sample does not contain fat.

ii) The sample contains saturated / unsaturated fat.

For Proteins:

i) The given sample contains proteins.

ii) The given sample does not contain proteins.

Common:

i) The given sample contains fat and protein body.

ii) The given sample contains carbohydrates and protein.

iii) The given sample contains carbohydrates, fat and protein.

14.7 CHECK YOUR UNDERSTANDING

1 Why are carbohydrates known as ‘hydrates of carbon’?

....

2. Define carbohydrates.

....

3. What is the general formula of polysaccharides?

....

4. What is meant by the term reducing sugar?

....

5. Name the compound formed as red precipitate when a carbohydrate is treated with Fehling’s solution.

....

6. Name the carbohydrate which is not digested in our body.

....

7. Which carbohydrate forms blue colour product when treated with iodine?

....

8. What are fats?

....

9. What products are obtained on hydrolysis of fats?

....

10. Write down the structural formula of Acrolein.

....

11. Name four sources of fats?

....

12. What is the difference in the physical state of saturated and unsaturated fats at room temperature?

....

13. A fat required more of Huble's solution of giving a permanent violet colour in the mixture? What inference will you draw from this observation?

....

14. Define proteins.

....

15. What is the main role of proteins in our body?

....

16. Name the bonding which unite amino acids to form a protein.

....

14.8 NOTE FOR THE TEACHER

1. Ensure that students work themselves with at least one sample of each kind of carbohydrates, (Glucose, Sucrose and starch), saturated and unsaturated fats.

2. After the students have performed the tests of all the samples, they may be asked to identify the unknown substance and write full details in the experiments sheet.

3. The reactions in all the experiments occur very easily. The students may be asked to performe slow addition and pay keen observation.

14.9 CHECK YOUR ANSWERS

1. Carbohydrates are called as hydrates of carbon because proportion of hydrogen and oxygen in carbohydrates is similar to that in water.

2. Carbohydrates are ployhydroxyaldehydes or ketones.

3. $(C_6H_{14}O_5)_n$

4. Sugars having free carbonyl group can reduce Tollen's reagent Fehling's solution to give metallic silver and Cu_2O respectively. Such sugars are called reducing sugars.

5. Cu_2O(Cuprous oxide)

6. Cellulose
7. Starch
8 Fats are triesters of long chain fatty acids and glycerol.
9 Fatty acid and glycerol

10. 

$CH_2{=}CH{-}CHO$

11. Cotton seed oil, coconut, milk, ghee
12. Saturated fats are solids and unsaturated fats are liquids at room temperature.
13. The given fat has more unsaturation.
14. Proteins are complex nitrogenous organic compunds.
15. Proteins are helpful in growth and maintenance of our body tissues and also regulate various physiological activities.
16. Amino acids join through peptide bonds making a polypeptide chain (protein).

EXPERIMENT-15

(a) preparation of solution of oxalic acid and ferrous ammouium sulphate of known molarity by weighing (non-evaluative). Use of chemical balance to be demonstrated.

(b) A study of acid-base titration (single titration only)

- **(i) To find out the Molarity of given NaOH solution by titrating against standard solution of oxalic acid. Both the solutions to be provided**

(c) A study of redox titrations (single titration only)

- **(i) To find out the Molarity and strength of given potassium permanganate solution by titrating against M/50 Mohr's salt (Ferrous ammonium sulphate) solution. Both the solutions to be provided.**
- **(ii) To find out the Molarity and strength of given potassium permanganate solution by titrating against M/10 oxalic acid solution. Both the solutions to be provided.**

OBJECTIVES

After performing this experiment, you should be able to:

- handle chemical balance properly;
- weigh chemicals accurately using a chemical balance;
- handle burette and pipette properly;
- pipette out a given solution correctly with the help of a pipette,
- prepare standard solutions of oxalic acid and ferrous ammonium sulphate;
- detect the sharp end point;
- perform acid-base (oxalic acid and sodium hydroxide) and, redox, (ferrous ammonium sulphate and potassium permanganate) titrations;
- calculate the Molarity and strength of the given solution by using appropriate formula.

15.1 WHAT YOU SHOULD KNOW

Volumetric analysis is quantitative analysis in which the results are expressed in a certain definite volume. It involves the use of at least one solution of known strength. It may be prepared by dissolving a definite amount of a solute in a solvent to get a known volume of solution. The volume of this solution which reacts with a volume of the solution of unknown strength of another substance is determined. The process is known as titration.

15.1.1 Handling the apparatus

In volumatric analysis, we deal with volumes of solutions. Therefore, these should be measured correctly. The glass apparatus must be clean and free from grease etc. Errors due to parallax in reading the level of a solution in burette, pipette and volumetric flask should be avoided. To read the volume in the container shown in Figure (15.1) the point shown by the arrow is the correct position.

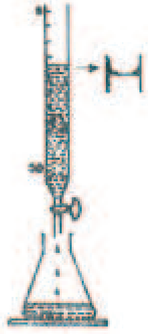


Fig. 15.1: *Correct way to note down the burette readings*

15.1.2 Pipette

Pipettes are available in various capacities (volumes) and a pipette of required volume is used during titration for delivering a liquid out of the pipette. It should be held vertically with its tip in contact with the wall of vessel. After the flow of liquid has ceased, a very small solution of the liquid remains in the lower portion of the pipette. It should not be blown out. For this, hold the bulb of the pipette in left hand palm with its upper tip closed with a finger. Touch the lower tip of pipette to the wall of the vessel. Handling of a pipette and correct way to drain out the solution are shown in set of figures 15.2a and 15.2b. Measuring of solution with pipette is shown in Fig. 15.3.

Fig. 15.2 *(a): Pipette* *(b) Handling of a pipette* *(c) Correct way to drain out the solution*

Fig. 15.3: *Measuring of solution with a pipette*

15.1.3 Chemical Balance Introduction

A chemical balance is commonly used in chemical laboratories to weigh an exact amount of the substance. The chemical reactions go to completion when exact mass of the substance are taken. Each molecule or atoms of the substance has its own importance. Hence it is necessary to use exact mass of the substance in each experiment. Therefore, the trip balance is not useful for reaction concerned. Chemical balance is used for weighing accurate mass of the substance.

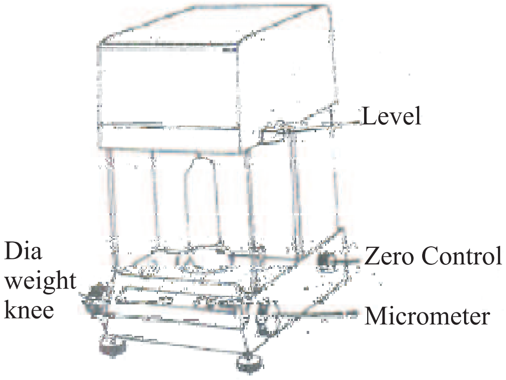


Fig. 15.4: *Single Pan Balance*

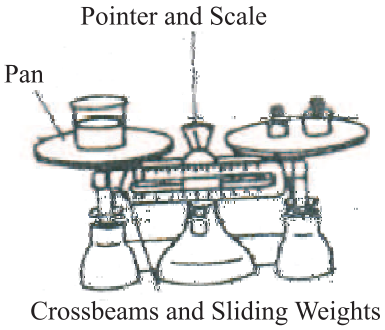


Fig. 15.5: *Rough Balance*

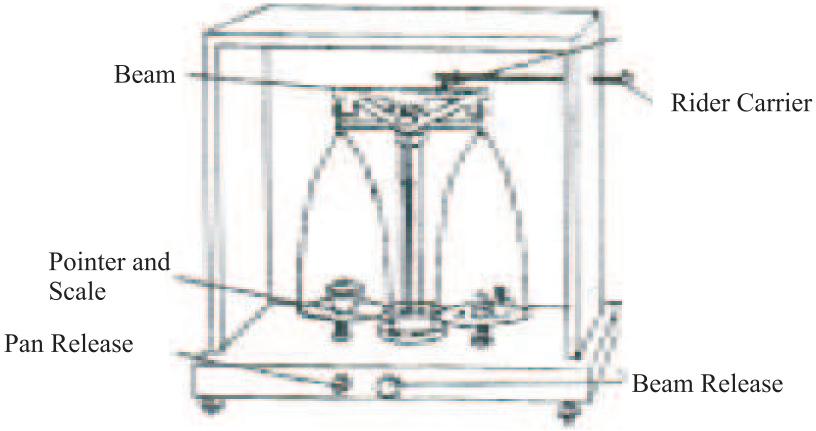


Fig. 15.6: *Analytical Balance*

The analytcal balance is an instrument for determining mass of a body by equilibrium of weights suspended from the opposite side of a bar having a fulcrum at its centre. It may be regarded as a rigid beam having a fulcrum at its centre and two arms of equal length. The chemical balance is shown in the Fig. (15.7).

A chemical balance consists of a light-weight beam having a mounted knife edge at its centre. It rests on a pure corrundum plate attached to the pillar. There are two knife edges mounted on the two ends of the beam which are equidistant from the central knife-edge. The two ends of the beam also have adjusting screws for Zero-adjustment. The centre of the beam is attached to a pointer which moves over the scale at the foot of the pillar. There are two levelling screws at the loose and one pumb-line suspended from the column. The beam is divided into 100 divisions, i.e. 50 divisions on each side of the fulcrum.

The whole arrangement is enclosed in a wooden case with glass sides.

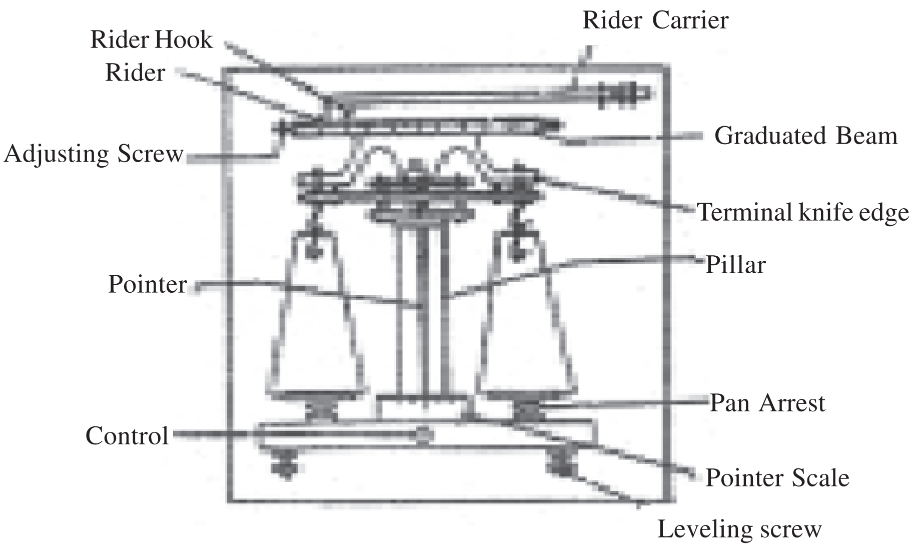


Fig. 15.7: *A chemical balance*

Weight-Box

A weight box is a wooden box having grooves of various sizes into which are placed different weights ranging from 1 to 100 as shown in Fig. 15.8a. These weights are made up of brass coated with nickel or chromium. Each weight is nearly cylindrical having a knob at its one end with the help of which it can be lifted with forceps.

The following is the order of weights placed in a weight box.

100g, 50g, 20g, 20g

10g ,5g, 2g, 2g, 1g

The weights are placed in the following sequence in a weight box.

Fractional weight box

Fractional weights are made up of aluminium or brass coated with chromium or nickel that range from 1 milligrams to 500 milligrams as shown Fig. 15.8b. The fractional weights iess than 10 milligrams are not used, instead the use of rider is recommended.

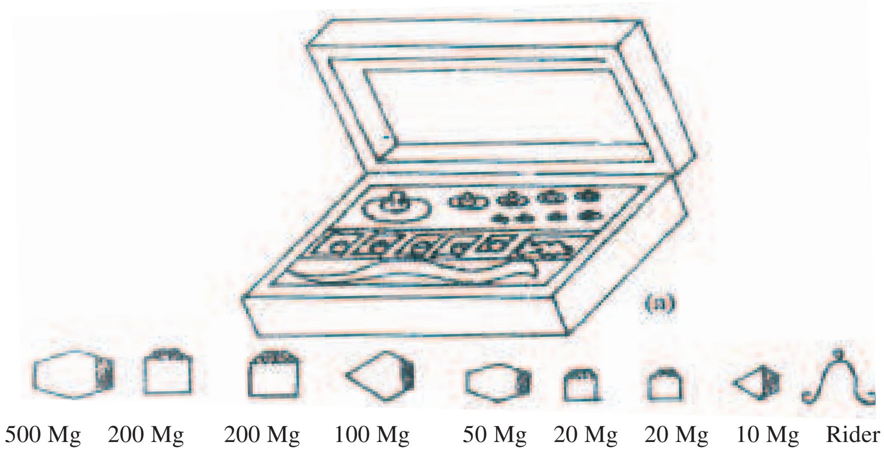


Fig: 15.8 *(a) A weight box, (b) Fractional weights*

Primary Standard

The standard solution of some substances can.be prepared directly by weighing. These substances are available in their pure forms and do not undergo chemical change on storing. These are known as primary standards.

The important properties of primary standards are as follows:

(i) They are easily available in pure and dry conditions.

(ii) They should not undergo any chemical change with air, oxygen and carbon dioxide.

(iii) They do not possess hygroscopic, deliquecent and efflorecent properties.

(iv) They ate easily soluble when added to the solvent (normally water).

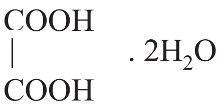
(v) They normally possess high molecular mass so that weighing errors are negligible.

(vi) The standard solution of these substances should react in a stoichiometric ratio with the volumetric titrants.

(vii) They don't react with impurities which are present in the solution to be titrated.

Examples of Primary Standard Substances

Oxalic acid



$$\begin{array}{l}COOH\\ |\\ COOH\end{array}\cdot 2H_2O$$

Mohr's salt $[FeSO_4(NH_4)_2SO_4 \cdot 6H_2O]$

Secondary Standards

Many chemical substances do not possess the primary standard properties (properties given above). Therefore, they cannot be used to prepare standard solutions. However, the solution of this type of substance are first prepared of approximate strength and then standardised by titrating with a solution of a primary standard.

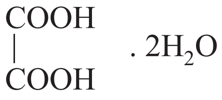
Example of Secondary Standard Substances

Sodium hydroxide (NaOH), potassium permanganate ($KMnO_4$).

15.2.4 Preparation of solutions of oxalic acid and ferrous ammonium sulphate of known molarity by weighing

Suppose you are asked to prepare **100 mL** 1.0M solution of oxalic acid;

As a first step you have to calculate the mass of oxalic acid required for preparing 100 mL of solution.



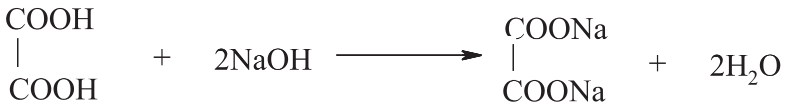
$$\begin{array}{l}COOH\\ |\\ COOH\end{array}\cdot 2H_2O \qquad \text{Molar mass} = 126g$$

126 g of oxalic acid is required to prepare 1 litre solution of molarity, 1 M.

To prepare 0.1 Molar 100 mL solution, you dissolve 1.26 of the oxalic acid in distilled water and make it upto 100 mL. Similarly, to prepare 0.1 M solution of ferrous ammonium sulphate, 3.92 grams of ferrous ammonium sulphate is dissolved in distilled water so as to get 100 mL solution

(a) Titration of oxalic acid solution against sodium hydroxide

In this acid-base titration, oxalic acid is completely neutralised by the base (NaOH) according to the following reaction.



$$\begin{array}{l}COOH\\ |\\ COOH\end{array} + 2NaOH \longrightarrow \begin{array}{l}COONa\\ |\\ COONa\end{array} + 2H_2O$$

According to this reaction, two moles of sodium hydroxide neutralises one mole of the acid for complete neutralisation. The end point is indicated by phenolphthalein indicator. It is colourless in acid medium and pink in the basic medium.

Now using the empirical relation you can calculate the strength of sodium hydroxide

$$a_1 M_1 V_1 = a_2 M_2 V_2$$

where,

a_1 = Acidity of sodium hydroxide = 1

M_1 = Molarity of sodium hydroxide = ?

V_1 = Volume of sodium hydroxide consumed (burette reading)

a_2 = Basicity of oxalic acid = 2

M_2 = Molarity of oxalic acid = 0. 1 M (known)

V_2 = Volume of oxalic acid taken for titration

Values of a_1, V_1, a_2, M_2, V_2 are known. By using the above relation you can calculate M_1

$$M_1 = \frac{a_2 M_2 V_2}{a_1 V_1}$$

(b) Titration of Ferrous Ammonium Sulphate solution against Potassium Permanganate solution

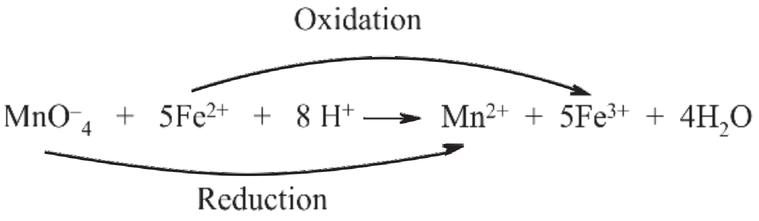
Potassium permanganate is an oxidising agent, both in alkaline and acidic medium. Oxidation is always accompanied by reduction. In this titration, the ferrous ion is oxidised to ferric ion by permanganate ion, [Mn (VII)] and at the same time permanganate ion is reduced to manganese (II) [Mn (II)] .

The following reactions take place

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$

The over all reaction is



$$MnO^-_4 + 5Fe^{2+} + 8\,H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

According to the stiochiometric relation, one mole of the oxidising agent, potassium permanganate, reduces 5 moles of reducing agent, ferrous ammonium sulphate.

Potassium permanganate is a self indicator, a pink colour appears and persists at the end point. To calculate the strength, the following relation is used:

$$a_2 M_1 V_1 == a_1 M_2 V_2$$

Here a_1 and a_2 are the change in oxidation number in oxidant and reductant respectively. For permanganate solution, $a_1 = 5$, M, and V, are its molarity and volume respectively $a_2 = 1$ for ferrous ammonium sulphate, M_2 and V_2 are its molarity and volume respectively.

15.2 MATERIALS REQUIRED

(1) Apparatus	**(2) Chemicals**
Analytical balance,	Oxalic acid, Sodium hydroxide,
Weight-box, Measuring flask	Ferrous ammonium sulphate (Mohr's salt),
Beaker, Glass rod, Conical flask,	Phenolphthalein, Distilled water,
Funnel, Burette stand, Wire gauze,	Potassium permanganate,
urette, Pipette	Sulphuric acid (dilute).

15.3 HOW TO PERFORM THE EXPERIMENT

To Prepare standard solutions of oxalic acid and ferrous ammonium sulphate, the following steps are followed

Weigh the required amount of substance (section 15.2) using an analytical balance. The substance should be weighed in a weighing bottle.

Transfer the weighed substance into a standard flask (100 mL) and dissolve in minimum amount of distilled water. Make the volume of solution upto the mark in the standard flask. Shake it by tilting the flask upside down. In case of ferrous ammonium sulphate, before making the solution upto the mark, dilute (sulphuric acid (~15mL) should be added to prevent the hydrolysis.

Preparation of 4(N) H_2SO_4

Dissolve 196g of conc. H_2SO_4 in 1000 ml of cold distilled water with constant stiring.

Preparation of standard solutions

(i) Oxalic acid

Mass of empty weighing tube =

Mass of weighing tube + substance =

Mass of weighing tube after transfer the substance into volumetric flask =

Mass of substance =

(ii) Ferrous ammonium sulphate

Mass of empty weighing tube =

Mass of weighing tube + substance =

Mass of weighing tube after transfer the substance into volumetric flask =

Mass of substance =

(b) Acid-base Titration

(i) To find out the Molarity of given NaOH solution by titrating against M/10 solution of oxalic acid. Both the solutions to be provided

Apparatus

Burette, pipette, clamp stand, white tile or paper, conical flask, wash bottle, beaker.

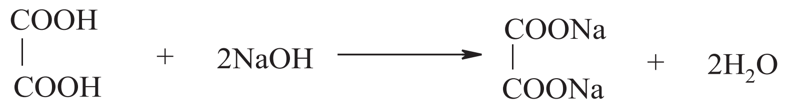
Chemicals required

M/10 oxalic acid solution, phenophthalein, sodium hydroxide solution.

Theory

In this experiment we standardise a solution of the strong base, NaOH by using weal oxalic acid $H_2C_2O_4.2H_2O$ as a primary standard solution.

The balanced chemical equation for this acid base titration is as



$$\begin{array}{c}\text{COOH}\\ |\\ \text{COOH}\end{array} + 2\text{NaOH} \longrightarrow \begin{array}{c}\text{COONa}\\ |\\ \text{COONa}\end{array} + 2H_2O$$

In this reaction two moles of NaOH reacts with one mole of oxalic acid.

Procedure

Take a, clean burette, rinse it with the given sodium hydroxide solution and clamp it vertically in a burette stand. Fill the burette with sodium hydroxide solution.

Ensure that no air bubbles are there in the stop cock. Note the initial reading (V_1). Rinse a clean 20 mL pipette with M/10 oxalic acid solution and then pipette out 20 mL of the given standard oxalic acid solution into a clean conical flask. Add a few drops phenolphthalein indicator. Hold the conical flask (as shown in figure 15.9) just below the nozzle of the burette and using your left hand, release sodium hydroxide solution into the conical flask drop by drop. Continuously swirl the contents of the conical flask smoothly and continue addition of NaOH solution dropwise till the appearance of pink colour. Note down the reading of the lower meniscus of NaOH solution. This is the final reading, (V_2). Repeat the titrations to get at least three concordant readings.

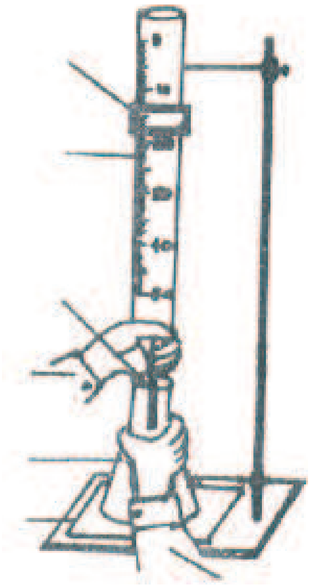


Fig. 15.9: *Carrying out a titration*

End point: colourless to pink colour.

Burette reading:

S.No.	Volume of M/10 oxalic acid solution taken (ml) V_1	Burettle reading		Volume of NaOH solution used difference of Reading $(a_2 - a_1)$	Concordant Reading volume (ml) V_2
		Initial Reading a_1	Final Reading a_2		
1.	20				
2.	20				
3.	20				
4.	20				
5.	20				

Calculation

Volume of oxalic acid solution taken in each titration, V = 20 mL

Molarity of oxalic acid = M_1 =

Volume of NaOH consumed (concurrent reading) = V_2

Molarity of Sodium hydroxide = M_2 = ?

From the chemical equation, it is clear that two moles of NaOH reacts with one mole of oxalic acid.

Oxalic acid   Base (NaOH)

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{2}$$

$$M_2 = \frac{2M_1V_1}{V_2} = x$$

Result

Molarity of the given sodium hydroxide is .... x mol/litre

(c) A study of redox titrations (single titration only)

(i) To find out the Molarity and strength of given potassium permanganate solution by titrating against M/50 Mohr's salt (Ferrous ammonium sulphate) solution. Both the solutions to be provided.

Apparatus: Burette, pipette, clamp stand, white tile or paper, conical flask, wash bottle, beaker.

Chemicals required: M/50 Mohr salt solution, dil (4N) H_2SO_4, $KMnO_4$ solution.

Theory: The Reaction between Mohr's salt and potassium permanganate is a redox reaction. In this reactino ferrous ion (Fe^{2+}) from Mohr's salt gets oxidised to (Fe^{3+}) and pink coloured Mn^{7+} gets reduced to colourless Mn^{2+}.

Molecular equation

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

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$[2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5$$

Ionic euqation

$$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

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

Indicator: $KMnO_4$ acts as self indicator

End point: Colourless to permanent pink

Procedure: Wash and rinse the burette and pipette with distilled water and then with the solution to be filled in them. fill the burette with the given $KMnO_4$ solution and pipette out 20 ml Mohr's salt solution (M/50) in a washed titration or conical flask. Add one test tube (~20 ml) full of dilute sulphuric acid (4 N) to the Mohr's salt solution taken in the conical flask. Note the intial reading of burette and start adding $KMnO_4$ solution from the burette till a permanent pink colour is imparted to the solution in the conical flask. Note the final reading. Repeat the process to get three concordant reading.

Observation table: Titration of Mohr's salt solution vs $KMnO_4$ solution.

S.No.	Volume of M/50 Mohr's salt solution taken (ml) V_1	Burettle reading		Volume of $KMnO_4$ solution used difference of Reading $(a_2–a_1)$	Concordant Reading volume (ml) V_2
		Initial Reading a_1	Final Reading a_2		
1.	20				
2.	20				
3.	20				
4.	20				
5.	20				

Concordant volume = *x* ml (say)

Calculation:

Molarity of given $KMnO_4$ solution = M_2 = ?

Volume of $KMnO_4$ solution used = V_2 ml

Molarity of given Mohr's salt solution = M_1 = 1/50

Volume of Mohr's salt solution taken = V_1 ml = 20 ml

From the chemical equations it is clear that one mole of $KMnO_4$ reacts with 5 moles of Mohr's salt.

$$\frac{M_1V_1}{5} \text{(Mohr's Salt)} = M_2V_2 \text{ (KMnO}_4\text{ Solution)}$$

$$M = \frac{M_2V_2}{V_1} \times 5 = y$$

Strength of $KMnO_4$ solution

Strength = Molarity × Molar Mass of $KMnO_4$ = y × 158 g/L = z

Result: The strength and molarity of given $KMnO_4$ solution is found out to be Z g/litre and y respectively.

(ii) To find out strength and Molarity of the given potassium permanganate solution by titrating against M/10 oxalic acid solution.

Apparatus: Burette, pipette, clamp stand, white tile or paper, conical flask, wash bottle, beaker, burner, tripod stand, wire net

Chemicals required: M/10 Oxalic acid solution, dil (4N) H_2SO_4, $KMnO_4$ solution.

Theory: This is a redox reaction taking place between oxalic and $KMnO_4$ solution. Here $C_2O_4^{2-}$ is oxidised to CO_2 and $KMnO_4$ ion is reduced to Mn^{2+} ion.

Ionic equation

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

The oxidation of oxalate ions by permanganate is very slow at room temperature. The reaction rate increases on heating (60–70°C) and once the reaction has started, its rate is automatically increase due to the formation of Mn(II) ions which catalyse the reaction (autocatalysis). Oxalic acid is a dibasic acid and one molecule of oxalic acid lose $2e^-$ so its equivalent weight can be calculated as

Molarity of provided $KMnO_4$ solution can be calculated using Molarity equation

$$\text{(Oxalic acid Solution)}\frac{M_1V_1}{5} = \frac{M_2V_2}{2}(KMnO_4\ \text{Solution})$$

Indicator: Potassium permanganate acts as self indicator

Endpoint: Colourless to permanent pink

Procedure: Rinse and fill the burette with given $KMnO_4$ solution. Pipette out 20 ml of oxalic acid solution in a washed titration flask, add one test tube (~20 ml) full of diluate sulphuric acid (4 N) and heat the flask to 60–70°C. Note the initial reading of the burette and start adding $KMnO_4$ solution from the burette till a permanent pink colour is imparted to the solution in the titration flask. Note the final reading of burette (Read upper meniscus beaceuse $KMnO_4$ solution is coloured). Repeat the above step to get three successive concordant reading.

Observation table: Titration of Standard M/10 oxalic acid vs unknown $KMnO_4$ solution

S.No.	Volume of M/10 Oxalic acid solution taken (ml) V_1	Burettle reading		Volume of $KMnO_4$ solution used difference of Reading (a_2-a_1)	Concordant Reading volume (ml) V_2
		Initial Reading a_1	Final Reading a_2		
1.	20				
2.	20				
3.	20				
4.	20				
5.	20				

Calculation:

Molarity of given $KMnO_4$ solution = $M_2 = ?$

Volume of $KMnO_4$ solution used = V_2 ml = n ml

Molarity of given oxalic acid solution = $M_1 = 0.1$

Volume of oxalic acid solution taken = V_1 ml = 20 ml

Molarity of given $KMnO_4$ solution

$$\frac{M_1V_1}{5} \text{ (oxalic acid)} = \frac{M_2V_2}{2} \text{ (KMnO}_4\text{ solution)}$$

$$M_2 = y$$

Strength of $KMnO_4$ solution

Strength = Molarity × Molar Mass of $KMnO_4$ = y × 158 g/L = z

Result: The strength and molarity of given $KMnO_4$ solution is found out to be Z g/litre and y respectively.

15.4 PRECAUTIONS

(i) Handle the Chemical Balance carefully.

(ii) While preparing standard solutions add distilled water into the flask slowly. (Otherwise you will easily miss the mark),

(iii) Chemicals should be pure (LR or AR).

(iv) Apparatus used should be clean and dry.

(v) Only 2 to 3 drops of indicator solution should be used,

(vi) At least two concordant readings should be taken for calculations,

(vii) While titrating, continuous swirling of the solution is required, to avoid incomplete reaction.

15.7 CHECK YOUR UNDERSTANDING

1. State the need of rinsing the burette and pipette with respective solutions to be used in the titration.

   ....

2. Why should pure chemicals be used for preparing a standard solution?

   ....

3. Why should only the lower meniscus be taken into consideration while reading the level of solution.

   ....

4. How the last (final) drop of solution in pipette can be taken out?

   ....

5. Why the secondary standard cannot be used in the standard solution preparation?

   ....

15.8 A NOTE FOR THE TEACHERS

(i) Teacher should demonstrate to the students the method to handle an Analytical Balance.

(ii) Teacher should ensure that the chemicals are pure enough and that distilled water is used in the titration. The appearance of the end point and the concept of concurrent readings should be made clear,

(iii) The reaction which is occurring in the titration should be explained to the students.

15.9 CHECK YOUR ANSWERS

1. To avoid error in the calculations.
2. The impurities may react and interfere in the reaction. Change in weights will lead to errors in the calculations.

3. The solution level in the burette is always in the curved manner (concave). Therefore if we take the upper meniscus, there will always be a loss in the volume of the solution.

4. After releasing all the solution just touch the edge of the pipette on the sides of the conical flask.

5. (a) Secondary standards are not available in the pure and dry forms.
   (b) It may undergo reaction with solvents
   (c) It may undergo hydration and alter its own weights during the process.
   (d) It may react with air or oxygen and carbon dioxide.

Notes

EXPERIMENT-16

Qualitative analysis of a salt involving detection of one anion and one cation from the following (salts insoluble in hydrochloric acid excluded)

Anions :

CO_3^{2-}, SO_3^{2-}, S^{2-}, NO_2^-, $C1^-$, Br^-, I^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, $C_2O_4^{2-}$, CH_3COO^-

Cations:

NH_4^+, Pb^{2+}, Cu^{2+}, As^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}

OBJECTIVES

After performing this experiment, you should be able to:

- explain the meaning of Qualitative Analysis;
- handle properly the chemicals and reagent bottles in the chemistry laboratory;
- perform simple experimental operations such as heating, testing of gas evolved, filtration and 'washing of residue etc.;
- observe the appearance/disappearance of colour, precipitate, turbidity etc. in reaction mixture;
- acquire an elementary idea of the pressence of an anion or a cation in the salt by carrying out dry test; and
- perform preliminary and confirmatory tests of anions and cations and analyse the given salt.

16.1 MATERIALS REQUIRED

(1) Apparatus	**(2) Chemicals**
Test tubes	Hydrogen Sulphide gas
Test tube holder	
Funnel	**Solution**
Glass rod	1) Lime water
Tripod stand	2) Silver nitrate $AgNO_3$(aq)
China dish	3) Lead acetate (aq)

Platinum wire/Nichrome wire
Boiling tube
Brush
Beaker
Wire gauze
Spatula
Watch glass

4) Sodium nitroprusside (aq)
5) Potassium iodide (aq)
6) Starch solution
7) Ammonium hydroxide
8) Barium chloride (aq)
9) Potassium chromate (aq)
10) Potassium ferrocyanide (aq)
11) Potassium sulphocyanide
12) Dimethyl glyoxime solution
13) Ammonium oxalate (aq)
14) Nesseler's reagent
15) Blue litmus solution.
16) Sodium hydroxide, (dilute and concentrated)
17) Hydrochloric acid (dilute and concentrated)
18) Sulphuric acid (dilute and concentrated)
19) Nitric acid (dilute and concentrated)
20) Acetic acid (dilute)

Solids

Ammonium chloride
Ammonium carbonate
Potassium dichromate
Ferrous sulphate
Ammonium Molybdate

16.2 WHAT YOU SHOULD KNOW

Qualitative analysis of an unknown salt consists of the detection and identification of the constituent ions. The inorganic salts on dissolving in water dissociate completely into positively and negatively charged ions. An positively charged ion is called *cation* or a basic radical and the negatively charged ion is called *an anion* or an acid radical. A number of tests are carried out to identify the ions.

Qualitative analysis is done by carrying out two kinds of tests (i) dry tests, and (ii) wet tests.

The dry tests are performed on solid inorganic substances. These tests should be performed before proceeding with wet tests.

I. During a dry test, we note

(i) physical examination of salt such as colour, smell and density of the salt gives valuable clues regarding the nature of some of the basic and acid radicals.

(ii) action of heat on dry salt

II. The wet tests are carried out in solution. In a wet test, we note

(i) the colour and smell of the gas evolved.

(ii) formation or disappearance of a colour of solution, (iii) formation or disappearance of a precipitate.

A test may be positive or negative. A positive test is the one which gives the result indicated in the theory and a negative test does not give the results as indicated in the theory.

For example, to test a carbonate ion, you add dilute sulphuric acid to the substance. The colourless gas evolved is passed through lime water which turns milky (a positive test). If the lime water does not turn milky then it is a negative test.

To detect the anion and cation in a salt, certain chemicals are used. These chemicals are called *Reagents.* When reagents react with salts, new compounds are formed with some observable properties such as colour, smell and characteristic appearance of precipitate.

Before carrying out systematic analysis, it is necessary to know few important laboratory techniques.

16.2.1 Laboratory Techniques

To identify an anion and a cation in a salt, some techniques have to be used. The techniques are as follows:

1. Heating of a salt or solution in a test tube

(i) While heating a salt or a solution in a test tube, hold the test tube in such a manner that the mouth of the test tube is away from yourself or any other person working in adjacent place.

(ii) Heat the test tube gently by placing its one side in the outermost zone of the flame. While heating, shake the test tube occassionally to avoid any spurtting.

(iii) Always heat the top layer of liquid in a test tube, so that it boils quickly. Never apply flame on the bottom of test tube, otherwise bumping will start. You may use a piece of procelein to avoid bumping.

(iv) While heating for a long time, use a test tube holder. Hold it between your thumb and the fingers if the volume in the test tube is less then half and you have to only warm the contents.

2. Use of a Reagent Bottle

Take out the desired reagent bottle from shelf. Remove the stopper and hold it in right hand. Hold the test tube between the thumb and first two fingers of the left hand. Now pour the required quantity of the reagent along the side of the test tube. Put the bottle back on the shelf and stopper it immediately. Never put the stopper on the table.

3. Testing of a gas evolved: On adding a reagent to a salt if effervescence are given out in cold or on heating it indicates the evolution of a gas.

The gas evolved can be tested in the following manner:

(i) Note the colour of gas evolved

(ii) Smell the evolved gas by puff of hand. Never inhale a gas by placing the nose directly into the vapour.

(iii) By bringing a filter paper strip or a glass rod with its end dipped into the testing reagent near the mouth of the test tube.

(iv) By passing the gas evolved for few seconds through a reagent taken in a test tube, shake the test tube well and observe the change.

4. Precipitation: Insoluble compound formed by addition of a reagent to a solution under the test or passing a gas through the solution under the test is called a precipitate and the process is called precipitation. As soon as a clear solution turns turbid, it is an indication that precipitate is formed.

In some cases the precipitate may dissolve in excess of precipitating reagent, in that case two observations should be taken, one on addition of precipitating reagent dropwise and second on adding excess of precipitating reagent.

5. Filtration: It is a process by which an insoluble compound is separated from a reaction mixture. To carry out filtration, first the filter paper cone is made. It is then opened in such a way that the three layers of paper are on one side, while the fourth layer is on the other side. By doing so a hollow cone of filter paper is obtained. The cone is then placed in funnel and by wetting with water, it is fixed properly but gently in funnel. The liquid mixture is then poured over the filter paper funnel along the side of a rod. Never fill the filter paper cone more than 2/3 rd of its capacity. Note that there should be no space between filter paper cone and glass funnel. It reduces the rate of filtration. The liquid passes through the pores of filter paper and collects in the vessel kept below the stem of the funnel. The clear liquid so collected is called Filtrate. The insoluble compound or precipitate, which remains over the filter paper is called residue.

6. Washing and collection of precipitable: It is essential to wash the precepitate before carrying out any test on it. The washing is done by slowly pouring distilled water over the precepitate while it is still in the runnel. After washing. carefully remove the filter paper from funnel open up and spread it on a dry filter paper and remove the precipitate carefully with the help of a spatula and collect it on a watch glass. Use a small portion of it eachtime for carrying out various tests.

7. Dry test: A number of tests can be carried out using the powdered salt. The information thus obtained often provides a clue to the presence or absence of certain radicals. With their knowledge, the course of wet analysis may be shortened or modified. Some of the important dry tests are given below:

(i) Physical examination: Examine the colour, smell and the density of salt

S.No.	Observation	Inferences
1.	**The colour of solid**	
	(i) Blue	Copper salt may be present
	(ii) Green (light or dark) present	Copper, nickel and ferrous salt may be
	(iii) Yellow	Ferric salt may be present
	(iv) Pink	Manganese salt may be present
	(v) Buff	Manganese salt may be present
	(vi) White	Salts of remaining cations may be present (Ca^{2+}, NH_4^+, Pb^{2+}, Zn^{2+})
2.	**Smell:** Rub a pinch of salt with the help of a spatula on a watch glass	
	smell of ammonia,	Ammonium salt may be present
	smell of rotten eggs	Sulphide salt may be present
3.	Density	
	Salt is light	Carbonates of zinc and calcium may be present

(ii) Dry heating test: The salt is heated gently and then strongly in a clean and dry test tube.

S.No.	Observation	Inferences
(1)	Solid melts and resolidifies	Salts of calcium may be present
(2)	Solid swells up	phosphate may be present
(3)	Solid decripitates (Cracking sound)	Lead nitrate may be present
(4)	Solid sublime and vapour are white in colour	Ammonium chloride may be presents

16.2.2 Precautions

(i) Use a perfectly dry test tube for performing this test.

(ii) Keep the mouth of the test tube away from yourself as well as from your neighbouring students.

(iii) During heating, do not heat the tube at one point but keep it rotating otherwise the tube may crack.

(iv) Do not smell the gases evolved by placing the nose directly over the mouth of the tube. Always smell the gas by puff of your hands.

16.3 DETECTION AND IDENTIFICATION OF ANIONS

List of anions : - CO_3^{2-}, SO_3^{2-}, S^{2-}, NO_2^-, $C1^-$, Br^-, I^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, $C_2O_4^{2-}$, CH_3COO^-

16.3.1 Preliminary tests

The method of detection of anions is not as systematic as that of basic radicals. It has not been possible to include acidic radicals (anions) into distinct groups as in the case of cations (basic radicals).

The process employed to detect an anion may be divided into two classes.

(A)Those involving the identification of volatile products obtained on treatment with acids.

This test can be further divided into the following two groups,

(I)Action of dilute sulphuric acid

(II) Action of concentrated sulphuric acid.

(B)Those dependent on reaction in solution

Before carrying out a confirmatory test in solution it is necessary to prepare a water solution. Or sodium carbonate extract of the salt

(i) Preparation of water solution for anion analysis: Take a pinch of given salt in a test tube. Add 2=3 mL of water and shake well.

(ii) Preparation of sodium carbonate of extract: If the salt is insoluble in water, preparation of sodium carbonate extract is necessary.

This is prepared as follows:

Mix the salt with nearly twice its weight of sodium carbonate. Add sufficient distilled water in a dish, boil and filter. The filtrate *is* known as sodium extract.

How to use sodium carbonate extract: Sodium carbonate extract always contains an excess amount of unreacted sodium carbonate which may interfere in the usual tests of acid radicals. It is absolutely necessary to destroy the excess of sodium carbonate. This is done by acidifying sodium carbonate extract with a suitable acid (choice depends upon the nature of the acid radical to be tested).

(A) Action of Acids

(I) Test with dilute sulphuric acid: The anions which can be detected by treating a salt with dilute H_2SO_4, are as follows :

CO_3^{2-} , S^{2-} and NO_2^-,

A gas is given out on adding dilute H_2SO_4 to salt. For observations and explanation follow the given table.

Anions	Observation	Explanation	Inferences
CO_3^{2-}	Brisk effervescence a colourless odourless gas is given out	$MCO_3 + H_2SO_4$ $\rightarrow M\,SO_4 + H_2O + CO_2$ carbon dioxide (colourless)	CO_3^{2-}
S^{2-}	Colourless gas with suffocating smell of rotten eggs is given out	$MS + H_2SO_4$ $\rightarrow M\,SO_4 + H_2S$ Hydrogen sulphide (colourless)	S^{2-} may be present
NO_2^-	A brown coloured gas is evolved	$2M\,NO_2 + H_2SO_4$ $\rightarrow M_2SO_4 + 2HNO_2$ nitrous acid (Colourless) $3MNO_2 \rightarrow H_2O + HNO_3 + NO$ $NO + O_2 \rightarrow 2\,NO_2$ Nitrogen dioxide (Reddish brown)	NO_2^- may be present

Do not boil the contents of the test tube. Over heating decomposes H_2SO_4 and gives sulphur dioxide.

(II) Confirmatory tests of CO_3^{2-}, S^{2-} and NO_2^- ions

(1) Carbonate ion CO_3^{2-}: On passing the gas through lime water, it turns milky due to the formation of calcium carbonate

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

Calcium carbonate

On passing excess of CO^{2+} the milkiness disappears and a clear solution is obtained.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

(2) ***Sulphide ion, S^{2-}:***

(a) Filter paper moistened with lead acetate turns black on exposure to gas.

$$Ph(CH_3COO)_2 + H_2S \longrightarrow 2CH_3COOH + PbS\downarrow$$

Black lead Sulphide

(b) **Sodium Nitroprusside test :** A violet colouration is obtained on adding freshly prepared solution of sodium nitroprusside to salt solution.

$$Na_2S + Na_2\,[Fe(NO)(CN)_5] \longrightarrow Na_2[Fe(CN)_5NOS$$

Sodium Nitroprusside Violet colouration

(3) ***Nitrite ion, NO_2^-:*** When a filter paper soaked in a mixture of KI + starch solution is exposed to the gas, it turns blue or violet in colour.

$$2NO_2 + 2KI \rightarrow 2KNO_2 + I_2$$

I_2 + Starch — Starch iodide complex, deep blue or violet.

(III) Test with concentrated sulphuric acid : This test is performed after performing the test with dilute $H_2\,SO_4$. Anions which give positive test with dilute H_2SO_4 will also react with concentrated H_2SO_4. On adding concentrated $H_2\,SO_4$ to a salt, if a gas is given out, follow the given table for drawing an inference.

I_{ON}	Observations	Explanation	Inferences
Cl^-	A colourless gas with pungent smell is evolved	$MCI + H,SO_4$ $MHSO_4 + HCl$ Hyderogen Chloride (colourless gas)	Cl^- may be present
Br^-	A brown gas with pungent smells is evolved, the Contents of the test solution turns redish brown	$MBr + H_2SO_4$ $\rightarrow MHSO_4 + H\,Br$ $2H\,Br + H_2SO_4$ $\rightarrow H_2O + SO_4 + Br_2$ Bromine (reddish brown gas)	Br^- may be present

I^-	Violet fumes with pungent smell evolved Black specks appeared on the sides of the test tube	$MI + H_2SO_4 \rightarrow MHSO_4 + HI$ $HI + 2H_2SO_4 \rightarrow 2H_2O + SO_2 + I_2$	I^- Iodide may be present purple (violet)
NO_3^-	brown coloured gas with pungent smell is evolved the gas intensified on adding copper turning	$2MNO_3 + H_2SO_4 \rightarrow M_2SO_4 + 2HNO_3$ $4\,HNO_3 \rightarrow 2H_2O + O_2 + 4NO_2$ $3Cu + 8\,HNO_3 \rightarrow 2Cu\,(NO_3)_2 + 2NO + 4H_2O$ $2NO + O_2 \rightarrow 2NO_2$	NO^-_3 may be present Nitrogen dioxide (light brown gas) Nitorgen oxide (colourless) (Brown gas)

Precautions

1. Do not boil the contents of test tube.
2. After the test is over, do not throw away the contents of test tube immediately into sink The reaction of concentrated H_2SO_4 with water is highly exothermic and generate a lot of heat.
3. Do not inhale the gas evolved during the test because they are corrossive in nature.
4. Concentrated H_2SO_4 should be handled carefully.

(IV) Confirmatory tests of Cl^-, Br^-, I^- and NO_2^-

(a) Chloride ion, (Cl^-)

(i) Silver Nitrate test: A curdy white precipitate insoluble in conc. HNO_3 is obtained on adding silver nitrate to water solution Acidify with dil HNO_3 before adding Ag NO_3 in case sodium carbonate extract in used.

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$

Curdy white precipitate is soluble in ammonium hydroxide.

$$AgCl + 2\,NH_4OH \longrightarrow [Ag(NH_3)_2]^+ + 2H_2O$$

Diammine silver chloride (Colourless)

Notes

(ii) Chromyl Chloride test

Yellow fumes of Chromyl Chlorides are obtained on heating a misture of salt and solid $K_2Cr_2O_7$ and concentrated H_2SO_4 in a dry test tube

$$2MCl_2 + K_2Cr_2O_7 + 3\,H_2SO_4 \longrightarrow 2MSO_4 + K_2SO_4 + 2CrO_2Cl_2$$

Chromyl chloride (Orangish red)

Chromyl chloride fumes turns dilute NaOH yellos

$$CrO_2Cl_2 + NaOH \longrightarrow Na_2CrO_4 \quad + \quad 2H$$

Sodium chromate (yellow)

A yellow precipitate of lead chromate, $PbCrO_4$ is formed on adding lead acetate to the yellow solution acidified with CH_3COOH

$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow PbCrO_4\downarrow \; + \; CH_3 \qquad 1$$

lead chromate (yellow precipitate)

(b) Bromide ion, Br^-

(i) Silver nitrate test: A light yellow precipitate is obtained on adding silver nitrate to water solution (after acidifying the sodium carbonate extract with dil HNO_3). The precipitate is partially soluble in ammonium hydroxide

$$Ag^- + Br^- \longrightarrow AgBr\downarrow$$

Silver bromide (light yellow)

$$AgBr + 2NH_4OH \longrightarrow [Ag\,(NH_3)_2]\,Br \;+\; 2H_2O \text{ in}$$

(ii) Organic layer test: The addition of chlorine water to water solution containing bromide liberates free bromine which imparts orange red colour to the test solution. On shaking with carbon tetrachlkoride, a reddish brown colour is imparted in CCl_4 layer. The organic layer of CCl_4 is obtained below the colourless aqueous layer.

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$$

Bromine, reddish brown in CCl_4

(c) Iodide ion, I^-

(i) Silver nitrate test: Iodide ion, (I^-) A yellow precipitate is obtained on adding $AgNO_3$ solution to acidified (with dil HNO) water solution, which is insoluble in NH_4OH

$$Ag^+ + I^- \longrightarrow AgI \downarrow$$

Silver iodide, yellow precipitate

(ii) Organic layer test: The addition of chlorine water to test solution liberates free iodine, which colours the solution, violet. On shaking with carbon tetra chloride, a violet colour is imparted to the organic layer.

$$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$$

Iodine (Violet Colour in $CC1_4$)

(d) Nitrate ion, (NO_3^-) :

Ring test: On adding concentrated. H_2SO_4 gradually along the side of the test tube to a mixture of salt solution in water or its sodium carbonate extract, acidified with dil.H_2SO_4, and freshly prepared ferrous sulphate solution, abrown ring is obtained at the junction of two layers.

$$\begin{aligned} M(NO_3)_2 + H_2SO_4 &\longrightarrow MSO_4 + 2HNO_3 \\ 6FeSO_4 + 2\ HNO_3 + 3\ H_2SO_4 &\longrightarrow 3Fe_2\ (SO_4)_3 + 4\ H_2O + \\ X\ FeSO_2 + Y\ NO &\longrightarrow (FeSO_4)_x\ (NO)_y \end{aligned}$$

Nitrosoferrous sulphate,

(brownring)

$$Fe^{2+} + 5H_2O + NO \longrightarrow [Fe(H_2O)_5\ NO]^{2+}$$

(B) Individual tests

(a) Sulphate ion, SO_4^{2-}: On adding $BaCl_2$ solution to acidified (dil HCl) salt solution or its sodium carbonate extract a white precipitate is obtained which is insoluble in concentrated HCl or concentrated HNO_3

$$Ba^{2-} + SO_4^{2-} \longrightarrow BaSO_4$$

Barium chloride white precipitate

(b) SO_3^{2-} sulphite ion

Take about 0.1 g salt in a test tube. Add 1 mL H_2SO_4. Punget smell due to the formation of SO_2.

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + H_2O$$

Take a small quantity of salt in a test tube. Add a little amount of $K_2Cr_2O_7$ and dil H_2SO_4. Warm the test tube green colour appeared in test tube SO_3^{2-} ion is confirm.

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + H_2O$$

$$SO_2 + K_2Cr_2O_7 + H^+ \longrightarrow Cr_2(SO_4)_3 + H_2SO_4 + H_2O$$

(c) $C_2O_4^{2-}$ Oxalate ion

Take a small quantity of salt (0.1 g) in a test tube. Add dil H_2SO_4 and a drop of $KMnO_4$ solution. Wamr the test tube. Colour of $KMnO_4$ dischage indicates the presence of C_2O4^{2-}

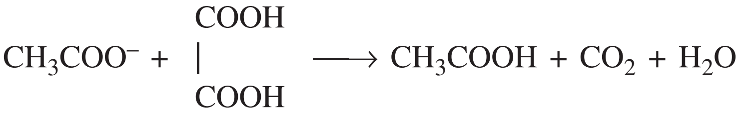
$$KMnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

$$2MnO_4^- + 16H^+ \longrightarrow 5C_2O_4^{2-} + 10CO_2 + 2Mn^{2+} + 8H_2O$$

(d) CH_3COO^- Acetate ion

Take a pinch of salt on your palm. Rub with a pinch of oxalic acid and a drop of water. Smell of vinegar confirm CH3COO⁻ ion



$$CH_3COO^- + \begin{array}{c} COOH \\ | \\ COOH \end{array} \longrightarrow CH_3COOH + CO_2 + H_2O$$

$$CH_3COO^- + H^+ + C_2H_5OH \longrightarrow \underset{\text{Ester}}{CH_3COOC_2H_5}$$

Take a small quantity of salt in a test tube. Add dil H_2SO_4 (1 ml) and C_2H_5OH (1 ml). First smell indicates the presence of CH_3COO^- ion

(e) Phosphate ion, (PO_4^{3-}): Salt or its water solution or its sodium carbonate extract is heated with concentrated, HNO_3 till the fumes no longer evolve. Contents of the test tube are diluted with water. A canary yellow precipitate of ammonium phosphomolybdate is formed on warming the above test solution with ammonium molybedate.

$$PO_4^{3-} + 12\,MoO_4^{2} + 24\,H^+ + 3\,NH_4^{4} \xrightarrow{\Delta} (NH_4)_3PO_4\ 12$$

Ammonium phosphomolybdate
canary yellow precipitate

Precautions

1. Some times on adding $BaCl_2$ solution, a thin white precipitate is obtained, it may be due to formation of barium phosphate which is soluble in concentrated HCl.
2. During the test of phosphate ion, use a small porcelain piece or pumice stones whiie heating the salt or water solution with concentrated. HNO_3, to avoid bumping of contents of test tube.
3. Use cone HNO_3 carefully.

16.4 IDENTIFICATION OF CATIONS

For identification of cations (excluding NH_4^+ ion belonging to group zero) have been divided into six groups depending upon the differences in solubility of chlorides, sulphides, hydroxides and carbonates. Of these ions, the cations are precipitated by adding some reagents called, group reagents.

The following table gives briefly the classification of basic radicals (cations) into groups. Group reagents and form in which they precipitate.

Groups	Cations	Group reagent	Form in precipitate which cation precipitate
O	NH^+_4	Cone. NaOH	No precipitate obtanied. A Colourless gas ammonia with pungent smell is evolved on worning
I	Pb^{2+}	dil. HCI	Chloride
II	Cu^{2+}, As^{3+}	$H_2S(g)$ in the presence of dil HCl	Sulphide
III	Fe^{3+}, Al^{3+}	excess of NH_4OH in presence of excess of $NH_4Cl(s)$	Hydroxide
IV	Co^{2+} Zn^{2+}, Mn^{2+}, Ni^{2+}	H_2S (g) in the presence of NH_4Cl (s) and NH_4OH excess	Sulphide
V	Ba^{2+}, Sr^{2+}, Ca^{2+}	$(NH_4)_2CO_3$ soln. in the presence of NH_4Cl and NH_4OH	Carbonate
VI	Mg^{2+}	$NH_4H_2PO_4$	Phosphate

Before proceeding to detect the cations the solution of the salt should be prepared.

Preparation of original solution: Take apinch of salt in a clean test tube. Add 2-3 mL of distilled water, shake well. If the solid is not soluble in cold water then heat the contents. If the salt is still not soluble in hot water add few drops of cone. HCI,

Precautions: Do not add excess of conc. HCI. This might create a problem during cation analysis.

(a) If on addition of cone. HCl a gas is evolved, wait till the effervescence ceases and then Add 2-3 drops more of conc. HCl.

(b) Use only distilled water to prepare original solution.

General rules for the procedure involving the analysis of cations (basic radicals)

(1) The group reagent should be added in the systematic order.

(2) Test for the higher group radicals are performed only when the radicals of a lower group are found absent.

(3) Slight excess of the group reagent should be added to ensure complete precipitation of group radicals.

(4) When a precipitate is obtained for a particular group, it is filtered and the residue is used for the analysis of the radicals of that group. Before carrying out the analysis, wash the residue two times with distilled water. Washings should be discarded.

(5) To find out the presence of a cation in a particular group, a small portion of the solution is used which is known as the test portion.

16.4.1 Cation Analysis

(a) Group zero, (Ammonium ion) NH_4^+

Ammonium ion, (NH_4^+): On warming with NaOH solution, a colourless gas with pungent smell of ammonia is evolved.

$$NH_4^+ + OH^- \xrightarrow{\Delta} NH_3 + H_2O$$

Ammonia (colourless)

Confirmatery test:

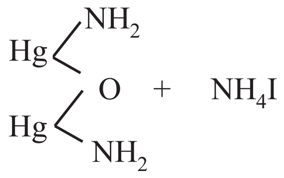
On passing the gas through Nessler reagent a reddish brown precipitate is obtained.

$$K_2HgI_4 \longrightarrow 2KI + HgI_2$$

Nessler's reagent

$$HgI_2 + 2NH_3 \longrightarrow Hg(NH_2)I + NH_4I$$

(Amino-mercuric iodide)



$$2Hg(NH_2)I + 2H_2O \longrightarrow \begin{matrix} Hg\langle^{NH_2} \\ \quad O \\ Hg\langle_{NH_2} \end{matrix} + NH_4I$$

Reddish brown, precipitate Iodide of

millons base

(b) Group-I (Pb^{2+})

If a white precipitate is obtained on adding dilute HCI to salt solution in water or while preparing original solution in dilute HCI, it indicates the presence of Pb^{2+} ions. White precipitates dissolves again on warning and reprecipitates on cooling.

$$Pb^{2+} + Cl^- \longrightarrow PbCl_2$$

Lead chloride (white precipitate)

Note: In case the original solution is prepared in dilute HCI, Group I is absent

(1) **KI test:** On adding KI to hot solution of lead chloride, a yellow precipitate is obtained.

$$Pb^{2+} + 2I^- \longrightarrow PbI_2 \downarrow$$

Lead iodide (Yellow precipi tate)

(2) Potassium chromate test: On adding K, CrO_4 solution to hot- solution of lead chloride, a yellow precipitate is obtained.

$$Pb^{2+} + CrO^{2-}_4 \longrightarrow PbCrO_4 \downarrow$$

Lead Chromate (Yellow precipitate)

(C) Group II: Cu^{2+}, As^{3+}

On passing hydrogen sulphide gas through acidified original solution obtained which indicates the presence of Cu^{2+} ions

$$M^{2+} + S^{2-} \longrightarrow MS \downarrow$$

Metal sulphide

(1) If no precipitate is obtained even on dilution of test portion, in that case gp II is absent.

(2) To obtain a granular precipitate pass H_2S for 2=3 minutes through hot solution.

Confirmatory test of Cu^{2+} ion: On heating black ppt of CuS with dilute HNO_3, a blue colour solution is obtained.

$$3CuS + 8\,HNO_3 \longrightarrow 3Cu\,(NO_3)_2 + 3S + 2NO\uparrow + 4H_2O$$

Copper nitrate,

(blue colour)

(1) On adding ammonium hydroxide, precipitate is obtained which is soluble in excess reagent to produce deep blue solution.

$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2$$

Copper hydroxide (Blue precipitate)

$$Cu(OH)_2 + 4\,NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$

Tetraammine cupric sulphate (deep blue colour)

(2) On adding acetic acid followed by potassium ferrocyanide to blue solution, a chocolate brown precipitate is obtained

$$2Cu^{2+} + K_4[Fe(CN)_6] \longrightarrow Cu_2\,[Fe(CN)_6] + 4K^-$$

Copper ferrocyanide,

(chocolate brown precipitate)

Confirmatory test of As^{3+} Arsenic ion

On passing H_2S in the solution of salt yellow ppt is obtained. It is soluble in yellow ammonium sulphide to form ammonium thioarsenate

$$As_2O_3 + 3(NH_4)_2S_x \longrightarrow 2(NH_4)_2AsS_4$$

On addition of dil HCl in the solution yellow ppt is form

$$(NH_4)_2AsS_4 + 6HCl \longrightarrow As_2S_3 + 6NH_4Cl + H_2S$$

Yellow ppt

Dissolve this ppt in con HNO_3 and then add ammonium molyblate canary yellow ppt indicates the presence of As^{3+} ion

$$As_2O_3 + 12HNO_3 \longrightarrow 2H_3AsO_4$$

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{Yellow ppt}}{(NH_4)AsS_4.12MoO_3} + 2NH_4NO_3 + 12H_2O$$

(d) Group III

(Fe^{3+} ions)

Preliminary test: To the origional solution add little concentrated HNO_3, and boil to oxidise Fe^{2+} to Fe^{3+} and then add excess of solid NH_4C1 followed by excess of ammonium hydroxide. White or reddish brown precipitate is obtained.

Reddish brown precipitate indicates the presence of Fe^{3+} ions.

Note: Addition of large excess of NH_4OH may start dissolving group III precipitates. Hence it should be avoided.

Confirmatory test of Fe^{3+} ion: Reddish brown precipitate of $Fe(OH)_3$ on dissolving in dilute HC1, preduces a yellow solution

$$Fe(OH)_3 + 3HCl \longrightarrow \underset{\text{Yellow solution}}{FeCl_3} + 3H_2O$$

(1) On adding $K_4\,[Fe(CN)_6]$ to yellow solution, a prussian blue precipitate is obtained.

$$4Fe^{3+} + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian blue}}{Fe_4\,[Fe\,(CN)_6]_3} + 12K^+$$

(2) On adding KCNS to yellow solution a red colouration is obtained

$$Fe^{3+} + 3SCN^- \longrightarrow [Fe(SCN)_3]$$

Ferric thiocyanate

(red colour)

(e) Group IV analysis (Co^{2+}, Zn^{2+}, Mn^{2+} & Ni^{2+} ions)

Preliminary test: Take the original solution and add NH_4OH to make it alkaline pass hydrogen sulphide, gas (H_2S) through the solution, a precipitate is obtained

Formation of white precipitate indicates the presence of Zn^{2+}

Formation of buff (flesh coloured) precipitate indicates the presence of Mn^{2+}

Formation of black precipitate indicates the presence of Ni^{2+}

$$M^{2+} + S^{2-} \longrightarrow \underset{\text{Metal sulphide}}{MS}$$

Note: Hydrogen sulphide gas should always be passed slowly, Otherwise black residue of FeS from kipps appratus enters the test solution and creates confusion.

(2) Solution should smell of ammonia before passing H_2S.

Confirmatory test Co^{2+} ion

To the original solution of the salt add NH_4Cl and NH_4OH. Now add a pinch of KNO_2 acidify with dil CH_3COOH. Yellow ppt indicate the presence of CO^{2+} ion

$$CH_3COOH + KNO_2 \longrightarrow CH_3COOH + HNO_2$$

$$Co(NO_2)_2 + 2HNO_2 \longrightarrow Co(NO_2) + H_2O + NO$$

$$Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6]$$

or on passing H_2S gas a solution black ppt is formed disssolve this ppt in aqua regia ($HCl : HNO_3$) 3 : 1. Neutralize by adding aqueous NH_3. Now add aqueous NH_4SCN. Appearance of blue colour indicates the presence of Co^{2+} ion

Confirmatory test; Zn^{2+} ion

On dissolving white precipitate of ZnS. in dilute HCI, a colourless solution is obtained Boil off H_2S.

$$ZnS + 2HCl \longrightarrow ZnCl_2 + HS_2$$

(1) On adding small amount of NaOH a white precipitate is obtained which is soluble in excess of NaOH

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$$

Zinc hydroxide, (white precipitate)

$$Zn(OH)_2 + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$$

Tetrahydroxozincate (II) ion

(2) Gray white precipitate is obtained on adding potassium ferrocyanide to solution of ZnS in dilute HCI..

$$2\,Zn^{2+} + K_4[Fe(CN)_6] \longrightarrow Zn_2[Fe(CN)_6] + 4K$$

grey white precipitate

Confirmatory test of Mn^{2+} Buff coloured precipitate of MnS dissolves in dilute HCI.

$$MnS + 2\,HCl \longrightarrow MnCl_2 + H_2S$$

Boil offhydrogen sulphide gas. To the solution obtained above, on adding NaOH, a white precipitate of Mn $(OH)_2$ is obtained. The precipitate rapidly oxidises on exposure to air turning brown.

$$MN^{2-} + 2OH^{-} \longrightarrow Mn(OH)_2$$

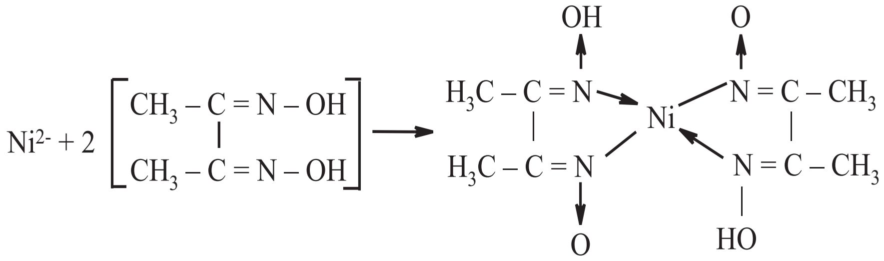
Manganese hydroxide (white precipitate)

$$Mn(OH)_2 + O_2 \longrightarrow MnO_2\,H_2O$$

Hydrated Manganese dioxide, (brown precipitate)

Confirmatory test: *Ni^{2+} ion*- Black precipitate of NiS is soluble in hot cone. HNO_r giving light green solution.On adding NH.OH and dimethylglyoxime reagent to above solution, a cherry red precipitate of nickel dimethylglyoxime is obtained.

$$3NiS + 2HNO_3 + 6H^{+} \longrightarrow 3Ni^{2+} 2NO + 4H_2O + 3S\downarrow$$



Nickel dimethylglyoxime Cherry red precipitate

(b) Group V (Ba^{2+}, Sr^{2+}, Ca^{2+} ion)

Preliminary test: A pinch of NH_4C1 is added to original solution. On adding excess of NH_4 OH to make the solution alkaline then add freshly prepared $(NH_4)_2$ CO_3 solution, a white precipitate is obtained

$$M^{2-} + CO_3^{2} \longrightarrow MCO_3$$

Metal carbonate (white precipitate)

White precipitate is soluble in acetic acid

$$MCO_3 + 2CH_3COOH \longrightarrow M(CH_3COO)_2 + H_2O$$

Metal acetate (Colourless)

A white precipitate of calcium oxalate is formed on adding ammonium oxalate to above solution.

$$Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 + 2CH_3C$$

(Calcium oxalate (white precipitate)

Ba^{2+} and Sr^{2+} ions

To the solution of salt add NH_4Cl, NH_4OH and $(NH_4)2CO_3$. Formation of white ppt indicate the presence of these radicals

$Ba^{2+} + CO_3^{2-} \longrightarrow BaCO_3$

$Sr^{2+} + CO_3^{2-} \longrightarrow SrCO_3$

$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$

Dissove this ppt in CH_3COOH and devide into three parts

Part 1 add K_2CrO_4 solution formaiton of yelolow ppt indicates the presence of Ba^{2+}

$$Ba^{2+} + CrO_4^{2-} \longrightarrow BaCrO_4$$

You can also perform flame test either with the salt or white ppt.

It gives grassy green flame.

Part II add $(NH_4)_2SO_4$ formationof white ppt indicate the presence of Sr^{2+} ion

$$Sr^{2+} + SO_4^{2-} \longrightarrow SrSOr$$

You can also perform flame test. It gives crimson red colour to the flame

(b) Group VI (Mg^{2+} ion)

Mg^{2+} ion

Take 5 ml original solution in a test tube. Add aqueous NH_3. Now add 1 mL solution of NaH_2PO_4 and scratch the walls of test tube with the glass rod. Formation of white ppt indicates the presence of Mg^{2+} ion

16.5 HOW TO PERFORM THE EXPERIMENT

Tabular Presentation of qualitative test

16.5.1 Acid Radicals

(i) Work sheet No. 1 Carbonate ion (CO_3^{2-})

Sulphide ion (S^{2-}) and

Nitrite ion (NO_2^-)

Experiment	**Observation**	**Interface**
(1) Carbonate ion,		
Take a small in a clean test tube. Add 1/mL of dilute H,SO_4.	Brisk effervescence Colourless, odourless,	Carbonate, (CO_3^{2-}) may be present
Lime water test Pass the gas evolved through 2-3 mL of lime water and shake well	Lime water turns milky	CO_3^{2-} confirmed
(2) Sulphide ion, (S^{2-}) Take a small amount of given salt in a clean test tube. Add 1 mL of dil H_2SO_4	Colourless gas with suffocating smell of rotten egg is given out	Sulphide, S^{2-}may be present
(i) Confirmative test: Bring a piece of filter paper moistened with lead acetate solution near the mouth of test tube	Paper turns black	Sulphide, S^{2-} confirmed
(ii) Sodium nitroprusside test: To 2 mL of Water solution of salt add 1 prepared sodium nitroprusside solution Shake well	A red colouration is obtained	Sulphide (S^{2-}) ion, confirmed
(3) Nitrite ion, NO_2^- Take a small amount of give salt in a clean test tube. Add 1 mL of dilute H_2SO_4	A brown coloured gas with pungent smell is given out	Nitrite, (NO_2^-) may be present
Test the gas evolved in Preliminary test with a filter paper soaked in mixture of KI and starch solution	Blue black or violet colour is obtained	Nitrite, (NO_2^-) ion confirmed

(ii) Work sheet No. 2: Chloride ion (Cl^-), Bromide ion (Br^-), Iodide ion (I^-) and Nitrate ion NO_3

Experiment	**Observation**	**Interface**
(A) Chloride ion, (Cl^-) Take a small amount of given	A colourless gas with pungent smell is	Chloride ion (Cl^-) may be present

salt in a clean and dry test tube. Add 2-3 drops of conc. H_2SO_4 carefully. Heat the test tube gently.	evolved	
(1) Chromyi Chloride test: Take a pinch of salt and solid potassium dichromate in a ratio of 1:3 in a dry test tube. Add 3-4 drops of concentrated H_2SO_4 and heat strongly.	orange-yellow fumes are given are out	
(ii) Pass the gas evolved through NaOH solution. Shake well.	A yellow solution is obtained	
(iii) Acidify the soln. obtained above with acetic acid neutralize with excess of NaOH and then add lead acetate solution to it. Shake well.	A yellow precipitate is obtianed	Cl^- confirmed
(2) Silver nitrate test: (i) To 5 mL of original solution add dil. HNO_3 to acidify it and then add 1 mL of $AgNO_3$ solution. Shake well.	Crudy white precipitate is obtained	Cl^- may be present
(ii) Filter the precipitate. After washing the precipitate add 2=3 mL of ammonium hydroxide solution to it. Shake well.	A colourless precipitate is soluble	Cl^- confirmed
(B) Bromide ion, (Br^-) Take a small amount of given salt in a clean and dry test tube Add 2-3 drops of concentrated H_2SO_4.Heat the test tube carefully.	A brown gas with pungent smell is evolved The contents of the test tube turns orange red	Bromide ion (Br^-) may be present

(i) $AgNO_3$ test: Acidify 2 mL of original soln.with dilute HNO_3 Add silver nitrate solution.	A light yellow precipitate is obtained which is partially soluble in excess of NH_4OH	Bromide ion (Br^-) confiremed
(ii) Organic layer test: To 2 mL of water solution add 1/2 mL of CCl_4 and add 3 mL of Chlorine water. Shake well.	Reddish brown organic layer is obtained	Bromide ion (Br^-) confirmed
(C) Iodide ion, I^- Take a small amount of given salt in a clean and dry test tube Add 2=3 drops of concentrated H_2SO_4 carefully. Heat the test tube gently.	Violet fumes with pungent smell evolved Black specks appeared on the side of the test tube	Iodide ion (I^-) may be present
(i) $AgNO_3$ test: To 2 mL of water solution add dilute HNO_3 to acidify it add 1 mL at $AgNO_3$ solution, shake well.	A yellow precipitate is obtained	
(ii) Add NH_4OH to the above solution ppt add 2-3 mL of ammonium hydroxide solution to it. Shake well	precipitate is insolube	Iodide ion (I^-) confirmed
Take 2 mL of water solution. add 1/2 mL of $CC1_4$. Then add 3=4 mL of Chlorine water. Shake well.	A violet organe layer is obtained	I^- confirmed
(D) Nitrate ion, NO_3^- Take a small amount of given salt in a clean and dry test tube Add 2-3 drops of concentrated	Bown coloured gas with pungent smell is evolved The gas intensified on	nitrate ion, (NO_3^-) may be present

H_2SO_4 carefully. Heat the test tube gently.	adding copper turnings, solution turns blue	
Take 2-3 mL of water solution in a test tube and add 2 mL of freshly prepared solution of ferrous sulphate, shake well.	A brown ring is obtained at the junction where the liquid surface meet each other	nitrate ion, (NO_3^-) confirmed
To this solution add few drops of concentrated H_2SO_4 gradually along the sides of test tube without disturbing the test tube.		

(iii) Work Sheet No.3 : Qualitative analysis of Sulphate ion (SO_4^{2-}) and Phosphate ion (PO_4^{3-})

Experiment	**Observation**	**Inference**
(A) Sulphate ion, (SO_4^{2-}) (i) Acidify the Na_2CO_3 extract or the salt solution in water with dil.HCl and then add $BaCl_2$ solution.	A whilte ppt insoluble in Conc.HCl is obtained.	SO_4^{2-} ion is confirmed
(B) Phosphate ion, (PO_3^{3-}) Acidify the Na_2CO_3 extract with dil. NHO_3 and then add solid ammounium molybdate Warm the test tube gently.	A canary yellow precipitate or colour is obtained	Phosphate ion (PO_4^{3-}) confirmed

16.5.2 Basic Radicals

(i) Work sheet No. 1: Ammonium ion (NH_4^+)

Experiment	**Observation**	**Inference**
Take a pinch of salt in a test tube. Add 2-3 mL. of NaOH solution. Heat the test tube gently and then strongly	A colourless gas with pungent smell is given out.	Ammonium ion (NH_4^+) may be present.

(if necessary) smell the gas evolved.		
Pass the gas evolved in the above test through Nessler's reagent for atleast 1 minute. Shake well.	A reddish brown precipitate is obtained.	Animonhim ion, (NH_4^+)confirmed.

(ii) Work Sheet No. 2 : Group-1: Lead (II) ion (Pb^{2+})

Experiment	**Observation**	**Inference**
Solubility in water Take a pinch of salt in clean test tube. Add 2-3 mL of water and then few drops of dilute HC1. Shake well. Carryout following tests with white precipitate obtained above.	A white precipitate is obtained.	Lead (II) ion (Pb^{2+}) may be present
Wash the precipitate and dissolve a small amount of precipitate in 5-6 mL of hot water. Divide the soln. into two parts.	A clear solution is obtained	
(a) Potassium iodide test: To one part of hot soln. add 1 mL Potassium iodide solution, shake well.	A yellow precipitate is obtained (PbI_2)	Lead(II) ion (Pb^{2+}) confirmed
(b) Potassium Chromate test To the second part of hot solution add 1 mL of K_2CrO_4 solution and shake well.	A yellow precipitate is obtained ($PbCrO_4$)	Lead(II) ion (Pb^{2+}) confirmed

(iii) Work Sheet No. 3: Group II Copper (II) ion (Cu^{2+})

Experiment	**Observation**	**Inference**
Take 2 mL of original solution in a test tube, add a few drops of dilute HCl. Pass H_2S gas through this solution.	black precipitate	(Cu^{2+}) may be present

Heat a small amount of precipitate in 1-2 mL of dilute HNO_3 and divide it into two parts.	A blue solution in obtained	(Cu^{2+}) may be present
(i) To one part add NH_4OH solution drop by drop till it is in excess.	A blue precipitate is obtained which dissolved to produce deep blue solution	(Cu^{2+}) confirmed
(ii) Acidify another portion with 2 mL acetic acid and then add 1 mL of potassium ferrocynide	A chocolate brown precipitate is obtained	(Cu^{2+}) confirmed

(iv) Experiment Sheet No. 4: Group III Ferric iron or Iron (III) ion, (Fe3+)

Experiment	Observation	Inference
Take 2 mL of original solution in a clean test tube. Add excess of NH_4C1 solid, shake well to dissolve it. Heat if necessary. To cold solution add NH_4OH drop by drop till it is in excess. **Iron (III)** ion, (Fe^{3+}) If a reddish brown precipitate is obtained, it indicates the presence of Fe^{3+} ion.	A reddish brown precipitate obtained	Fe^{3+} ion may be present
Dissolve the precipitate in 2-3 mL of dilute HCI. and divide it into two parts.	A yellow solution is obtained	
(i) To one part of solution add 1 mL potassium ferrocyanide. Shake well.	A prussian blue colour is obtained	Fe^{3+} confirmed
(ii) To the second part of solution add 1 mL of potassium sulphocyanide.	Blood red colour is obtained	Fe^{3+} confirmed

(v) Work Sheet No. 5 : Group IV-Zinc(II) ion (Zn^{2+}), Manganese(II) ion (Mn^{2+}) and NIckel(II) ion (Ni^{2+})

Experiment	Observation	Inference
Take a 2-3 mL of original solution in a tube, add excess of NH_4OH to make the solution alkalline. Warm the contents of the test tube. Pass H,S gas through it for 1/2 minute		
(A) Zinc (II) ion, Zn^{2+}: Formation of white or dirty white ppt indicates the presenc of Zn^{2+}ions.	White precipitate is obtained	Zn^{2+} may be present
Dissolve the washed white precipitate in 1 mL of dilute HCI. Dilute it with 2-3 mL of water, Divide the solution into two parts	A clear soln. is obtained	
To one part of the solution add dilute NaOH solution drop by drop till it is in excess.	White precipitate is obtained which dissolves in excess to produce colourless soln.	Zinc (II) ion (Zn^{2+}) confirmed
To another part of solution add 1 mL of potassium ferrocyanide.Shake well.	A grey white precipitate is obtained	Zinc (II) ion (Zn^{2+}) confirmed
(B) Mangnese(II)ion(Mn^{2+}) Formation of buff coloured precipitate indicates the presence of Mn^{2+} ions,	Buff precipitate obtained	Manganese (II) ion (Mn^{2+}) may be present
Dissolve the buff coloured precipitate into 1mL of dilute HCI. Dilute it with 2-3 mL of water.	A clear solution is obtained	
To this solution add dilute NaOH solution drop by drop till it is in excess.	A white precipitate is obtained which turns brown due to aerial oxidation	(Mn^{2+}) ion confirmed
(C) Nickel (II)ion,(Ni^{2+}) Formation of black precipitate indicates the presence of Ni^{2+} ion.	Black precipitate is obtained	Ni^{2+} ion may be present

Take a small amount of washed precipitate in a china dish. Add 1-2 mL of concentated HNO_3 to it. Boil it. Evaporate the contents of china dish to dryness.	A yellowish green residue is obtained	
Cool down the china dish Add 2-3 mL of water. Shake well. Transfer this solution to a clean test tube.	A light green solution is obtained	
Add excess of NH_4OH solution and then 1 mL of dimethyl glyoxime. Shake well.	A cherry red precipitate is obtianed	Ni^{2+} ion is confirmed

(vi) Work Sheet No. 6: Group V Calcium (II) ion.

Experiment	**Observation**	**Inference**
Take 2 mL of original solution in a clean a test tube. Add a pinch of solid NH_4Cl and ot excess of NH_4OH. solution and then 2 mL of freshly prepared NH_4CO_3. solution, shake well.	A white precipitate is obtained	Calcium (II) ion (Ca^{2+}) may be present
Formation of white precipitate indicates the presence of Ca^{2+}ion.		
Take a small amount of white precipitate and add 1 mL of acetic acid.	A clear soln. is obtained	
To the above solution add 2 mL of ammonium oxalate solution. Shake well.	A white precipitate slowly appears	Calcium (II) ion (Ca^{2+}) confirmed

An Illustration of identification of cation and anion in a given sample of salt.

AIM: To find out the presence of an anion and a cation in the given salt

Experiment	**Observation**	**Inference**
1. Physical Examination (i) Colour of salt	white	May contain salts of NH_4^+, Pb^{2+}, Zn^{2+}, Ca^{2+}

(ii) Heat small amount of salt in a clean dry test tube.	salt sublimates	May contain NH_4^+ ions
(a) Anion analysis		
2. A pinch of salt was taken in a clean test tube 2 mL of dilute H_2SO_4 was added to it and heated first gently and then strongly.	No observable changes took place	CO_3^{2-} S^{2-} and NO_2^- absent
3. A pinch of salt was taken in a clean and dry test tube. Add few drops of conc. H_2SO_4 to it, heated gently, few copper turning were added and contents were heated again.	A brown gas with pungent smelll is given out and solution turns brown	Nitrate ion (NO_3^-) ion may be presnet
4. Confirmation test of NO_3^- ion : 2 mL original soln, were taken in a test tube. To this 2mL of freshly prepared $FeSO_4$ (aq) was added. Shaken well, add a few drops of concentrated H_2SO_4 along the side of test tube without disturbing the test tube.	Brown ring at the junction of H_2SO_4	NO_3^- confirmed
(b) Cation Analysis		
5. A pinch of salt was taken in a test tube. 2-3 mL water was added to it-followed by 3-4 drops of dil. HCl. Shake well.	Clear solution	Group I absent
6. To the above solution pass H_2S gas		
7. 2 mL of original solution was taken in a test tube. Solid NH_4C1 was added in excess, followed by addition of excess NH_4OH solution warm gently.	No ppt	Group II absent Group III absent

8. Passed H_2S gas through group III solution.		
9. 2 mL of original soln. was taken in a test tube. A pinch of NH_4Cl solid was added.		Group IV absent
Excess of NH_4OH solution was added followed by addition of 2 mL freshly prepared $(NH_4)_2CO_3$ solution. Shake well.	White precipate is formed	Group V Present
Confirmation test of Cation		
10. Filtered and washed precipate was dissolved in 2 mL of acetic acid.	ppt is soluble	Ca^{2+} may be
11. 2mL of $(NH_4)_2CO_3$ soln. was added to above obtained solution.	White PPt is obtained	Ca^{2+} is confirmed
Result : The given salt contains Anion – NO_3^- Cation - Ca^{2+}		

Precautions

1. Use acids carefully.
2. Avoid using large quantities of acids and salt.
3. Keep the materials ready for testing the gas evolved.
4. Performed the test on the gas evolved immediately. If for any reason the testing is delayed, then add a little amount of salt and test the gas immediately
5. Addition of group reagents should be followed in correct order.
6. Analysis of anion should be carried out before cation analysis.
7. Pass H_2S gas through hot solution.
8. Always use a pinch of NH_4Cl in group V.

Observations

The students should record the observations and inference during the analysis of given salt (s),

16.6 CONCLUSION

The given salt contains

(i) Acid radical ....

(ii) Basic radical ....

The given salt is ....

16.7 CHECK YOUR UNDERSTAING

1. What is meant by qualitative analysis?

   ....

2. What is meant by the terms positive test and negative test?

   ....

3. What happens when carbon dioxide is passed through $Ba(OH)_2$ solution instead of calcium hydroxide solution?

   ....

4. What happens when an acid is over boiled?

   ....

5. Why is it necessary to keep the test tube dry during chromyl chloride test?

   ....

6. Why Bromine (Br_2) Iodine (I_2) (g) is more soluble in organic solvent such as $CC1_4$ than in water?

   ....

7. How will you distinguish between Br^- and NO_3^- in qualitative analysis?

   ....

8. Why can HNO_3 not be used to prepare original solution of a salt?

   ....

9. What is a group reagent?

   ....

10. What chemicals are used in kipps apparatus to make hydrogen sulphide gas?

    ....

11. What is the group V reagent?

    ....

12. Why is it necessary to add concentrated H_2SO_4 along the sides of the test tube during ring test of NO_3 ion?

    ....

13. Can group V precipitate dissolve in dilute HCl instead of acetic acid?

    ....

16.8 NOTE FOR THE TEACHER

1. Teacher should explain important terms used during experiment.
2. Teacher should demonstrate all the techniques explained in the experiment.
3. In qualitative analysis, students use concentrated acids, alkali and other laboratory reagents. The Teacher should be cautious and ensure that all students follow proper precautions
4. Freshly prepared soln. of (a) $FeSO_4$ (b) sodium nitroprusside (c) $(NH_4)_2CO_3$ should be used.
5. Following combination of anions and cations should not be given

   (i) Halide ions and Pb^{2+},

   (ii) SO_4^{2-} ion and Pb^{2+}, Ca^{2+}

   (iii) PO_4^{3-} and gp III onwards

   (iv) NO_3^- and group II

   (v)S^{2-} and group II and group IV cations
6. The teacher may ensure that the students carry out the analysis of given salts systematically.
7. Follow all the precautions given in this experiments and general precautions of a chemistry laboratory.
8. Get sufficient practice of analysis of salts. The students may use their note-books to records the practicals.

16.9 CHECK YOUR ANSWERS

1. Qualitative analysis is the scheme of the detection and identification of the constituent ions of an unknown salt.

2. A positive test is the one which gives the observations, needed for that radical. A negative test does not give the required observations for a test.

3. $Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O$

4. $2H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + O_2$

5. If dry test tube is not taken. Concentrated H_2SO_4 gets diluted and chromyl chloride test can not be performed properly.

6. Being covalent in nature Br_2 or I_2 are more soluble in non-polar solvent such as $CC1_4$

7. Bromide ions, (Br^-) gives reddish brown vapour of Br_2 and solution turns red in colours on treatment with concentrated H_2SO_4 NO_3^- ion gives brown fumes of NO_2 which intensified on heating with copper turning.

8. HNO_3 is an oxidising agent. It oxidises H_2S to S (sulphur),

9. The cations in their respective group are precipitated by adding certain chemicals under definite condition of acidic or alkanity. These chemicals are called group reagents.

10. FeS and dilute H_2SO_4

11. Group V reagent $(NH_4)_2\,CO_3$ solution in the presence of NH_4C1 and NH_4OH

12. If the concentrated H_2SO_4 is added directly, then solution turn reddish brown.

13. Ca^{2+} ion is precipitated as calcium oxalate, (CaC_2O_4) on adding ammonium oxalate $(NH_4)_2C_2O_4$. This precipitate is highly soluble in dilute HCl. Hence calcium (II) ion will not be precipitate out in presence of dilute HCl.

EXPERIMENT-17

To Identify the Functional Groups present in the given organic compounds and perform:

(i) Test for unsaturation.

(ii) Test for carboxylic, phenolic, aldehydic and ketonic groups.

OBJECTIVES

After performing this experiment, you should be able to:

- detect the presence of unsaturation in a given organic compound by simple tests;
- differentiate between saturated and unsaturated compounds;
- detect the presence of the following functional groups in the given organic compounds: carboxylic, phenolic, aldehydic and ketonic groups;
- differentiate between the pairs of compounds containing (a) carboxylic and phenolic groups and (b) aldehydic and ketonic groups;
- explain the acidic nature of carboxylic and phenolic groups;
- write the reactions involved in the various tests.

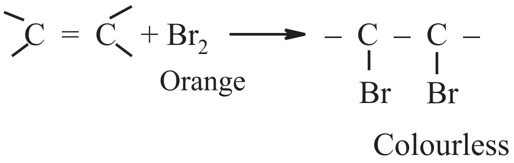
17.1 WHAT YOU SHOULD KNOW

In an organic compound, unsaturation is due to the presence of double ($>C=C<$) or triple ($-C \equiv C-$) bonds in the molecule. The presence of unsaturation is tested by the following two methods.

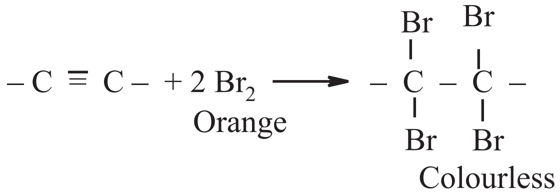
(i) Bromine water test

(ii) Baeyer's test (using 1 % alkaline potassium permanganate solution)

(i) Bromine water test: The organic compound is treated with bromine water dropwise. The decolourisation of bromine water shows the presence of unsaturation in the organic compound.

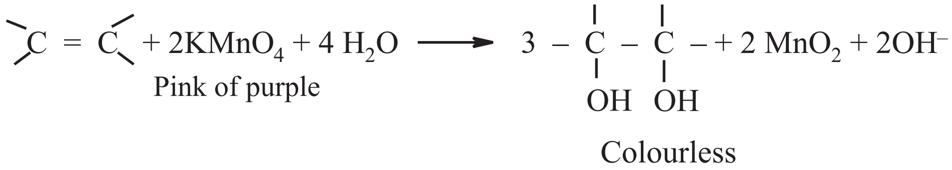


$$>C=C< + \underset{\text{Orange}}{Br_2} \longrightarrow \underset{\text{Colourless}}{-\underset{Br}{\underset{|}{C}}-\underset{Br}{\underset{|}{C}}-}$$



$$-C\equiv C- + \underset{\text{Orange}}{2\,Br_2} \longrightarrow \underset{\text{Colourless}}{-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-}$$

(ii) **Baeyer's test:** The organic compound is treated with an aqueous solution of alkaline potassium permanganate (Baeyer's reagent). The disappearance of the pink colour of potassium permanganate shows the presence of unsaturation.



$$>C=C< + \underset{\text{Pink of purple}}{2KMnO_4 + 4\,H_2O} \longrightarrow 3\ \underset{\text{Colourless}}{-\overset{|}{\underset{OH}{\underset{|}{C}}}-\overset{|}{\underset{OH}{\underset{|}{C}}}-} + 2\,MnO_2 + 2OH^-$$

Precautions

1. Do not inhale the bromine water or bromine in carbon tetrachloride.
2. If the comppund is soluble in water, use bromine water for testing. If the compound is insoluble in water, then dissolved 5 mL of the compound (liquid) or a pinch of the solid in 1 mL of carbon tetrachloride and test it with bromine in carbon tetrachloride solution.
3. Add the reagents dropwise.

17.1.1 Functional Group

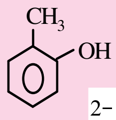
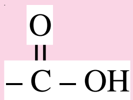
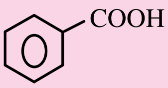
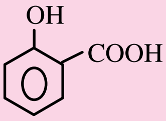
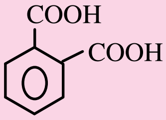
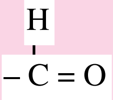
A functional group is that part of the compound which contains an atom or a group of atoms and shows specific reactions. It is the reactive part of a given compound whereas the hydrocarbon part is the non-reactive part. For example, in $CH_3-CH_2-CH_2-COOH$

$CH_3-CH_2-CH_2$ - is the non-reactive hydrocarbon chain, while- COOH is the functional group called carboxylic acid group.

All the reactions of $CH_3CH_2CH_2COOH$ are due to the presence of- COOH group.

In the following section, we shall discuss the chemistry of four functional groups, phenol, carboxylic (-COOH), aldehyde (-CHO) and ketone $>C=O$ The examples of compounds containing these groups are given in the following table.

Notes

Functional Group	**Class of the Compound**	**Specific Example**
C_6H_5-OH Phenolic	Phenols	C_6H_5-OH  2- cresol
 $-\overset{O}{\overset{\|}{C}}-OH$ Ethanoic acid Carboxylic acid group	Carboxylic acid	CH_3COOH  Benzoic acid  Salicylic acid  Phthalic acid
 $-\overset{H}{\overset{\|}{C}}=O$ Aldehydic	Aldehydes	CH_3CHO Ethanal C_6H_5CHO Benzaldehyde
$>C=O$ Ketonic	Ketones	CH_3COCH_3 Propanone 

(A) Test for Carboxylic Group

The carboxylic group can be tested by the tests as given below.

(i) **Litmus test:** Put a drop of an aqueous solution of the compound on blue litmus paper. If the blue litmus turns red, acidic nature is indicated.

(ii) **Sodium hydrogen carbonate test:** Add a saturated solution of sodium hydrogen carbonate to an aqueous solution of the compound. If brisk effervesence appear due to evolution of CO_2 gas, the carboxylic group is confirmed.

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 \uparrow + H_2O$$

(iii) **Esterification test:** The given organic compound is mixed with absolute ethanol in equal amounts and a few drops of conc. sulphuric acid are added. The mixture is warmed on a water bath. If a fruity smell (pleasant sweet smell) is obtained, the presence of carboxylic group is confirmed.

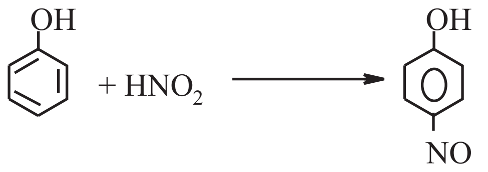
$$CH_3COOH + C_2H_5OH \xrightarrow[\text{}]{\text{Few drops of Conc. } H_2SO_4} \underset{\text{warm ester (fruity smell)}}{CH_3COOC_2H_5} + H_2O$$

(B) Tests for phenolic group

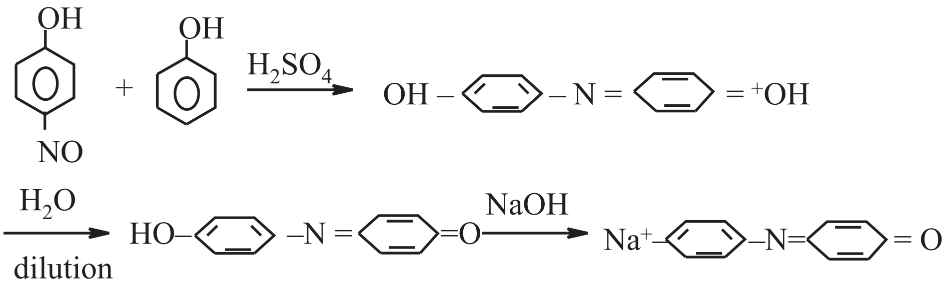
(i) **Ferric chloride test:** Dissolve a pinch of organic compound in water or alcohol. A few drops of this solution are mixed with neutral ferric chloride solution. If a red, blue or violet colouration appears, then the presence of phenolic group is confirmed.

For example, thus, red colouration is obtained with phenol while, with 0, m- and p-cresol, it is violet. With Resorcinol, gives blue colouration whereas catechol gives green colouration.

(ii) **Liberamann's Test:** The organic compound is mixed with solid sodium nitrite (2-3 crystals) and gently warmed for a few seconds. The mixture is cooled and cone sulphuric acid is added. The solution appears red in colour on dilution with water and the colour changes to blue / green on treatment with sodium hydroxide. The above observation confirms the presence of phenolic group in the given compound.



4-nitrosophenol



Indophenol
(red)

Indophenol
(blue)

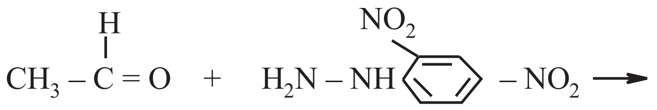
(C) Tests for Aldehydes and Ketones

Both aldehydes and ketones contain the carbonyl group (> C = O). The carbonyl group can be confirmed by:

(i) 2, 4- dinitrophenyl hydrazine (2,4-DNP test)

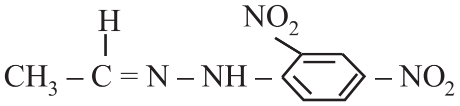
(ii) Sodium bisulphite

(i) 2, 4 - DNP test: The organic compound is treated with 2,4-DNP reagent and warmed over a water bath. Formation of yellow or orange crystals indicate the presence of a carbonyl group (aldehydic orketonic).

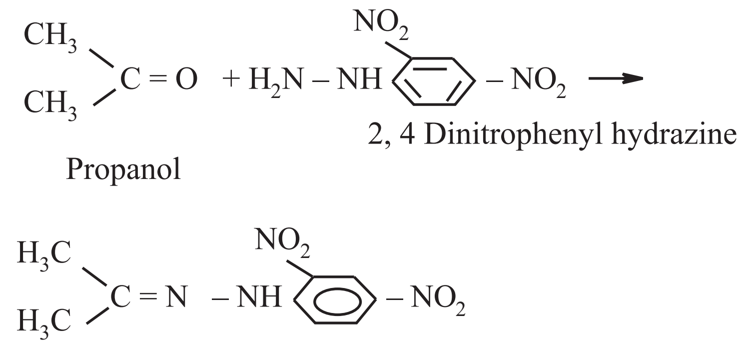


Ethanal

2,4- Dinitrophenylhydrazine

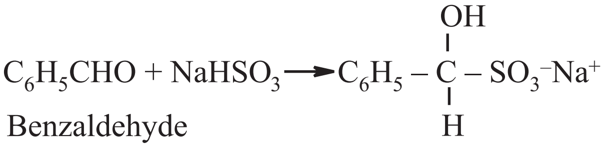


2,4- Dinitrophenylhydrazine
of the aldehyde



2, 4 Dinitrophenyl hydrazone of the ketone

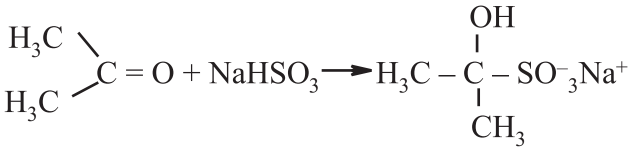
(ii) **Sodium bisulphite test:** The organic compound is treated with a saturated solution of soduim bisulphite. The mixture is shaken well and left for 15 minutes. The formation of a crystalline precipitate indicates the presence of a carbonyl group.



$$C_6H_5CHO + NaHSO_3 \longrightarrow C_6H_5-\underset{H}{\overset{OH}{C}}-SO_3^-Na^+$$

Benzaldehyde

Addition product



$$(H_3C)_2C=O + NaHSO_3 \longrightarrow H_3C-\underset{CH_3}{\overset{OH}{C}}-SO^-{}_3Na^+$$

Addition product

(A) Tests for Aldehydes

(i) **Fehling's test:** The organic compound is treated with Fehling's solution and warmed over a water bath. Appearance of a red / orange precipitate confirms the presence of aldehyde group.

$$CH_3CHO + 2Cu^{2+} + 5OH^- \rightarrow CH_3COO^- + Cu_2O\downarrow + 3H_2C$$

Acetaldehyde Fehlings Solution Red precipitate

The aldehyde reduces the Cu^{2+} (cupric ions) to cuprous state (Cu_2O cuprous oxide).

3. **Tollen's Reagent test:** To the organic compound, an equal amount of Tollen's reagent is added and the mixture is warmed on a water bath. Appearance of shining silver mirror on the inner walls of the test tube confirms the presence of aldehydic group.

$$CH_3CHO + \underset{\text{Tollen's Reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \rightarrow CH_3COO^- + \underset{\text{Silver mirror}}{2Ag} + 4$$

The Tollen's reagent (ammonical silver nitrate solution) contains silver ions. These are reduced by aldehydes to metallic silver.

(B) Test for ketone

Ketones do not give Fehling's and Tollen's tests. Ketones give the following two tests which are not given by aldehydes:

1. ***m*-Dinitrobenzene test:** To a mixture of finely powdered *m*-dinitrobenzene and an equal amount of organic compound, add dilute sodium hydroxide solution. The appearance of red colour indicates the ketonic group.
2. **Sodium nitroprusside test:** To the given organic compound, add sodium nitroprusside solution and a little sodium hydroxide solution. Appearance of red- violet colour confirms the presence of ketonic group.

17.2 MATERIALS REQUIRED

(1) Apparatus	(2) Chemicals
Test tubes, Test tube stand, Test tube holder, Water bath, Tripod stand.	Samples of organic compounds. Bromine water. Alkaline potassium permanganate solution, Neutral ferric chloride solution, Sodium nitrite (solid). Litmus paper, Sodium hydrogen carbonate. Alcohol, Conc. sulphuric acid, 2,4-Dinitrophenylhydrazine solution, sodium bisulphite solution, *m*-Dinitrobenzene solid, Sodiumnitroprusside, Sodium hydroxide (10% solution), Fehling's reagent, Schiffs reagent and Tollen's reagent.

17.3 HOW TO PERFORM THE EXPERIMENT

The tests should be performed systematically as described in the following table. All functional groups should be tested. The experiments performed should be recorded as shown below:

Table 1: Tests for Unsaturation

Experiment	Observations	Inference
(a) To a solution of 0.2 g of the organic compound in water or CCl_4, add bromine water or bromine in CCl_4 dropwise. Shake the mixture after each addition.	Bromine is decolourised or Bromine is not decolourised	Unsaruration present or Unsaturation absent
(b) To the organic compound (0.5 g) add 1 mL of 0.5% aq. $KMnO_4$ solution dropwise	$KMnO_4$ solution is decolourised or $KMnO_4$ solution is not decolourised	Unsaturation present or Unsaturation absent

Table 2: Test for phenolic hydroxyl group

Experiment	Observations	Inference
(a) Dissolve 50 mg of organic compound in 1-2 mL of water or alcohol. Put a drop of the solution on blue litmus paper.	Blue litmus turns red or No change	Compound is acidic in nature; May be phenolic OH group or carboxylic acid or phenolic OH or carboxlic group abscent
(b) To a solution of the compund in water or alcohol add a drop of freshly prepared neutral ferric chloride solution	blue, green, violet or pink colouration appears or (no (characteristic colouration)	Phenolic OH group present or Phenolic OH group absent
(c) (i) Heat about 50mg of the organic compound with sodium nitrite (2-3 crystals) gently for 30 seconds in a dry test tube. To the cooled mixture, add 1 mL conc. H_2SO_4	Deep blue or green colouration appears	Phenolic group present
(ii) Addabout2-3 mL water to the above mixture	The colour changes to red	Phenolic OH group present
(iii) Add NaOH solution to the above mixture	Blue or green colour or negative test	Phenolic OH group absent if the test is negative

Precautions

1. Phenol is highly corrosive. It causes blisters on the skin Always handle it carefully.
2. Neutral ferric chloride should be freshly prepared, see Appendix for details.
3. Phenol turns blue litmus red. Carboxylic acids also give the test but phenol does not decompose sodium hydrogen carbonate.
4. Instead of phenol, naphthols may be given for test for phenolic group.

Table 3: Test for carboxylic acids

Experiment	**Observations**	**Inference**
(a) The aqueous solution of the organic compound is put on a blue litmus paper	Blue litmus turns red or No change	- COOH group may be present - COOH group absent
(b) To the 0.2 g organic compound, add saturated solution of sodium hydrogen carbonate	Effervescences seen or No effervescences	- COOH group present or - COOH group absent
(c) *Ester formation* To 0.2 g of the organic compound, add an equal amount of ethyl alcohol and a drop of cone, sulphuric acid. Warm the mixture on a water bath.	Fruity odour develops or No fruity odour	- COOH group present - COOH group absent

Table 4: Tests for aldehydes and ketones

(a) To the solution of the organic Compound (1mL) add 5 mL. 2, 4- dinitrophenylhydrazine reagent. Heat the solution in a water bath,	Yellow or orange precipitate	carbonyl group present (–CHO or > CO) >C = O
(b) The organic compound (0.5 g) is shaken with 2 mLof saturated sodium bisulphite solution.	white precipitate	–CHO, > C = O present
(c) To a solution of equal volumes offering's A and Fehling's B, add 0.2 g of the organic compound. Heat the mixture for 5 minutes in a water bath.	Red precipitate of Cu_2O	Aldehyde (–CHO) group present

(d) To 1 mL of $AgNO_3$ solution, add a drop of dil. NaOH solution. To this, add ammonium hydroxide dropwise fill the precipitate dissolves. To the resulting solution add 0.1 g of the organic compound. Heat for 5 minutes in a water bath. red colour	Silver mirror is formed on the inner side of the test tube.	Aldehyde (- CHO) group present
(e) Add I mL of sodium nitroprusside solution to 0.5 g of the organic compound. Shake the mixture and add NaOH solution dropwise	red colour	Ketone (< C = O) group present
(f) Mix 0. lg of the organic compound with 0.1 g m-dinitrobenzene. Add I (mL dil. NaOH soln. and shake	Violet colour fades slowly	Ketone (< C = O) group present

Precautions

1. Tollen's reagent should be freshly prepared.
2. Benzaldehyde reacts very slowly and a grey precipitate is generally obtained. Shake the tube vigorously to break the oily globules from time to time.
3. Wash the test tube thoroughly with warm sodium hydroxide solution followed by washing it with a large amount of water.

Specific Examples

(This is not a part of the experiment.)

Example 1:

Aim of the Experiment: To identify by chemical tests which one of the samples, A and B is benzaldehyde and which one is acetone.

Apparatus: Test-tubes

Chemicals: Silver nitrate solution, Ammonium hydroxide, Iodine solution and Sodium hydroxide.

Observations: Perform the following chemical tests with compounds A and B.

Experiment	**Observation**	
	Compound A	**Compound B**
1. Colour and physical state	Colourless liquid (turns yellow on standing)	Colourless liquid
2. Odour	Odour of bitter almonds	Pleasant smell
3. Solubility in		
(i) Water	Immiscible	Miscible
(ii) Sodium hydroxide solution	Immiscible	Immiscible
(iii) 5%$NaHCO_3$ solution	Immiscible	Immiscible
(iv) Cone. HC1	Immiscible	Immiscible
4. **Chemical Test**		
(i) **Tollen's Test:** (a) Place 1 mL of silver nitrate solution in a clean test-tube and add 1 drop of dil. NaOH solution. A brown ppt. is formed. Add ammonia solution dropwise until the brown ppt. just redissolves. To this add about 0.5 mL of liquid A and warm the test-tube in a beaker of boiling water for 5 minutes.	A shining silvermirror forms	
(b) Repeat this test with liquid B		No silver mirror
(ii) **Sodium nitroprusside test:** Add 1 mL of sodium nitroprusside to 0.5 mL of the liquid A and B in separate test tubes. Add NaOH Solution to both the test tubes and shake them.	No charateristic colour	Red colour formation
(iii) (a) Mix 0.5 mL of the liquid B with 0.5 g of solid *m*-dinitrobenezene Add NaOH and shake the contents.	Violet colouration appears that fades slowly	
(b) Repeat the same with liquid A	No characteristic colour	

Conclusion: Compound A is benzaldehyde and Compound B is Acetone.

Example 2:

Aim of the Experiment: To identify by chemical tests which one of the samples C and D is phenol and which one is benzoic acid.

Apparatus: Test tubes

Chemicals: Sodium nitrite, Sodium hydrogen carbonate

Observations

Experiment	Observation	
	Compound A	**Compound B**
1. Colour and physical state	Colourless or pink crystalline solid	White solid
2. Odour	Carbolic	Odourless
3. Solubility in:		
(i) Water	Sparingly soluble, forms an emulsion	Sparingly soluble
(ii) Dil. NaOH solution	insoluble	Soluble
(iii) 5% $NaHCO_3$ solution	Insoluble	Soluble
(iv) Conc. HCl	Insoluble	Soluble
4. Blue litmus test	Turns red	Turn red
5. **Chemical tests**		
(i) **Libvermann's test.**		
(a) Perform Libermann's test with protion of compound C. For procedure, see experiment in table	Deep blue or green colour	
(b) Repeat this test with a portion of compound D		No colouration
(ii) **Sodium hydrogen carbonate test**		
(a) Place 3 mL of 10% $NaHCO_3$, soln. in a clean test-tube and add a portion or the compound C. Warm it.		No effervescences
(b) Repaet this test with a portion of compund D.		Strong effervescences

Conclusion

The given organic compound was found to contain..................functional group.

17.5 CHECK YOUR UNDERSTANDING

1. Name the functional group (s) present in the following compounds. Phenol, benzoic acid, sallicylic acid and acetone.

   ....

2. How will you distinguish the following pairs of compounds?

   (a) Acetic and acetaldehyde.

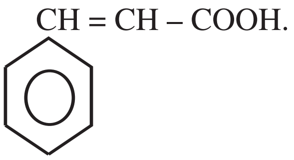
   (b) Acetic acid and phenol.

   ....

3. Write the reaction for bromine water test on $C_6H_5 - CH = CH_2$

   ....

4. What tests would be given by the following compound?



$C_6H_5-CH = CH - COOH.$

   ....

5. What is Baeyer's reagent?

   ....

6. Why should Tallen's reagent be freshly prepared?

   ....

7. Which compound is more acidic. Phenol or benzoic acid?

   ....

8. How -will you differentiate between phenol andcresols?

   ....

9. How will you infer the presence. of carbonyl group in a compound?

   ....

10. Give an example of aromatic compound which is known methyl ketone.

   ....

17.5 NOTE FOR THE TEACHER

1. The students may be given enough number of samples of the same functional group for proper practice.
2. Phenol is highly corrosive. Test for phenolic groups, the students may be given - Naphthol, β - Naphthol, or o -, m, - p - cresols etc. Avoid giving phenol directly to the students without proper precautions of handling.
3. Students should be told to wear lab coats and use gloves when corrosive substances are being handled.
4. The students and the assistant should be instructed to keep inflammable liquids away from the burner.
5. A sample worksheet is given in this section. The students may be asked to record the experiments in this format.

17.6 CHECK YOUR ANSWERS

1. The functional groups present in the following compounds are:

   Phenol - Phenolic group.

   Benzoic acid - Carboxylic acid group

   Salicylic acid - Phenolic group and carboxylic group.

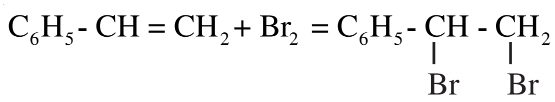
   Acetone - Ketonic group.

2. Acetone and Acetaldehyde can be distinguished by any of the following tests.
   - (i) Fehling's test
   - (ii) Tollen'stest
   - (iii) Sodium nitroprusside test
   - (iv) *m*-dinitrobenzene test

The changes observed are tabulated below :

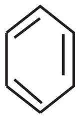
S.No.	Test performed	Acetaldehyde	Acetone
a.	Fehling's test	red colouration appears	×
b.	Tollen's test	Silver mirror is formed	×
c.	sodium nitroprusside test	×	Violest colouration
d.	*m*-dinitrobenzene test	×	red colouration

Ans. 3.



$$C_6H_5\text{-}CH = CH_2 + Br_2 = C_6H_5\text{-}\underset{\displaystyle Br}{\underset{|}{CH}}\text{-}\underset{\displaystyle Br}{\underset{|}{CH_2}}$$

4. $CH_2 = CH - COOH$ will give the following test:



   (i) Positive test for unsaturation due to the double bond,

   (ii) Positive test for carboxylic group.

   The compound will therefore, give positive test with bromine water and positive test with sodium hydrogen carbonate.

5. Baeyer's reagent is an alkaline solution of potassium permanganate, (please see appendix for details)

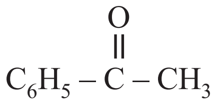
6. Tollens reagent is a solution of ammoniacal silver nitrate. It should be freshly prepared because it is unstable as it can easily decompose to Ag_2O and finally to silver, on standing.

7. Benzoic acid is a stronger acid than phenol. Benzoic acid will give brisk effervescences with sodium hydrogen carbonate solution due to the liberation of carbon dioxide gas. Phenol does not give positive test with sodium hydrogen carbonate as it is a weak acid.

8. Phenol and cresois can be differentiated by neutral ferric chloride test. Phenol will give red colouration, o-, m- and p-cresol will give violet colouration.

9. Carbonyl compounds give 2,4- dinitrophenylhydrazine test and sodium bisulphite test. Crystalline precipitates are formed in both cases.

10. Acetophenone is an example of methyl ketone. It has the formula



$$C_6H_5 - \overset{\overset{\large O}{\|}}{C} - CH_3$$

17.7 CHECK YOUR ANSWERS

1. Multiple scratches, if made on the glass tube will cause a rough and irregular cut.

2. The outer diameter of the borer should be equal to the inner diameter of the tube to be inserted into the bore.

3. To avoid cracking of the cork and to get a smoother bore, it is moistened with water and pressed in a cork presser.

4. The edges should be heated gently by rotating on a flame.

Appendix

Preperation of Common Laboratory Reagents

1. **Bromine water:** Shake 5 mL of liquid bromine with 100 mL of distilled water in a conical flask. Decant off the clean solution into a bottle and stopper it.

2. **Bromine in $CC1_4$:** Shake 4 mL of liquid bromine with 100 mL of carbon tetrachloride and stopper the bottle.

3. **Alkaline potassium permanganate solution :** (Baeyer's Reagent) Dissolve 1 g of solid potassium permanganate in 100 rnL of distilled water, then add 1 Og of anhydrous sodium carbonate. Shake the mixture to dissolve it and stopper the bottle.

4. **Neutral ferric chloride :** Place 2 mL ferric chloride solution in a clean test tube. Add ammonium hydroxide until a brown precipitate just appears. Now add the original ferric chloride solution until the precipitate just disappears. (Prepare fresh for a day)

5. **2,4- dinitrophenyl hydrazine (2,4 - DNP) :** Dissolve 2 g of 2,4-DNP in 100 mL methanol to which 4 mL of conc. sulphuric acid is added. Filter if necessary.

6. **Sodium bisulphite solution :** Dissolve 30 g of sodium bisulphite in 100 mL of distilled water.

7. **Schiff s reagent:** Dissolve 0.1 g of fuschine (p-rosaniline hydro chloride) in 100 mL water. Pass sulphur dioxide gas until its red colour is discharged. Filter and use the filtrate.

8. **(a) Fehling's solution A:** Dissolve 35 g of crystalline copper sulphate in 500 mL water. Add 3 mL of concentrated sulphuric acid to it.

   (b) Fehling's solution B: Dissolve 173 g of Rochelle salt (sodium potassium tartarate) and 60 g of sodium hydroxide in 500 mL of water.

Note: (i) Fehling's solution A and Fehling's solution-B are available in the market also, (ii) Mix equal volumes of A and B solutions just before performing the test.

9. **Tollen's Regent:** Place 2 mL of silver nitrate solution in a clean test tube Add two drops of sodium hydroxide solution (10% solution). A brown precipitate is formed. Now add dilute ammonium hydroxide solution dropwise until the brown precipitate of silver oxide just redissolves.

10. **Cone, sulphuric acid** 18M as supplied may be used.

11. **Cone, hydrochloric acid** 12M as supplied maybe used.

12. **Cone, nitric acid** 16 M as supplied may be used.

13. **Acetic acid (glacial** 11M as supplied may be used.

14. **DiL sulphuric acid 12M:** Pour 111 mL of cone, sulphuric acid slowly and with constant stirring in 500 mL of distilled water. Cool and make up the volume to 1 litre.

15. **Dil. hydrochloric acid 4M:** Add 333.3 mL of conc. HCl in the distilled water and make up the volume to 1 litre.

16. **Dil nitric acid 4M:** Add 250 mL of Cone. HNO_3 in the distilled water and make up the volume to litre.

17. **Dil. acetic acid 2M:** Add 182 mL of glacial acetic acid in distilled water and make up the volume to 1 litre.

18. **Ammonia solution** 15M as supplied may be used.

19. **Dil. ammonia solution 4M:** Pour 266.6 mL of the cone, ammonia solution in distilled water and make up the volume to 1 litre.

20. **Ammonium chloride 4M:** Dissolve 214g of the salt in one litre of water.

21. **Ammonium carbonate 2M:** Dissolve 192g of Ammonium carbonate in 1 litre distilled water.

22. **Ammonium acetate 3M:** Dissolve 231g of the salt in a litre of distilled water.

23. **Ammonium sulphate lM:** Dissolve 132g of the salt in 1 litreof distilled water.

24. **Ammonium oxalate 0.5M:** Dissolve 71g of the saltin 1 litre of distilled water.

25. **Ammonium molybdate 0.5M:** Dissolve 88g of the salt in a mixture of 120 mL of cone, ammonia solution and 80 mL of distilled water. Add 240 g of ammonium nitrate and dilute it to 1 litre water.

26. **Barium chloride 0.2 M:** Dissolve 48.8g of the salt in distilled water and make up the volume to 1 litre.

27. **Chlorine water:** Take one litre of distilled water and saturate it with chlorine gas and keep the solution in a dark coloured bottle.

28. **Calcium chloride 0.2 M:** Dissolve 43.8g of the salt in distilled water and make up the volume to 1 litre.

29. **Copper sulphate 0.5M:** Dissolve 124.75g of the salt in distilled water. Add a few drops of dilute acetic acid and make up the volume to 1 litre.

30. **Cobalt nitrate 0.15M:** Dissolve 43.65g of the salt in distilled water and make up the volume to 1 litre.

31. **Dimethyl glyoxime 1 %:** Dissolve 10g of the solid in ethyl alcohol and make up the volume to 1 litre with distilled water.

32. **Ferric chloride 0.5M:** Dissolve 135g of the salt in distilled water. Add 20mL of conc. hydrochloric acid and make up the volume to 1 litre.

33. **Ferrous sulphate 0.5M:** Dissolve 138.5g of the salt in distilled water conatining 10mL of conc. sulphuric acid and make up the volume to 1 litre.

34. **Iodine solution 0.05M:** Dissolve 12.7g of iodine crystals in distilled water containing 20 g of potassium iodide and then dilute it to 1 litre.

35. **Lime water:** Dissolve some amount of calcium oxide in distilled water, filter the solution after sometime and keep it in a reagent bottle.

36. **Litmus solution (Blue):** Dissolve 10g of litmus in distilled water and make up the volume to 1 litre.

37. **Litmus solution (Red):** To the blue litmus solution add about 10 drops of dilute hydrochloric acid.

38. **Lead acetate 0.1M:** Dissolve 37.9g of the salt in 500 mL of distilled water containing a little acetic acid and make up the volume to 1 litre.

39. **Methyl orange:** Dissolve 1 g of the solid in distilled water and make up the volume to 1 litre.

40. **Mercuric chloride 0.1M:** Dissolve 27.2g of the salt in the water and make up the volume to 1 litre.

41. **Nesslers reagent:** Dissolve 23g of mercuric iodide and 16 g of potassium iodide in distilled water and make up the volume to 100 mL. Add 150 mL of 4M $NaOH$ solution. Allow it to stand for 24 hours and decant the solution. Solution should be stored in a dark coloured bottle.

42. **Potassium chromate 0.2M:** Dissolve 38.8g of the salt in distilled water and make up the volume to 1 litre.

43. **Potassium dichromate 0.1M:** Dissolve 29.4g of the salt in distilled water and make up the volume to 1 litre.

44. **Potassium iodide 0.2M:** Dissolve 33.2g of the salt in water and make up the volume to 1 litre.

45. **Potassium thiocyanate 0.2M:** Dissolve 19.4g of the salt in distilled water and make up the volume to 1 litre.

46. **Potassium permanganate 0.02M:** Dissolve 6.32g of the salt in distilled water and make up the volume to 1 litre. Heat the solution and filter it.

47. **Potassium ferrocyanide 0.1M:** Dissolve 42.2g of the salt in distilled water and make up the volume to 1 litre.

48. **Potassium ferricyanide 0.2M:** Dissolve 65.8g of the salt in distilled water and make up the volume to 1 litre

49. **Pheuolphthalein 0.1%:** Dissolve 0.25g of the solid in 125 mL of ethyl alcohol and then add 125 mL of distilled water.

50. **Sodium hydroxide 4M:** Dissolve 160g of the sodium hydroxide pellets in distilled water

50. **Sodium hydroxide 4M:** Dissolve 160g of the sodium hydroxide pellets in distilled water and make up the volume to 1 litre.

51. **Silver nitrate 0.1M:** Dissolve 17g of the salt in distilled water and make up the volume to 1 litre and store it in a brown coloured bottle.

52. **Starch** Prepare paste of about 1g of starch in cold water and pour it in 100 mL of boiling water with constant stirring. Allow it to cool.

53. **Disodium hydrogen phosphate 0.1M:** Dissolve 35.8 g of the salt in distilled water and make up the volume to 1 litre.

54. **Sodium nitroprusside 0.03M:** Dissolve 1g of the solid in 100 mL of distilled water.

55. **Sodium cobaltinitrate 0.16M:** Dissolve 64.64g of the solid in distilled water and make the volume to 1 litre.

56. **Stannous chloride 0.5M:** Dissolve 113g of salt in 200 mL of concentrated hydrochloric acid by heating (if necessary). Add several pieces of metallic tin and make up the volume to 1 litre.

57. **Yellow ammonium sulphide:** Take about 200 mL of concentrated ammonia solution in a bottle and saturate it with H_2S gas. Add 10g of flowers of sulphur and shake well untill sulphur is completely dissolved. Dilute the solution to one litre with distilled water.