स्वाध्याय स्वमन्थन स्वावलम्बन

UTTAR PRADESH RAJARSHI TANDON OPEN UNIVERSITY

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Indira Gandhi National Open University

UP Rajarshi Tandon Open University

UGCHE-(L)-6
Chemistry Lab-I
Chemistry Lab-II

FIRST BLOCK : Quantitative Analysis-I

SECOND BLOCK : Quantitative Analysis-II

FIRST BLOCK : Inorganic Preparations and Gravimetry

SECOND BLOCK : Quantitative Inorganic Analysis

Shantipuram (Sector-F), Phaphamau, Allahabad - 211013

UTTAR PRADESH
RAJARSHI TANDON OPEN UNIVERSITY

Block

1

QUANTITATIVE ANALYSIS-I

COURSE INTRODUCTION

'Chemistry Lab-I' is the first laboratory course in chemistry. It is designed for students of Bachelor's Degree Programme (B.D.P.) in Science who have a background in science and mathematics. This manual gives the procedural details about various experiments you are required to perform. Appropriate conceptual basis has also been laid for each experiment to make this manual complete in itself.

Two common tools, a scientist uses, are observation and reasoning. An experiment is a controlled observation. We perform an experiment having some aim in our mind. We make observations and draw conclusions by logically analysing these observations. Chemistry has been defined as 'the integrated study of the preparation, properties, structure and reactions of the chemical elements and their compounds, and of the systems which they form.' As such experimental work forms an essential part of chemistry which has, indeed, been defined as an experimental science. One type of experiments in chemistry, known as analytical experiments, deal with analysing various materials to find the nature and the amount of components constituting them. The other type of experiments deal with synthesis of substances.

Broadly, analytical experiments are divided into two types, viz., qualitative, concerned with the identification and separation of chemical substances, and quantitative, concerned with the determination of the amount of a chemical substance present, either alone or in a simple or complex mixture with other substances. Quantitative analysis is further classified into various types, e.g., gravimetric analysis, volumetric or titrimetric analysis, etc. In gravimetric analysis, the component to be estimated is converted into a stable and insoluble precipitate, which is collected, dried and weighed accurately. Knowing the chemical reaction involved, the mass of the precipitate can be used to find the amount of the substance under investigation. You would be doing such experiments in a later course.

In titrimetric analysis, the material to be estimated is dissolved in a suitable solvent and is titrated against a standard solution of an appropriate reagent. Volume of the above solution along with the volume and concentration of the standard solution are then used to estimate the amount of the material. In colorimetric analysis, light absorbing property of a substance is used for its estimation using a colorimeter.

This lab course is designed to enable you to understand the principle, practice and application of titrimetric analysis in an integrated way. Here, we shall try to analyse a given material by more than one titrimetric method. In other words, we shall attempt to see how different types of titrimetric analyses can be exploited to analyse a compound. In this process, we will be making use of some instrumental methods too, viz., conductometry, potentiometry and colorimetry using the instruments conductometer, pH meter and colorimeter, respectively. Except colorimetry, the other two instrumental methods are based on titrimetric principles only. However, these methods take advantage of some physical properties of the compound, i.e., conductance, pH or colour.

This course contains two blocks. In Block 1, we begin by explaining the basic concepts involved in titrimetric analysis. We discuss the principles of acid-base titrations potentiometry and conductometry, and set experiments for you to do using titrimetric, pHmetric and conductometric methods.

In Block 2, we take up redox titrations, explaining first their principles and then experiments involving the estimation of iron and copper. We also discuss the principle of colorimetry and show how to estimate copper in a given solution using this technique. Lastly, we take up the analysis of a sample of water to find out its hardness, alkalinity and dissolved oxygen.

Objectives

After studying this course and performing the experiments set in it you should be able to

- explain the basic concepts involved in titrimetric analysis,
- explain the principles of acid-base, redox and complexometric titrations,
- work out the stoichiometric relations based on the reactions involved in the above,
- select and use appropriate apparatus/equipment for titrimetric, potentiometric, conductometric and colorimetric

- take observations and calculate results after performing the experiments set in the course and
- compare the results obtained with those expected, point out sources of error and suggest measures for improvement.

Study Guide

In this lab course, you would be doing twelve experiments which involve quantitative determination of different substances using both the conventional titrimetric and instrumental methods.

Each experiment contains the following six sub-sections :

Principle
Requirements
Procedure
Observations
Calculations
Result

Write up on each experiment starts with a discussion of the theoretical principles on which the experiment is based. We would like you to go through this carefully before starting the experiment. We have introduced self assessment questions (SAQs) at appropriate places, which will enable you to see whether you have understood this part. Space has been provided for answering the SAQs, so that you can refer back to them whenever necessary. In case you want to supplement your study by consulting other reference books, a list is given at the end of Block 2.

The sub-section, 'Requirements' gives you an idea of the apparatus and chemicals you would be needing for the experiment. You may have to prepare some solutions yourself, for which detailed procedures have been given. In addition, some solutions may be provided, which you may collect from the laboratory staff.

The next three sub-sections, i.e., 'Procedure, Observations and Calculations' tell you how to carry out the experiment, take observations, tabulate them and calculate the result. In case an instrument has to be used in an experiment, a brief description of the instrument as well as operating instructions have been given. We would like you to go through these carefully, discuss with your counsellor and be confident about handling these instruments. Chemical analysis is becoming more and more instrument oriented and we would like you to be familiar with some of the basic instruments like pH meter, conductometer, colorimeter, etc. In the last sub-section, 'Result', you are required to discuss your result and compare it with the known value, your counsellor will give you.

With the result for each experiment you have to mention % error which you can calculate using the following formula,

$$\% \text{ error} = \frac{\text{Experimental Value} - \text{Correct Value}}{\text{Correct Value}} \times 100$$

We want you to see where the source(s) of error are, so that you can improve your performance. For example in a titration experiment, possible explanation for the experimental low values for the molarity include (a) error in weighing of primary standard, (b) in preparation of standard solution, (c) in taking the burette readings (d) in observing the colour change of indicator, etc.

Last but not the least, check the apparatus as it is given to you, especially the burette, it should not leak. Clean the glass apparatus thoroughly as indicated. The analytical balance may also need to be set, you can take your counsellor's help in this. After you finish the experiment, clean the apparatus again. You should leave your bench as clean as you got it. We have given elementary precautions that need to be observed in the laboratory. Read them carefully and observe them. Mind you, chemicals are safe if handled properly.

Laboratory Notebook

An important part of your scientific training is the maintenance of a complete and up to date record of your laboratory work. For recording experimental data, laboratory notebooks are available in the market. You need a 30-40 page chemistry notebook for this lab.

You should prepare the pages for recording data before you come to the lab. For each experiment, you should write down the title of the experiment, important chemical reactions involved and observations. The observation Tables, as given with the experiment in your manual, should be given on the left-hand page. Calculations and results are reported on the right-hand page. You may do the calculations after the lab and record the result in your notebook.

The laboratory notebook must be submitted to the counsellor for corrections and grading. Marks have been allocated for doing the experiment and for recording it properly. Your counsellor may also conduct a viva-voce to judge how much you have learnt. There are marks for this too.

We want you to share the thrill of learning by doing. There is no better way to learn.

So, best of luck.

BLOCK INTRODUCTION

In this block we introduce the basic concepts related to titrimetric analysis, particularly, acid-base titrations using acid-base indicators, pH metric and conductometric methods.

In Unit 1 you would be introduced first to the basic skills, such as, how to weigh a sample, measure volumes and perform a titrimetric experiment. Perhaps you have learnt these skills in your previous classes. This unit is an important review and extension. In this unit, you will also learn the handling of lab reagents and safety measures to be observed while working in the laboratory. As you know, many of the operations conducted in chemistry laboratory are potentially hazardous and, therefore you must observe certain safety precautions.

In Unit 2 and Unit 3, we shall discuss the basic theory of acids and bases, the principles of acid-base titrations, potentiometry and conductometry. In Unit 2, you will learn how to perform acid-base titrations using conductometry. In Unit 3, you will learn to analyse a mixture of two bases by indicator method.

Objectives

After studying this block and performing the experiments set in it, you should be able to:

- explain the basic principle of acid-base titrations, potentiometry and conductometry,
- prepare standard solutions from primary standards and standardise other solutions,
- estimate acetic acid in vinegar solution using acid-base indicator, pH meter and conductometer,
- determine the strength of sodium carbonate and sodium hydroxide in a given solution and compare the results obtained by different methods, and
- design experiments employing the techniques of acid-base indicators, potentiometry and conductometry for analysis of acid base contents of commercial products.

UNIT 1 LABORATORY TECHNIQUES AND PROCEDURES

Structure

1.1 INTRODUCTION

As you know by now, in titrimetry we estimate a substance in solution by titrating it against the standard solution of an appropriate substance. Here, we would be dealing with weighing masses of substances and measuring volumes of their solutions accurately. We, therefore, first of all introduce you to the apparatus commonly used in titrimetric analysis, and explain its correct use. We also tell you how to make a standard solution and express its concentration. A titrimetric analysis involves the detection of the equivalence point where the quantities of reactants balance stoichiometrically, for this, methods using indicators and also various instrumental methods are available. We briefly introduce you to these leaving details for the actual experiment. A sample titration has also been described.

Finally, we introduce you to the common laboratory reagents and the safety measures one should observe in a chemistry laboratory.

Objectives

After reading this unit, you will be able to:

- measure and deliver sample volumes by selecting and using appropriate equipment for titrimetric measurement,
- determine the mass of a sample by correctly using analytical balance,
- perform basic laboratory skills, including pouring reagents and transferring solids, preparing solutions of known concentrations,
- organise and interpret experimental data by effectively tabulating the data and also plotting it as a graph, and
- record the observations and do the calculations.

1.2 APPARATUS COMMONLY USED

Titrimetric analysis involves reliable and accurate measurements of volumes of solutions. Three pieces of apparatus, namely, a pipette, a burette and a volumetric flask are

indispensable for this purpose. Their use is described here. Before doing the experiment you should go through the instructions given below carefully and work accordingly.

1.2.1 How to Use a Pipette

Pipette is used to measure and transfer known volume of a liquid from one container to another.

Pipettes which can measure volumes of less than 1 cm^3 are also available with special accessories.

A pipette is shown in Fig. 1.1 (a). As you can see, it is a long tube with a bulb in the middle. On the narrow upper part of the pipette a horizontal line is marked. This line indicates the level to which the pipette has to be filled to deliver the liquid equal to the volume indicated on the bulb when used in the way described below. Pipettes can be of different capacities like 1, 2, 5, 10, 20, 25, 50 cm^3, etc. You will use pipettes mostly of 10 and 20 cm^3 for your experiments.

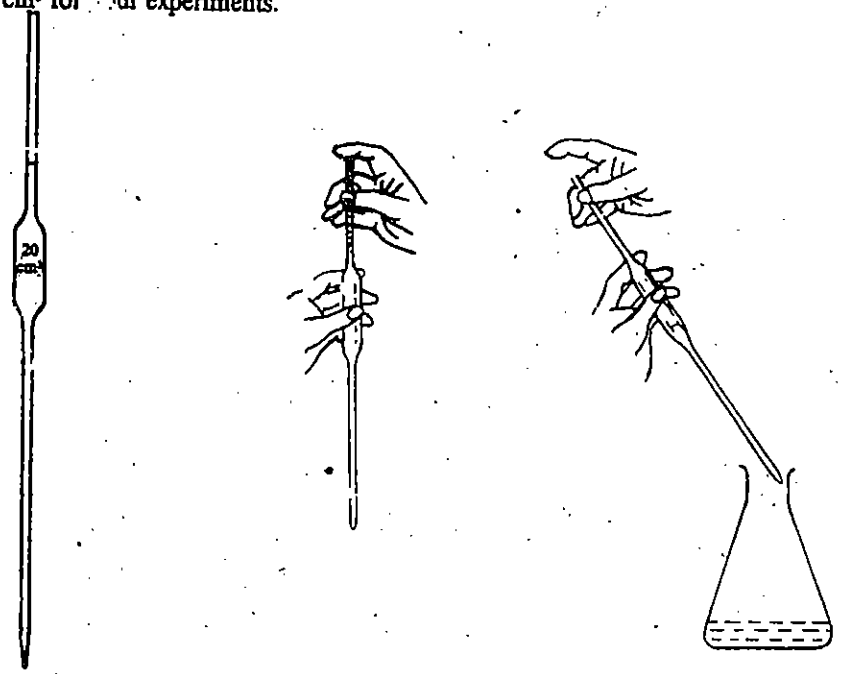

Fig. 1.1 : (a) Pipette. (b) Handling of a pipette. (c) Correct way to drain out the solution.

CAUTION!
Do not suck corrosive liquids like strong acids and alkalies by mouth. You can use a rubber teats.

Concave meniscus
Convex meniscus

The curved surface of a liquid in a container is known as the meniscus. The meniscus in case of liquids which stick to the container, is concave, e.g., for water and aqueous solutions, while it is convex in case of liquids which do not stick to the container, e.g., for mercury.

Fig. 1.2 : Graduated Pipette.

Before using a pipette, it has to be thoroughly washed with a good quality detergent followed by plenty of water and finally with distilled water. This removes all the grease. It is then rinsed with the solution which has to be measured. For rinsing, the solution is taken in a clean and dry beaker. The pipette is dipped deep into the solution and the solution is sucked into the pipette to fill it up to about half its volume. It is then taken out and the solution is made to wet it completely from inside by moving the solution up and down and also around its axis. The solution is drained out and the whole process is repeated. The pipette is then filled with the solution until the level is about 2 cm above the mark. The top of the pipette is then quickly closed by slightly moist (not wet) index finger; see Fig. 1.1 (b). The pressure of the finger is slowly released so as to allow the solution to run out until the lower **meniscus** just touches the mark. The solution from the pipette is transferred into the container in which titration has to be done. The solution is allowed to run out on its own. The last drop of the solution which does not seem to drain out by itself is taken out gently by touching the tip of the pipette with the walls of the container for about 3-4 seconds; see Fig. 1.1 (c). **Do not blow out the last drop.** The volume of the liquid thus transferred through the pipette is equal to the volume marked on the pipette.

Another type of pipette is designed to deliver definite but different volumes of a liquid. It is called a **graduated pipette,** Fig. 1.2. It has got markings corresponding to different volumes. It is also used in a similar fashion, with the only difference that the liquid is not completely drained out; instead the volume required is transferred.

SAQ 1

Why should you not blow the last drop out of the pipette?

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1.2.2 How to Use a Burette

A burette is designed to transfer definite but variable volumes of a liquid into another container.

A burette is a long glass tube, commonly of 50.0 cm^3 capacity in 0.1 cm^3 unit graduation marks, Fig. 1.3. It has a stop cock at the lower end to control the amount of solution drained. The burette also has to be washed, first with a detergent followed by plenty of water and finally by distilled water. It is then rinsed with the solution to be measured. For rinsing it is filled a little less than half with the solution and by repeatedly rotating and tilting the burette, the solution is made to wet it completely from inside. This solution is discarded. The burette is then mounted on the stand in an upright position and is filled carefully with the help of a funnel. After taking out the funnel, the meniscus is adjusted to a definite graduation mark by drawing out some solution through the stop cock. The bottom of the meniscus should just touch the graduation mark. While reading the solution level in the burette, your eyes should be on level with the graduation mark, otherwise there would be error due to parallax, Fig. 1.4. It is not necessary to adjust the meniscus at the zero mark level, if it is too high for the level of your eyes. You can adjust it at, say 10.0 cm^3 or any other convenient level.

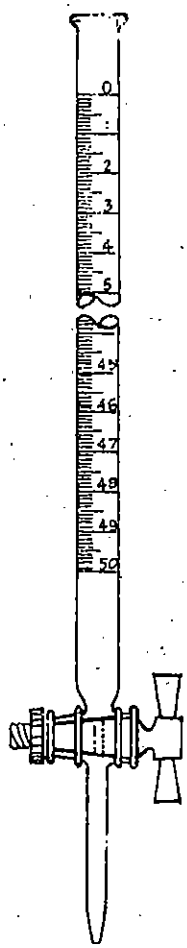

Fig. 1.3 : Burette.

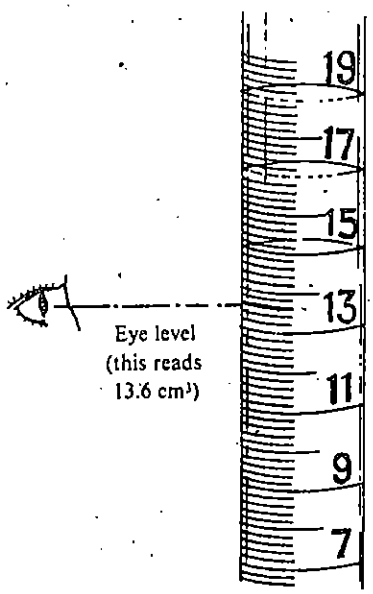

Fig. 1.4 : Eye level for burette reading.

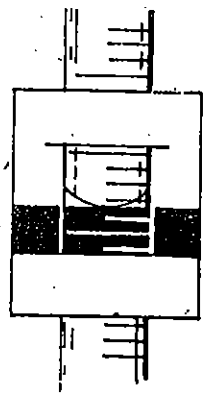

Fig. 1.5 : Reading the burette : the black portion of the parallax card is adjusted to make the meniscus plainly visible.

Error in burette reading is among the most common sources of error in titrimetric analysis. To make the meniscus more distinct and to ensure that it looks the same always, it is convenient to place a screen behind the burette as shown in Fig. 1.5. This can be made from a small piece of cardboard covered with white paper with the lower half blackened with ink. The black part is to be held downward. This is called a **parallax card.** You can ask your counsellor to show you how to make a parallax card.

After adjusting the meniscus, the level of the solution in the burette is recorded. This is called the **initial reading** or initial volume. Then the titration is performed and at the end of the titration, the level of the solution is recorded. It is called the **final reading** or final volume. The difference of the two readings, (final reading – initial reading), gives the

volume of the solution transferred to the titration flask. The correct way of delivering a liquid from burette is shown in Fig. 1.6.

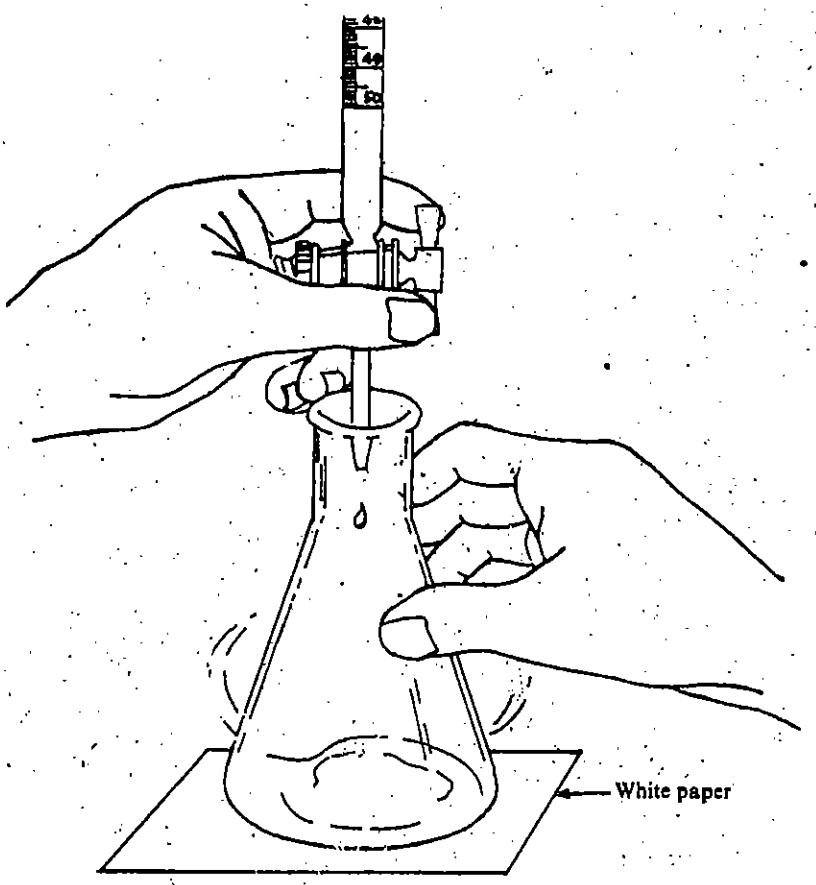

Fig 1.6 : Delivery of liquid from a burette.

1.2.3 How to Use a Volumetric Flask

A volumetric flask is used to prepare a definite volume of a solution of precisely known concentration.

Volumetric or measuring flask has a flat bottom with a long, narrow neck, Fig. 1.7. It has a calibration mark on its neck which indicates the level up to which the flask is to be filled to get a volume equal to the one indicated on the flask.

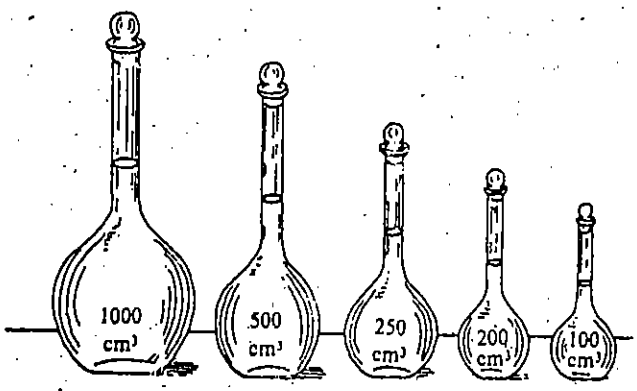

Fig. 1.7 : Volumetric flasks

PRECAUTION!
No standard apparatus is to be heated above 298 K.

You will be using volumetric flasks of 100 cm^3 and 250 cm^3 capacity. The flask, before use, is cleaned thoroughly, washed with distilled water and allowed to drain. The weighed compound is transferred into the flask with the help of a funnel. It is first dissolved in just enough water; the solution is then made up to the mark by carefully adding more distilled water. This can be done with a wash bottle or better with a pipette. The flask has to be stoppered tightly and shaken well before use to get a homogeneous solution.

1.2.4 How to Use an Analytical Balance

In titrimetric analysis, you will invariably have to prepare a standard solution. You would be required, for this purpose, to weigh a solid accurately by using an analytical balance. It is very important to learn the use of an analytical balance because accurate weighing is important for the accuracy of any titrimetric experiment.

A commonly used analytical balance is shown in Fig. 1.8. The various parts of the balance are labelled in the figure. Before using the balance, you have to first determine the **zero point** of the balance. For this purpose, the side doors of the balance are closed and the arrest knob (1) is slowly and carefully turned counter-clockwise. **Avoid jerks as they may disturb the setting of the balance.**

Zero point is the point on the scale at which the pointer of the unloaded balance comes to rest.

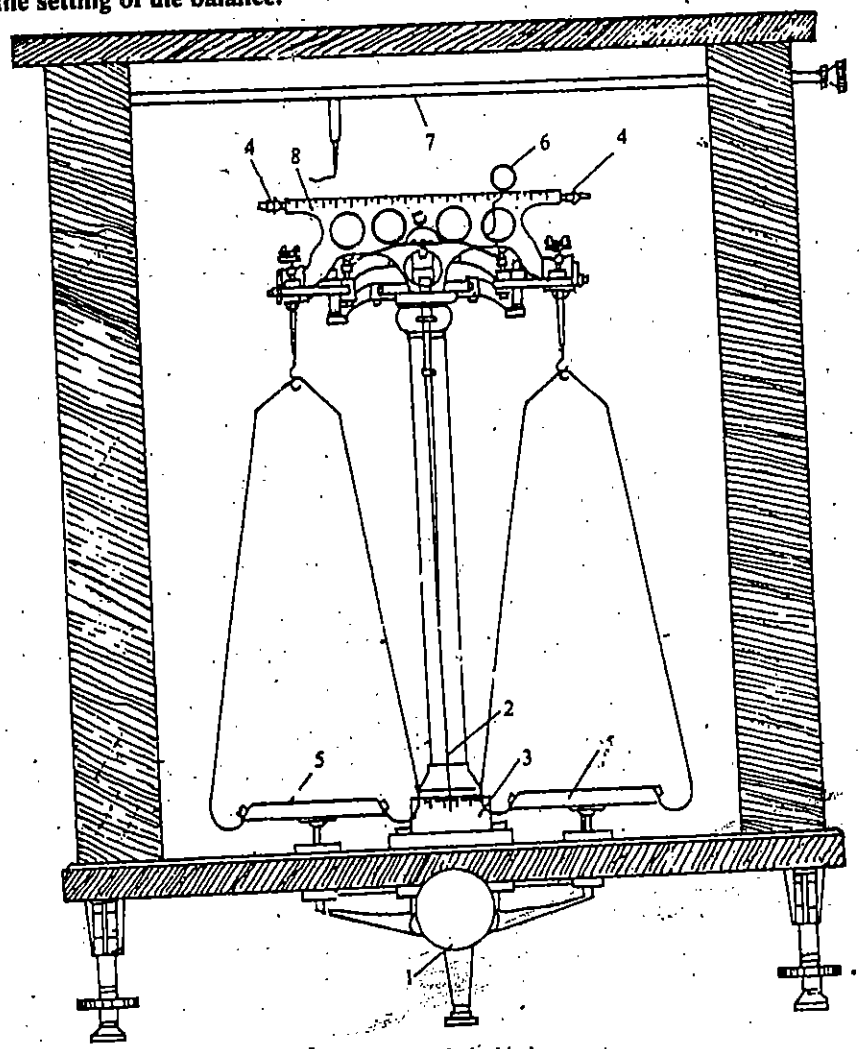

Fig. 1.8 : Analytical balance

When the arrest knob is turned fully to the left, the pointer (2) starts swinging around the centre of the scale (3). The first two swings are ignored and starting with the third swing, the extreme positions of the swing are noted. The swings to the right are positive and those to the left are negative. The readings to the left and right are averaged separately and the mean of these averages is found, which is the zero point. The following example will make it clear.

Ideally the zero point should coincide with the middle or the zero of the scale.

	Reading on the Left	Reading on the Right
1.	− 5.0	+ 5.0
2.	− 4.0	+ 4.0
3.	− 3.0	+ 3.0
4.	− 2.0	
	− 14.0	+ 12

$$\text{Average} = \frac{-14.0}{4} = -3.5 \qquad \frac{12.0}{3} = 4$$

$$\text{Mean Value} = \frac{-3.5 + 4}{2} = 0.25$$

The zero point is 0.25, i.e., 0.25 units to the right.

Such small discrepancies between the zero point and the middle of the scale may be ignored as they are insignificant. However, if the deviation is large, e.g., greater than 1.5 units, the balance must be adjusted by means of the screws (4), for which you may request your counsellor.

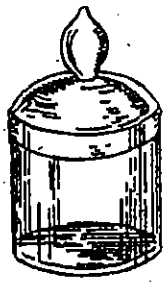

Fig. 1.9 : Weighing bottle

After adjusting the zero point of the balance (if necessary), we come to actual weighing. For this purpose, we use a glass or a plastic weighing bottle, Fig. 1.9. First of all, the weighing bottle is weighed on a rough balance to find its approximate mass to the nearest gram. Then, the left side door of the analytical balance is opened and the weighing bottle is kept on the left side pan (5) and the door is closed. Similarly, through right side door, weights equal to the approximate mass of the weighing bottle are transferred to the right side pan from a weight box; Fig. 1.10.

You must close both the doors of the balance before raising the pans with the arrest knob.

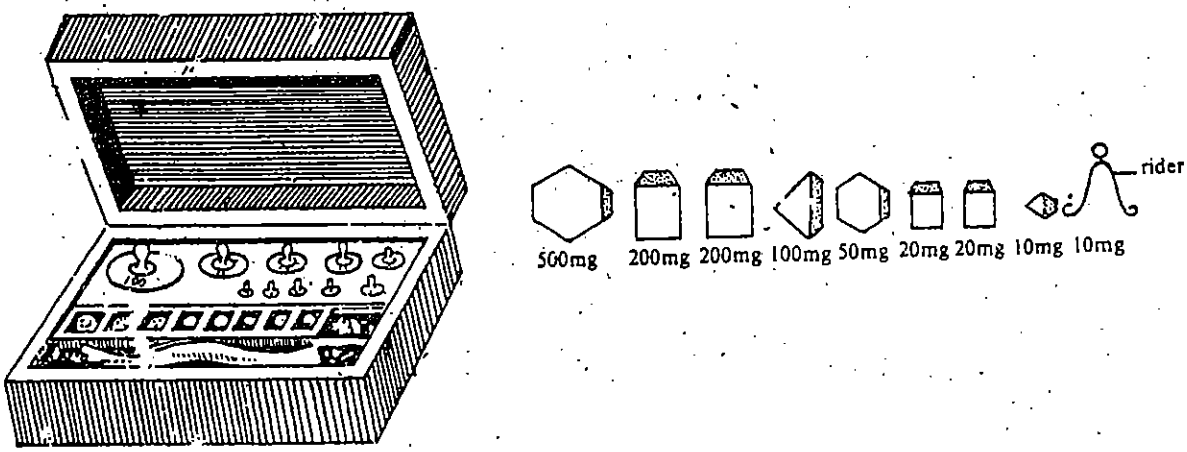

Fig. 1.10 : Weight box and weights

Always use forceps to transfer the weights. **Refrain from using your hands.**

The arrest knob is once again turned to the left and the movement of the pointer is seen. If it moves more to the left, then the weights transferred are in excess of the mass of the bottle. In that case some weights have to be removed. On the other hand, if the pointer moves to the right, then the added weights are not sufficient and we need to add more weights. Arrest the movement of the beam by turning the arrest knob fully towards the right and open the right side door to add or remove some weight(s), as the case may be. Recheck the movement of the pointer by turning the arrest knob. Continue this process till the addition of 1 gram weight makes the right hand pan heavier while its removal makes it lighter, e.g., if the weight is say 15.5 g, then 15 g weight would be lighter and 16 g weight would be heavier. After this, the fractional weights marked in mg, have to be added in the order of decreasing weight till the two sides are balanced. Do not use fractional weights of less than 10 mg, you should use a rider in such cases. A rider, Fig. 1.10, is a thin metallic wire suitably bent to be seated on the beam of the balance. It is normally put on the right hand side of the beam (6) with the help of the rider carrier (7). By varying the position of the rider on the beam (8), the rest point is found, i.e., the two pans are balanced.

A rider is used for mass adjustments below 10 mg/.01 g.

The beam scale has got markings from 0-10 on either side. It is calibrated in such a way that each main division is numerically equal to mass in milligram, when the rider is put on it. Each main division is further divided into 5 subdivisions and each subdivision is equivalent to 0.2 mg. Thus the accuracy of such an analytical balance can be only up to 0.2 mg. The mass of an object can be calculated using the following formula:

Mass of the object = (Weights added in grams)
+ (Fractional weights added × 0.001) g
+ (Main division of the rider position × 0.001) g
+ (Subdivision of the rider position × 0.0002) g

Let us illustrate the use of this formula. Suppose that while weighing an object, the weights added to the right side pan are 15 g, 200 mg and 2 × 20 mg. Let the rider position be 2 on the main divisions and 3 on the subdivisions.

Then the mass of the object
= 15.00 g + (240 × 0.001)g + (2 × 0.001)g + (3 × .0002)g
= 15.2426 g.

You have, so far, seen how to weigh an object accurately. If we want to weigh a substance in the weighing bottle, we make use of the method of weighing by difference. For this, the weighing bottle is first approximately weighed. The substance to be weighed is put into the bottle (a little more than required) and weighed accurately (m_1 g). The substance is transferred into a volumetric flask and the bottle is again weighed accurately (m_2 g). The difference of the two masses, i.e., $(m_1 - m_2)$ gives the exact amount of the compound transferred (m g).

Mass of the substance (m) = Mass of the bottle with substance (m_1) − Mass of the bottle after transferring the substance (m_2)

$m = m_1 - m_2$ g

Having learnt about the general apparatus to be used in the experiments for the first lab course, let us now understand the various terms and concepts used in these experiments. Before this, try the following SAQ.

SAQ 2

What is the mass of a substance if the following weights are needed to weigh it?

g	mg	position of rider
5	200	8.2
2	100	
1	50	

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1.3 EXPRESSION OF CONCENTRATION

In a qualitative sense, the term concentration deals with the "crowdedness" of the particles of **solute** in a **solution.** A solution having more number of solute particles per unit volume; is said to be more concentrated. In quantitative analysis, one very often comes across this term. Before we give an expression for this, it would be worthwhile to recapitulate a few relevant fundamental concepts here.

Solute is the dissolved substance in a solution. **Solvent** is the substance in which the solute is dissolved. **Solution** is the homogeneous mixture of a solute and a solvent.

Mole, denoted as mol, is the amount of a substance that contains as many elementary entities as are there in 0.012 kg of C^{12} isotope of carbon. The mole may be of atoms, ions, molecules, electrons or any other entity. The number of elementary entities in a mole of any substance is fixed and is given by a constant called the **Avogadro's number,** N_A which equals 6.022×10^{23}

The number of C^{12} atoms in 0.012 kg of C^{12} is equal to 6.022×10^{23}

Relative Molecular Mass (Molecular Weight) denoted as M_r, is the mass of one molecule in atomic mass unit (a.m.u.) relative to 1/12th of the mass of the pure C^{12} isotope (12.000 a.m.u.). For most titrimetric analyses, purpose of this is the same as the old atomic mass and molecular mass. We find it by multiplying the atomic mass of each element in the molecule by its subscript in the formula and then adding the total for each element to get the grand total, e.g., one molecule of CO_2 has relative molecular mass of 44, which is calculated as:

$[12.000 + (16 \times 2)] = (12 + 32) = 44$

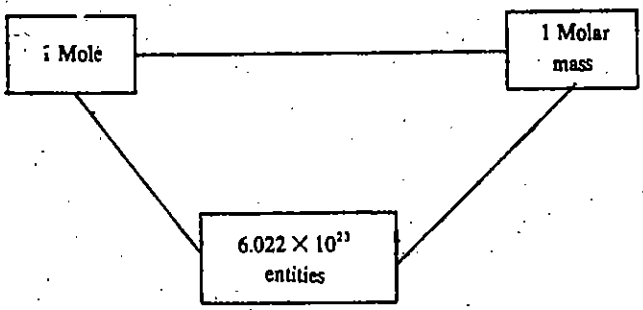
Relative molecular mass being relative is unitless.

Molar Mass, denoted by symbol M_m, is the mass of one mole of a given substance. It is numerically equal to the relative molecular mass but is expressed in g mol^{-1} units. The following illustration explains this point.

Although SI unit of molar mass is kg mol^{-1}, it is more convenient to use g mol^{-1} for titrimetric calculations.

The relative molecular mass of oxalic acid dihydrate $[(COOH)_2.2H_2O]$ crystals = 126. The molar mass of oxalic acid dihydrate crystals = 126 g mol^{-1}

The amount of a substance having mass equal to molar mass is called a **mole**. Thus we see that mole, molar mass and Avogadro's number are interrelated. A schematic representation of the relationship among these is shown below:



For titrimetric purposes we express concentration in terms of **molarity** denoted by symbol M which is defined as the number of moles present in one dm^3 of the solution. It can be expressed as :

$$\text{Molarity } (M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in dm}^3\text{)}}$$

Thus, if you dissolve 126 g of oxalic acid dihydrate (molar mass = 126 g mol^{-1}) in water and make the volume up to 1 dm^3, then the solution would be 1 M.

The molarity, M, of a solution containing m g of the solute in V cm^3 of a solution can be calculated as follows :
Let the molar mass of the solute be M_m g mol^{-1}

$$\text{Number of moles of a solute} = \frac{\text{Its mass}}{\text{Molar mass}} = \frac{m \text{ g}}{M_m \text{ g mol}^{-1}}$$

$$= \frac{m}{M_m} \text{ mol}$$

Volume of the solution = V cm^3
Since 1000 cm^3 = 1 dm^3,

$$\text{Volume of the solution} = \frac{V \text{ cm}^3}{1000 \text{ cm}^3 \text{ dm}^{-3}}$$

$$= \frac{V}{1000} \text{ dm}^3$$

Hence by definition,

$$\text{Molarity of the solution } (M) = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in dm}^3}$$

$$= \frac{m}{M_m} \text{ mol} \times \frac{1}{\frac{V}{1000} \text{ dm}^3}$$

i.e., $$\boxed{M = \frac{1000\, m}{M_m . V} \text{ mol dm}^{-3}} \qquad \text{...(1.1)}$$

1 ml = 1.000028 cm^3.

The pipettes and burettes are calibrated in cm^3 units (actually in ml which is almost equal to cm^3). **Hence, by substituting the volumes of the solutions in cm^3 units in the above expression, molarity of a solution can be calculated.**

Though molarity is being accepted more and more as the way of expressing concentrations, another related term, viz., **normality** is still in use. Here equivalent mass is used in place of molecular mass . Normality is defined as the number of gram equivalents of the solute per dm^3 of the solution. In other words,

$$\text{Normality } (N) = \frac{\text{Number of equivalents of solute}}{\text{Volume of solution (in dm}^3\text{)}}$$

The molar mass of a substance is an inherent property. It is independent of the nature of the chemical reaction it may be undergoing. Hence, a given solution containing a known amount of the solute will have the same molarity under all conditions. Normality, on the other hand, can change as the gram equivalent of a substance depends on the chemical reaction involved in the titration. For example, $KMnO_4$ can have a gram equivalent of 158.04, 52.68 or 31.6 depending on the reaction conditions. In the light of the above, it is advisable to use molarity rather than normality. We would be using molarity throughout our experiments. However, percentage, formality, molality, mole fraction and ppm are some other ways of expressing concentration and are briefly explained here.

Percentage : The percentage of a **solute** in a given solution can be expressed in three different ways depending upon the nature of the solute and the solvent. Let us illustrate by taking some examples.

(a) If we take 10 g of, say, NaCl and dissolve it in water to make a volume of 100 cm^3, then we get a 10% mass by volume, i.e. 10% *m/V* solution of NaCl in water..

Mass per cent can also be called parts per hundred (pph).

(b) If instead of preparing 100 cm^3 of solution, we add enough water to prepare 100 g of solution, then we get 10% mass by mass, i.e. 10% *m/m* solution of NaCl in water.

(c) In cases where the solute is also a liquid, it is possible to represent concentration as volume by volume. For example, if we mix 10 cm^3 of methanol (solute) with H_2O (solvent) to prepare 100 cm^3 of the solution, then we get 10% volume by volume, i.e. 10% *V/V* solution of methanol in water.

Mathematically percentage is given as :

$$\text{Percentage} = \frac{\text{Amount of solute}}{\text{Amount of solution}} \times 100$$

The units would depend on the units of the amount of solute and solvent.

Formality : In certain ionic compounds, e.g., NaCl, which are completely dissociated in solution, it is less accurate to talk of one molecule or of molecular mass. In such cases, a different term, viz., formality is considered. Formality is defined as the number of gram formula masses dissolved per dm^3 of the solution Here, it is, therefore, more appropriate to talk of formality than of normality or molarity.

Molality : The molality of a solution is the number of moles of the solute per kilogram of the solvent contained in a solution. It is given by the following expression :

$$\text{Molality} = \frac{m_1 \times 1000}{m_2 \times M_m}$$

where,
m_1 = mass of the solute
m_2 = mass of the solvent
M_m = Molar mass of the solute

The molality scale is useful for experiments in which physical measurements, e.g., freezing point, boiling point, vapour pressure, etc., are made over a wide range of temperatures.

Mole fraction : The mole fraction (x) of any component in a solution is defined as the number of moles(n) of that component divided by the total number of moles of all the components in the solution. The sum of mole fractions of all the components of a solution is unity. For example, for a two component solution :

$$x_1 \text{ (solvent)} = \frac{N}{n+N}$$

$$x_2 \text{ (solute)} = \frac{n}{n+N}$$

$$x_1 + x_2 = \frac{n+N}{n+N} = 1$$

where n is the number of moles of the solute and N is that of the solvent. Mole fraction scale is mostly used in theoretical work.

Parts per million (ppm) : This unit is particularly useful for expressing very small concentrations. We find this unit by using :

$$\frac{\text{mass of solute}}{\text{mass of solute + mass of solvent}} \times 1{,}000{,}000 = \text{ppm}$$

1 mg mass of a solute dissolved in 1 dm^3 is one ppm.

ppm = $mg\ dm^{-3}$
= $\mu g\ cm^{-3}$
= $10^{-3}\ g\ dm^{-3}$

The masses of solute and solvent should be expressed in the kg unit. The concentrations of air and water pollutants are often given in parts per million.

Various ways of expressing concentrations are given here just to make you aware of these. Though in modern texts, by and large, the concept of molarity is being used, you would come across other expressions also.

SAQ 3

What is the molarity of sodium hydroxide solution made by dissolving 4.000 g of solute in a volumetric flask and adding water to the calibrated volume of 500 cm^3? (M_m of NaOH = 40 $g\ mol^{-1}$).

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SAQ 4

How many grams of $AgNO_3$ will have to be weighed to make 1 dm^3 solution of 0.1 mol dm^{-3} molarity? (M_m for $AgNO_3$ = 169.87 $g\ mol^{-1}$).

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1.4 STANDARD SOLUTION

The concentration terms being clear to you, you must know something about a standard solution.

A standard solution is defined as the one whose concentration (strength) is known accurately, i.e., we know exactly how much of the solute is dissolved in a known volume of the solution. A standard solution may be prepared by dissolving an accurately weighed, pure stable solid (solute) in an appropriate solvent. Preparation of a standard solution is generally the first step in any quantitative experiment, so it is important to know how to prepare a standard solution.

Primary and Secondary Standards

In titrimetry, certain chemicals are used frequently in defined concentrations as reference solutions. Such substances are classified as **primary standards** or **secondary standards**. A primary standard is a compound of sufficient purity from which a standard solution can be prepared by weighing a quantity of it directly, followed by dilution to give a definite volume of the solution. The following specifications have to be satisfied for a substance to qualify as a primary standard :

1. It must be easily available and easy to preserve.
2. It should not be **hygroscopic** nor should it be otherwise affected by air.
3. It should be readily soluble in the given solvent.
4. The reaction with a standard solution should be stoichiometric.
5. The titration error should be negligible.

Hygroscopic substances are those which have a tendency to absorb moisture.

Few available primary standards for acid-base, redox and complexometric titrations are :

Potassium hydrogen phthalate (KHP) $C_8H_5O_4K$	M_r = 204.23 Acid-base
Anhydrous sodium carbonate Na_2CO_3	M_r = 106 Acid-base
Potassium dichromate $K_2Cr_2O_7$	M_r = 294.19 Redox
Arsenic (III) oxide As_2O_3	M_r = 197.85 Redox
Potassium iodate KIO_3	M_r = 214.00 Redox
Sodium oxalate $Na_2C_2O_4$	M_r = 134.00 Redox
Sodium Salt of EDTA	M_r = 372.3 Complexometric

Solutions prepared from the primary standards are called primary standard solutions.

Substances which do not satisfy all the above conditions, are known as secondary standards. In such cases a direct preparation of a standard solution is not possible. Examples are alkali hydroxides and various inorganic acids. These substances cannot be obtained in pure form.

Therefore, concentration of these can be determined by titrating them against primary standard solutions. This process is called **standardisation** and the solution so standardised is called a secondary standard solution.

Preparation of a Standard Solution

To prepare a standard solution of volume, V cm^3, of known molarity, M mol dm^{-3}, the mass of the solute required, m g, of molar mass M_m, can be calculated by rearranging Eq. 1.1 as follows :

$$\text{Mass of the solute } (m) = \frac{M \,.\, M_m \,.\, V}{1000} \text{ g} \qquad \ldots(1.2)$$

The solute is then weighed on an analytical balance as explained before (Sec 1.2.4), transferred into a standard flask and dissolved first in a small quantity of the solvent, the solution is then made up to the mark and shaken thoroughly to get a homogeneous solution.

In preparing a standard solution whose concentration is, say, around 0.1 M, the amount of the substance weighed need not be exactly equal to that corresponding to 0.1 M. It can be slightly less or more, but the weighing must be accurate. From the weight of the solute actually taken, molarity of the solution can be calculated using Eq. 1.1.

SAQ 5

On what criteria do

(a) sodium hydroxide and

(b) benzoic acid

fail as primary standards according to the criteria given in the text.

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1.5 TITRATION

In titrimetric analysis, one determines the volume of a standard solution which is required to react quantitatively with a known volume of the other solution, the concentration of which is to be determined. For this purpose, an **aliquot** of the solution to be estimated is pipetted out and is transferred to a conical flask. The standard solution is added dropwise from a burette to the solution in the conical flask.

The conical flask is continuously shaken to enable the two solutions to mix thoroughly. Standard solution is added till the two solutions react quantitatively. This process is called **titration**. The solution in the conical flask is called the **titrand** and the one in the burette is called the **titrant**. The total volume of titrant used in the reaction is called the **titre**.

We have said above that in a titration, the titrant is added till it reacts quantitatively with the titrand. Such a stage, at which the quantities of titrant and titrand are in their

Aliquot is the volume of the solution delivered by the pipette in a titration. If you use a 20 cm^3 pipette everytime during a titration, the aliquot contains 20 cm^3 of the solution.

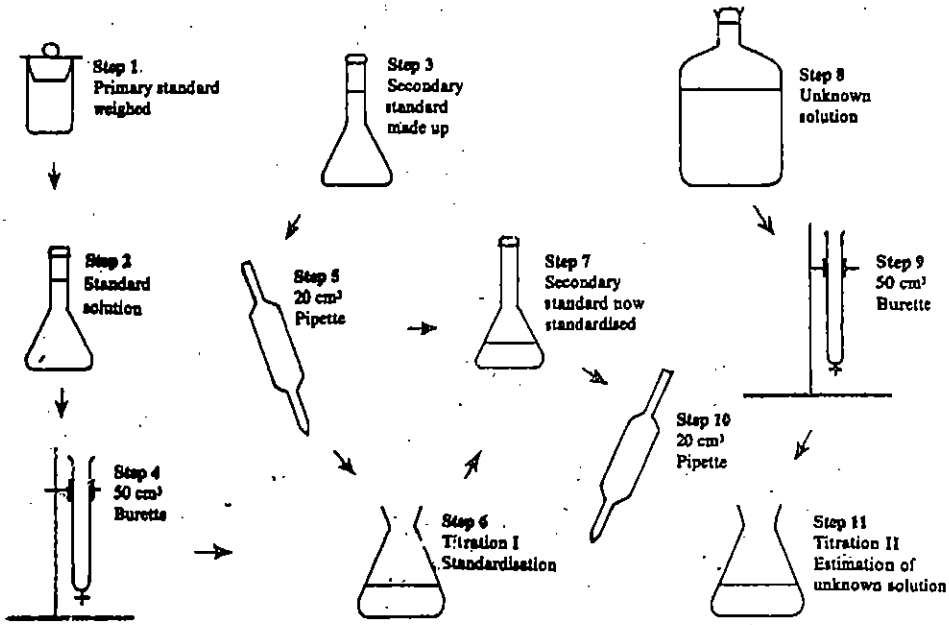


Fig. 1.11 : Steps in a titrimetric estimation

stoichiometric proportions (in terms of equivalents or moles), is called the **equivalence point.** A question arises now, as to how do we know that the equivalence point has been reached? At what stage shall we stop adding the solution from the burette? Essentially we need some substance which can indicate this stage by a change in a physical property like colour. A substance which is used to indicate the equivalence point of a titration through a colour change is called an **indicator**. Equivalence point so obtained is called **end point.** It is not necessary that the end point is coincident with the equivalence point, because of the delay in getting the indicator to show the change, and other factors. Ideally end point and equivalence point should be as close as possible. The indicator, to be used in a given titration, would depend on the nature of the chemical reaction involved between the two reacting solutions. The basic requirement for an indicator is that it should have distinctly different colours before and after the end point because we need to know the end point visually. If no visible indicator is available, the detection of equivalence point can often be achieved by following the course of the titration by measuring the potential difference between an indicator electrode and a reference electrode or the change in the conductivity of the solution.

End point is the point usually indicated by a change of colour of an indicator. At the end point particular reaction is completed. Equivalence point is the point at which the number of equivalents of reactants are equal to each other.

1.5.1 Types of Indicators

The indicators can be of three types depending upon their usage :

i) **Internal indicators :** These have to be added into the reaction solution. Examples are : phenolphthalein, methyl orange, diphenylamine, etc.

ii) **External indicators :** These are not added into the solution. The indicator is kept out on a plate. A drop of the solution being titrated is taken out with the help of a rod and put on the indicator. A change in colour indicates the end point. Potassium ferricyanide is one such example.

iii) **Self-indicators :** Sometimes either the titrand or the titrant changes its colour at the end point and acts as a self-indicator. The example is potassium permanganate used in permanganatometry.

1.5.2 Types of Titrations

Depending upon the nature of the chemical reaction involved in a titration, the latter can be classified into the following types :

i) **Acid-base Titrations** or **Neutralisation titrations :** The reaction in which an acid reacts with a base to give salt and water is called a **neutralisation reaction** and the

titration involving such a reaction is called **neutralisation titration.** An example is the reaction between NaOH and HCl,

$$NaOH + HCl \rightarrow NaCl + H_2O$$

The indicators used in these titrations, depend upon the pH at the end point, the familiar examples are phenolphthalein and methyl orange.

ii) **Oxidation-Reduction or Redox Titrations :** Titrations involving oxidation-reduction reactions, i.e., those in which one component gets oxidised while the other gets reduced are known as **redox titrations.** An example is the titration between oxalic acid and potassium permanganate in acidic medium, in permanganatometry. In this case, potassium permanganate gets reduced to Mn^{2+} while oxalic acid gets oxidised to CO_2 and water. In this titration potassium permanganate acts as a self-indicator. The following equation represents the reaction :

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

Chromatometry and iodometry which are discussed in this course are also redox titrations.

iii) **Precipitation Titrations :** In certain reactions, when the two components react, a precipitate is formed. The end point is indicated by the completion of precipitation. Such reactions are termed as **precipitation reactions** and the titrations as the **precipitation titrations;** an example is the titration between potassium chloride and silver nitrate as per the following equation :

$$KCl + AgNO_3 \rightarrow AgCl + KNO_3$$

Titrations involving $AgNO_3$ are also called **argentometric titrations.**

iv) **Complexometric Titrations :** A complexation reaction involves the replacement of one or more of the co-ordinated solvent molecules, which are co-ordinated to a central metal ion, M, by some other groups. The groups getting attached to the central ion are known as ligands, L.

$$M(H_2O)n + nL = ML_n + nH_2O$$

The titration involving such type of a reaction is called a **complexometric titration.** For example, you will be using ethylenediaminetetraacetic acid (EDTA) as the complexing agent in your experiments. The indicator used in this case is eriochrome black T.

1.6 SAMPLE TITRIMETRIC EXPERIMENT : DETERMINATION OF THE STRENGTH OF GIVEN SODIUM HYDROXIDE SOLUTION

Having learnt about titration in general, types of titrations and indicators, you would now like to learn how you would do an experiment, make observations, record data and calculate the result. It is also important to examine the result critically, compare it with known or expected value, look for the sources of error so that improvement can be made. We will illustrate all this in the following example. Of course, you will have to perform various experiments according to the procedure given in each case. We consider here a simple titration involving a strong acid and a strong base, viz., HCl and NaOH, using methyl orange as the indicator.

Objectives

After performing this experiment you should be able to :

- state the principle involved in the experiment,
- find out the exact concentration of given NaOH solution in mol dm^{-3}, and
- find out the strength of this solution in g dm^{-3}.

1.6.1 Principle

In this experiment, you are required to find the strength of NaOH solution. First you must write the chemical equation involved in the reaction :

$$NaOH + HCl \rightarrow NaCl + H_2O$$

According to this equation one mole of NaOH would react completely with one mole of HCl at the end point.

$$\frac{\text{Number of moles of HCl used}}{\text{Number of moles of NaOH used}} = \frac{1}{1} = 1 \qquad \ldots(1.3)$$

Note Eq. 1.3 relates the ratio of the number of moles of two reactants to the ratio of their stoichiometric quantities.

If the molarity of HCl is M_1 mol dm^{-3} and volume of HCl used is V_1 cm^3 then the,

$$\text{Volume of HCl} = V_1 \text{ cm}^3 = \frac{V_1}{1000} \text{ dm}^3$$

$$\text{Number of moles of HCl used} = \frac{M_1 V_1}{1000} \text{ mol} \qquad \ldots(1.4)$$

Let us assume that the molarity of NaOH solution is M_2 mol dm^{-3} and the volume used is V_2 cm^3. Similarly,

$$\text{Number of moles of NaOH used} = \frac{M_2 V_2}{1000} \text{ mol} \qquad \ldots(1.5)$$

Substituting Eq. 1.4 and 1.5 in Eq. 1.3:

$$\frac{\frac{M_1 V_1}{1000}}{\frac{M_2 V_2}{1000}} = 1 \implies \frac{M_1 V_1}{M_2 V_2} = 1 \qquad \ldots(1.6)$$

or $M_1 V_1 = M_2 V_2$ $\qquad \ldots(1.7)$

Eq. 1.7 is the basic equation used in titrimetric calculations.

In general, for a titration between two substances A and B yielding C and D, as per the stoichiometric equation :

$pA + qB \rightarrow rC + sD$.

where, p, q, r and s are the number of moles of each substance involved in the reaction. It is possible to generalise Eq. 1.3 and write,

$$\frac{M_A V_A/1000}{M_B V_B/1000} = p/q$$

i.e., $$\boxed{\frac{M_A V_A}{M_B V_B} = p/q} \qquad \ldots(1.8)$$

1.6.2 Requirements

Apparatus

Burette (50 cm^3) — 1
Pipette (20 cm^3) — 1
Conical flask (250 cm^3) — 1

Solutions provided

Sodium hydroxide solution (≃ 0.1 *M*)
Hydrochloric acid solution (0.1 *M*)
Methyl orange indicator solution

1.6.3 Procedure

To perform the titration, 20 cm^3 of the NaOH solution is pipetted out into a clean conical flask. Two drops of methyl orange indicator are added to this solution and it is stirred thoroughly. An orange colour is obtained.

The burette is filled with hydrochloric acid solution and the level of the solution in the burette is adjusted to a convenient number graduation. As said before it is advisable to adjust the level close to the level of your eyes (Fig. 1.4). Do not forget to put a parallax card (sub-sec. 1.2.2). After recording the initial burette reading in the observation Table I, you have to start adding HCl slowly from the burette into the conical flask. Addition of HCl has to be continued till the orange colour changes to the red colour. This shows the end point of the titration. You have to stop addition of HCl from the burette and note the burette

reading in the observation Table I. The difference between the final and initial readings of the burette gives a rough idea of the titre value. Refill the burette with HCl and set its volume to a level equal to or near the previous setting. Repeat the experiment, i.e., take another clean conical flask and pipette out a fresh aliquot of NaOH. Add the indicator. In this titration you can add the solution from the burette as in the first titration, up to a volume about 1 cm^3 less than the titre in the first reading. Thereafter do not add the solution continuously, instead, add just one drop at a time and shake the flask. Continue this process till the orange colour changes to red with the addition of just one drop. Record this reading too.

Repeat the above process till you get 2-3 **concordant readings.**

Consecutive readings which are repeated are called **concordant readings.**

1.6.4 Observations

A model presentation for recording the data for this experiment is given here. You will have to record your data in a similar way for your titrimetric experiments.
Indicator used = Methyl orange

Observation Table I

HCl Vs. NaOH

Sl. No.	Volume of NaOH in cm^3	Burette reading		Volume of HCl in cm^3
		Initial	Final	
1	20	10.0	29.7	19.7
2	20	11.0	30.2	19.2
3	20	10.0	29.2	19.2

Thus, volume of HCl solution used = titre value = 19.2 cm^3

1.6.5 Calculations

You will have to proceed the following way to calculate, first the molarity of NaOH solution and then the mass of NaOH in 1 dm^3 of the solution.
Volume of NaOH solution taken = $V_2 = 20\ cm^3$
Molarity of NaOH solution = $M_2 = ?$
Volume of HCl solution consumed = $V_1 = 19.2\ cm^3$
Molarity of HCl solution = $M_1 = 0.1\ M$
According to Eq. 1.8,

$$\frac{M_1V_1}{M_2V_2} = \frac{p}{q}$$

Substituting the values of M_1, V_1, V_2, p and q,

$$\frac{0.1 \times 19.2}{M_2 \times 20} = \frac{1}{1}$$

$$M_2 = \frac{0.1 \times 19.2}{20}\ \text{mol dm}^{-3}$$

$$= 0.096\ M$$

Molar Mass of NaOH = 40 g mol^{-1}

Strength of NaOH
$= M_2 \times$ molar mass g dm^{-3}
$= 0.096 \times 40$ g dm^{-3}
$= 3.84$ g dm^{-3}

This can also be expressed in other way as :
Mass of NaOH in 1 dm^3 (1000 cm^3) of the solution
(as per Eq. 1.2)

$$= \frac{\text{molarity} \times \text{molar mass} \times \text{volume of the solution in cm}^3}{1000}\ \text{g}$$

$$= \frac{0.096 \times 40 \times 1000}{1000}\ \text{g}$$

$= 3.84$ g

1.6.6 Result

For the given sample experiment,
i) The molarity of the NaOH solution is 0.096 mol $d.n^{-3}$
ii) Strength of NaOH = 3.84 g dm^{-3}

1.7 INSTRUMENTAL DETERMINATION OF EQUIVALENCE POINT

In HCl vs. NaOH titration described in the last section, determination of the equivalence point of the titration was detected by colour change of an indicator. Suppose we don't want to use an indicator or many a times suitable indicator may not be available for a titration or the concentration ranges may be smaller than those required for colour change using an indicator. What should we do in these situations?

In these cases, instrumental methods which measure some physical property of the solution are used to detect the equivalence point. You will be using three instruments for this purpose. These are conductometer, potentiometer and colorimeter which measure the conductance, the potential and the colour intensity of the solution, respectively. Instrumental methods are quicker and more accurate. It would be worth comparing the results you obtain by titrimetry with those of the instrumental methods.

1. Conductometric Titrations

In conductometric titrations, the conductance of the solution being titrated is measured as a function of the volume of the titrant using a conductometer and a graph is plotted between the two (Fig. 1.12). You will learn the use of conductometer in Unit 2.

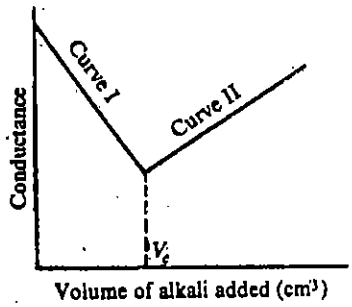


Fig. 1.12 : Conductance curve : Titration of NaOH against HCl

The change in the slope of the conductance vs. volume curve indicates the equivalence point.

The point of intersection of conductance curves for the titrand having excess of hydrochloric acid (curve I) and excess of sodium hydroxide (curve II) is the equivalence point.

2. Potentiometric Titrations

In potentiometric titrations, solution, the concentration of which is to be determined, is made the electrolyte in a half cell using an appropriate electrode. The potential of the half cell with respect to a reference electrode is measured as a function of the volume of the titrant. The change in slope of the potential vs. volume curve indicates the end point (Fig. 1.13).

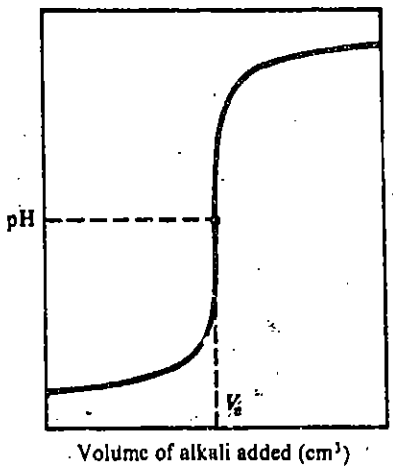


Fig. 1.13 : pH metric titration of HCl vs. NaOH

A special case of potentiometry where hydrogen ion concentration, i.e., pH is measured is referred to as pH metry. We get a curve of the type shown in Fig. 1.13 on plotting pH vs. the volume of the titrant. The region where a sharp change in pH takes place, in this case pH 7, indicates the end point.

Colorimetry

Besides the above two instrumental methods which have been explained as part of the titrimetric procedures, you will be using yet another instrumental method, viz., colorimetry. This is based on the measurement of the absorption of light of a suitable wavelength by a given solution. The amount of light absorbed is directly proportional to the concentration of a given absorbing species. This property is made use of in determining the concentration of the absorbing solution.

Use of Instruments

Instructional manuals for the instruments, would be provided to you. The detailed theory of these instrumental methods will be described along with the respective experiments.

SAQ 6

Tick √ on the correct statement/s.

Instrumental methods are preferred over indicator methods because

i) very small concentrations of substances can be estimated using instrumental methods.

ii) Instruments are not very expensive.

iii) Instrumental methods require a lot of time and do not give accurate results.

iv) Instrumental methods do not require indicators.

1.8 COMMON LAB REAGENTS

You will be using a number of reagents and chemicals during your experiments. There are lab assistants to help you to get these reagents. Most of these chemicals are kept in the reagent shelves and are properly labelled. The bench shelves have mostly the liquid reagents which include hydrochloric, sulphuric and nitric acids. Besides these, other solutions like silver nitrate, ammonium hydroxide, sodium hydroxide, barium chloride, etc., may also be kept there. You have to be very careful while using all these, especially, the acids. Mishandling any chemical may result in injury. You should thoroughly read the next section in the unit before starting your experiments which tells you about some safety measures in the laboratory.

The solid reagents are usually kept on a common table. You should use a spatula and take only the required amount of the compound from the bottle or the pack. Don't waste any chemical. The liquid reagents should be taken with the help of droppers.

The special chemicals and solutions required for any particular experiment will be provided by your counsellor at the time of performing the experiment.

1.9 SAFETY MEASURES IN THE LABORATORY

An important aspect in a chemistry laboratory is your own and your fellow workers' safety. Accidents occur in the laboratory because of carelessness and inadequate knowledge about the chemicals being used. Though accidents cannot be fully eliminated, yet these can be prevented to some extent by knowing in advance some general precautionary measures. The following dos' and don'ts in the laboratory would help you to avoid accidents.

The Do's :

- Wear a lab coat or an apron when working in the lab.
- Keep the test tube pointing away from yourself and others while heating it on a burner.
- Use splinters and not a paper to light a burner.
- You should know where the fire extinguishers are located in the laboratory and how to use them.

- Always use safety goggles for protecting your eyes from a dangerous operation, e.g., distillation of an inflammable liquid or while doing sodium ignition test.
- Wash your hands with soap when you leave the laboratory after doing an experiment.
- Carry out the reactions involving pungent or noxious fumes under a fume hood.
- Ensure that gas and water taps are closed before leaving the lab.

The Don'ts :

- Don't wear loose clothes specially the synthetic ones while working in the laboratory.
- Don't taste any chemical, not even sucrose; it may be contaminated.
- Don't pipette out corrosive liquids by sucking with your mouth.
- Don't put the reagents back into the bottles or packs after use. These should be poured into another glass bottle kept specially for the waste liquids.
- Don't try to insert glass tubing or thermometer into corks forcibly.
- Don't inhale the vapours of any chemical deeply which might cause suffocation and choking; be alert and quick in perceiving the smell of the vapours, keeping the test tube in a slanting position.
- Don't keep inflammable solvents like petrol, ether, alcohol, etc. near a burner.
- Don't add pumice stones to a boiling liquid; add them before beginning to heat the liquid.
- Don't ever perform unauthorised experiments and never work alone in the laboratory.
- Don't touch electric switches with wet hands.

However, even if you are a careful worker and follow the general rules of safety, the accidents can occur—that's why they are called accidents. For such occasions, you must be fully equipped and must know what to do in such a case. There should be a first-aid box in every laboratory containing some common things like Dettol, Burnol, Band-aid, bandages, cotton, etc. Generally, the most common accidents that occur are cuts, burns, fires, poisoning and rarely, an explosion. Let us see one by one, what first aid should be given to a student, when such a mishap occurs.

Table 1.1 : List of hazardous chemicals and their effects

Hazardous Chemical	Effect
Salts of Ag, As, Ba, Cu, Hg, Ni, Pb, Sb, Tl, V, $C_2O_4^{2-}$, F^-, MnO_4^-	Most of these are very dangerous but only if swallowed, $AgNO_3$ causes caustic burns.
H_2S	Almost as poisonous as HCN. Exposure dulls the sense of smell.
SO_2, NO_2, Cl_2, Br_2, I_2, HNO_3, H_2SO_4, HF	All are dangerous as well as unpleasant. When concentrated, all cause rapid destruction of the skin; HF is especially dangerous.
$HClO_3$, $HClO_4$ and their salts	Highly oxidising.
Chlorinated alkanes, e.g., $CHCl_3$, CCl_4	Most of these are norcotic, causing mental confusion.
Benzene	Toxic vapours causing dizziness.
Benzoyl chloride	Irritant.
Ether, ethanol	Very highly inflammable.
Nitrobenzene	Toxic vapours.
Phenol	Burns the skin.

i) **Cuts :** The most common accidents in the chemistry lab are cuts from broken glassware. If you have a cut, wash the wound well with cold water immediately. If bleeding is severe, apply pressure directly on to the wound to stop the bleeding. Then an antiseptic cream can be applied to the wound with a proper dressing.

ii) **Burns :** Burns generally caused by hot equipment can be treated as the cuts are treated, that is, wash the burnt part with cold water for sometime and then apply Burnol to it.

Burns are very often caused by chemicals too. Table 1.1 gives you a list of hazardous chemicals and their effects.

iii) **Fire :** A small fire in a beaker, caused by the vapours of an inflammable liquid, can be extinguished by covering it with a watch glass.

If the clothes catch fire one should lie on the floor and fire can be smothered by wrapping a blanket around the body.

Poisoning : If one happens to swallow a poisonous chemical, plenty of water should be given if the person is conscious. For a corrosive poison, calcium hydroxide solution (lime water) should be given as soon as possible. An antidote should be given only in the case of non corrosive poisons.

v) **Explosion** : Sometimes a faulty technique during the experiment can lead to an explosion. 'You should work with highly oxidising or explosive chemicals only under strict supervision'

Table 1.2 gives the remedies for a few common chemical reagents used in the laboratory.

Table 1.2 : Remedies for a few chemical reagents

Chemical	Neutralising wash
Acids like HNO_3, H_2SO_4, HCl	$NaHCO_3$ or 2*M* ammonium carbonate (leaves no residue on clothes), then apply vaseline or a soothing cream.
Alkalies, e.g., NaOH, KOH etc.	1*M* acetic acid, then apply vaseline or a soothing cream.
Bromine	2*M* Ammonia, keep the affected part dipped in $NaHSO_3$ till bromine is washed off, then apply vaseline.
Phenol	Ethanol and then hospital treatment.
Sodium	Ethanol on a cotton wool pad.

1.10 ANSWERS TO SAQs

1. The pipette is calibrated to include the liquid column trapped at the tip. Further, blowing it makes it dirty and CO_2 in the breath may react with the solution being pipetted.

2. $(5 + 2 + 1)\ g + (200 + 100 + 50) \times 0.001\ g + 8 \times 0.001\ g + 2 \times .0002\ g.$
   $= 8\ g + .350\ g + .008\ g + .0004\ g$
   $= 8.3584\ g$

3. From Eq. 1.1, $M = \dfrac{1000\ m}{M_m.V}\ \text{mol dm}^{-3}$
   Where $M_m = 40\ \text{g mol}^{-1}$
   $m = 4.000\ \text{g}$
   $V = 500\ \text{cm}^3$
   Therefore,
   $M = \dfrac{1000 \times 4.000}{40 \times 500}\ \text{mol dm}^{-3}$
   $= 0.200\ \text{mol dm}^{-3}$
   Thus, molar concentration $= 0.200\ M$

4. Again consider Eq. 1.1,
   $M = \dfrac{1000\ m}{M_m V}\ \text{mol dm}^{-3}$
   Where $M_m = 169.87\ \text{g mol}^{-1}$
   $V = 1\ \text{dm}^3 = 1000\ \text{cm}^3$
   $M = 0.1\ M$
   On substituting these values in the above equation, we have
   $m = \dfrac{0.1 \times 169.87 \times 1000}{1000}$
   $= 16.987\ \text{g}$
   Thus, mass of $AgNO_3$ required for 0.1*M* solution = 16.987 g.

5. (a) i) NaOH is hygroscopic,
   ii) It is not available in pure form as it combines with CO_2 from the air and some part of it is converted into sodium carbonate.

   (b) Benzoic acid fits most of the criteria, but its solubility in water is low, although in non-aqueous solvents such as ethanoic acid (acetic acid) or ethanol it is not so.

6. i) ✓
   ii) ×
   iii) ×
   iv) ✓

UNIT 2 ACID-BASE TITRATIONS-I

Structure

2.1 INTRODUCTION

In Unit 1, we have discussed different types of quantitative analysis and also defined acid-base titration. In this unit and in the next unit we will present a fairly detailed description of acid-base titrations.

Acid-base titration is a quick and accurate method of determining acidic or basic substances in analytical samples. A standard solution of a strongly basic titrant, such as sodium hydroxide, is used to titrate acids. Bases are titrated with standard solution of hydrochloric acid or some other strongly acidic titrant. Most commonly, the end point of an acid-base titration is detected by observing the colour change of an indicator. However, for more accurate results, electrochemical methods, such as pHmetry and conductometry are used to locate the equivalence point.

In this unit, we shall first discuss the basic theory of acids and bases and the principle of acid-base titrations. After that you will be introduced to the actual experiments in which you will use the acid-base indicator method, pHmetry and conductometry to estimate acetic acid in vinegar solution.

Objectives

After reading this unit and performing the experiments you should be able to :

- define acids and bases,
- define K_w and derive equation for calculating the pH of an aqueous solution,
- derive equations useful in calculating dissociation constant of an acid (K_a) and a base (K_b),

- select and use primary standards for acid-base titrations correctly,
- select and use acid-base indicators for the acid-base titrations,
- estimate acetic acid in vinegar solution using an acid-base indicator,
- define potentiometry and describe the essential features and working of a pH meter,
- estimate acetic acid in vinegar solution using a pH meter,
- define conductometry and describe the essential features and working of a conductometer, and
- estimate acetic acid in vinegar solution using a conductometer.

2.2 THEORY OF ACIDS AND BASES

You may have studied about acids and bases in your previous classes. We are summarising the theory of acids and bases here to enable you to recall it. This will help you in understanding the basic principle of acid-base titrations.

2.2.1 Definition of Acids and Bases

There are three common definitions of acids and bases.

The first one is given by Arrhenius (1884). He defined an acid as any compound that releases protons, H^+, in water and a base as any compound that gives OH^- ions in water. This definition has several limitations. For example, this definition applies only to aqueous solutions.

According to the second definition proposed by Brönsted and Lowry (1923), an acid is a proton donor and a base is a proton acceptor. The main advantage of this definition over the earlier one is that the acid-base reactions are not limited just to the combination of H^+ and OH^- ions. Further, it applies both to aqueous and non-aqueous solutions.

The third definition was proposed by Lewis in 1938. He stated that an acid is a substance that can accept an electron pair and a base is one that can donate an electron pair. The significance of this definition is that the acid-base concept can be extended to many organic and inorganic reactions in which a proton is not involved.

Out of these definitions, we find Brönsted-Lowry definition the most suitable one for the purposes of explaining acid-base titrations. As said earlier, according to this definition, an acid is a proton donor and a base is a proton acceptor. An acid and a base react to give a conjugate base and a conjugate acid, respectively. This is illustrated by the reaction between acetic acid and water, here acting as a base, yielding acetate ion and hydronium ion. The acetate ion which can accept a proton, is the conjugate base of acetic acid. Similarly, hydronium ion, which can donate a proton, is the conjugate acid of water.

Conjugate acids and bases are related by the gain or loss of one proton.

$$\underbrace{\text{Acid}_1 + \text{Base}_2}_{\text{Conjugate pair}} \rightleftharpoons \underbrace{\text{Acid}_2 + \text{Base}_1}_{\text{Conjugate pair}}$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Water}}{H_2O} \rightleftharpoons \underset{\text{Hydronium ion}}{H_3O^+} + \underset{\text{Acetate ion}}{CH_3COO^-} \quad \ldots (2.1)$$

Such chemical equations involving conjugate acid and base pairs help us in defining ionic product of water and dissociation constants of acids and bases, which we will discuss in the following sections.

Before proceeding further, answer the following SAQs.

SAQ 1

Label the conjugate acid-base pair in the following reactions :

(a) $HI + H_2O \rightleftharpoons H_3O^+ + I^-$

(b) $CO_3^{2-} + H_2O \rightleftharpoons OH^- + HCO_3^-$

(c) $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

(d) $NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$

2.2.2 Ionisation of Water and the pH Concept

Water undergoes **autoionisation**, i.e., two molecules react giving hydronium and hydroxide ions; in this reaction one molecule acts as an acid, the other as a base, i.e.,

$$H_2O + H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad \ldots (2.2)$$

Many other solvents like NH_3 also undergo autoionisation.

$NH_3 + NH_3 \rightleftharpoons \underset{\text{Ammonium ion}}{NH_4^+} + \underset{\text{Amide ion}}{NH_2^-}$

This equilibrium is very important as it occurs in any aqueous solution, simultaneously with other reactions. We can write an equilibrium expression for Eq. 2.2 as,

$$K = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

where, K is the equilibrium constant and quantities written within square brackets denote equilibrium molar concentrations.

The molar concentration of water, which appears in the denominator of the above expression, is very nearly constant ($\simeq 55.6$ mol dm^{-3}) in both pure water and in dilute aqueous solutions. Therefore, $[H_2O]^2$ can be included with the equilibrium constant, K, on the left side of the equation. This gives,

$$K[H_2O]^2 = [H_3O^+][OH^-]$$

In place of the product of K and $[H_2O]^2$, we can use a new term K_w, thus,

$$K_w = K[H_2O]^2 = [H_3O^+][OH^-]$$

Table 2.1 : Temperature dependence of K_w

Temperature (K)	K_w (mol dm^{-3})
273	0.11×10^{-14}
298	0.01×10^{-14}
323	5.47×10^{-14}
373	51.3×10^{-14}

or $\boxed{K_w = [H_3O^+][OH^-]}$ ... (2.3)

Since $[H_3O^+][OH^-]$ is the product of ionic concentration, K_w is called the **ionic product** of water, or simply the **ionisation constant** or **dissociation constant** of water. At 298 K, $K_w = 1.0 \times 10^{-14}$, and this varies with temperature (see Table 2.1).

To simplify, we generally write H^+ for hydronium ion, therefore, the Eq. 2.2 and the expression for the ionisation of water becomes,

$$H_2O \rightleftharpoons H^+ + OH^- \quad \ldots (2.4)$$

$$K_w = [H^+][OH^-] \quad \ldots (2.5)$$

It is important to remember that in any aqueous solution, the relationship expressed in the above equation must always be satisfied, regardless of any other equilibria that may also exist in the solution.

You may recall the Arrhenius concept of acids and bases, according to which, acidic properties of a solution depend on H^+ ions, and basic properties on OH^- ions. Thus, the concentration of these ions should be equal in pure water and in all neutral aqueous solutions. Therefore,

$$[H^+] = [OH]^- = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

In an acid solution $[H^+] > [OH^-]$, i.e., $[H^+] > 10^{-7}$ and $[OH^-] < 10^{-7}$
In a basic solution $[OH^-] > [H^+]$, i.e., $[OH^-] > 10^{-7}$ and $[H^+] < 10^{-7}$

Suppose we prepare an acid solution by addition of an acid to water. In this solution, expectedly, the concentration of H^+ is higher and, therefore, the concentration of OH^- is correspondingly lower; thus Eq.2.5 is obeyed which means that the product of $[H^+]$ and $[OH^-]$ remains 1×10^{-14} mol dm^{-3}. In general if $[H^+]$ is greater than 10^{-7}, the solution is acidic, and if it is less than 10^{-7}, the solution is basic.

The relation $K_w = [H^+][OH^-]$ is important, since, if either one of $[H^+]$ or $[OH^-]$ is known, the other can be calculated.

The pH Concept

From the above you can see that it is quite cumbersome to express acidity or basicity in terms of hydrogen ion concentration or hydroxide ion concentration. These concentrations may range from relatively high values to very small ones, for example, 10 mol dm^{-3} to 10^{-14} mol dm^{-3}. A very convenient concept called, pH, was proposed by Sorensen (1909). He defined pH by the relationship,

$$\boxed{pH = \log_{10} \frac{1}{[H^+]} = -\log_{10}[H^+]} \quad (2.6)$$

In a solution where the hydrogen ion concentration is 10^{-3} mol dm^{-3}, we, therefore, have

$$pH = -\log(10^{-3}) = -(-3)$$
$$pH = 3$$

Following the same approach for the hydroxide ion concentration, we can define the pOH of a solution as

$$pOH = -\log[OH^-] \quad \ldots (2.7)$$

The notation pH was originally used for 'potential of hydrogen'. The 'p' notation can be applied to other quantities and always means "minus $\log_{10}$ of", for example :

$pK_a = -\log_{10}K_a$

$pK_b = -\log_{10}K_b$ and so on.

pH gives a convenient scale for expressing $[H^+]$ of a solution.

Just as the H^+ and OH^- ion concentrations in a solution are related to each other, so also are the pH and pOH. From the equilibrium expression for the dissociation of water,

$$\log K_w = \log[H^+] + \log[OH^-]$$

Multiplying by -1 gives

$$(-\log K_w) = (-\log[H^+]) + (-\log[OH^-])$$

If we follow our definition, $-\log K_w = pK_w$. Therefore,

$$pK_w = pH + pOH \quad \ldots (2.8)$$

Since $K_w = 1.0 \times 10^{-14}$, $pK_w = 14.00$. This gives the useful relationship,

$$\boxed{pH + pOH = 14.00}$$

In a neutral solution, $[H^+] = [OH^-] = 10^{-7}$ mol dm^{-3}, and pH = pOH = 7.0, so that in a neutral solution, we say, that the pH = 7.0. In an acidic solution the $[H^+]$ is greater than 10^{-7} mol dm^{-3} and the pH is less than 7.0. By the same token, in a basic solution, the $[H^+]$ is less than 10^{-7} mol dm^{-3} and pH is greater than 7.0. This is summarised below :

	$[H^+]$	$[OH^-]$	pH	pOH
Acidic Solution	$> 10^{-7}$	$< 10^{-7}$	< 7	> 7
Neutral Solution	10^{-7}	10^{-7}	7	7
Basic Solution	$< 10^{-7}$	$> 10^{-7}$	> 7	< 7

From the above discussion you can see that acidity or basicity of a solution can be expressed conveniently in terms of pH.

The measure of the acidity of an aqueous solution is the actual concentration of hydrogen ions in the solution.

The measure of basicity, on the other hand, is the actual concentration of hydroxide ions.

So far we have discussed the pH concept and ionic equilibrium of water. In the next section, we will discuss acid-base equilibria, which exist when a weak acid or a weak base is dissolved in water. In case of a weak acid or a weak base we cannot determine hydrogen ion concentration of the acidic solution, or hydroxide ion concentration for the basic solution using original analytical concentration as can be done in the case of strong acid or strong base. These concentrations are always less in aqueous solutions than the stoichiometric acid or base concentrations. The extent of the difference is determined by the degree of dissociation or ionisation of the weak acid or base and is represented by the respective dissociation constant or ionisation constant. Hence, the equilibrium constant expression must be used in any calculations dealing with weak acids and bases.

2.2.3 Dissociation of Weak Acids and Weak Bases

Acetic acid, CH_3COOH, is a typical example of a weak acid. In water it is only partially ionised and the molecules of the acid exist in equilibrium with the ions produced in the ionisation reaction :

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

The equilibrium expression for this reaction is

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

In dilute solution, the concentration of H_2O is not appreciably different from that in pure water, so we may safely take it to be a constant and include it with K. That is,

$$K \times [H_2O] = K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

where we have used K_a to represent the **acid dissociation constant** or **ionisation constant**. The same equilibrium expression can be obtained if we simplify the equation by omitting

the solvent. Thus, for the dissociation of acetic acid we can write,

$CH_3COOH \rightleftharpoons H^+ + CH_3COO$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad \ldots (2.9)$$

In general, for any weak acid, HA, the simplified equation for the dissociation reaction can be written as,

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

$$\boxed{K_a = \frac{[H^+][A^-]}{[HA]} \text{ mol dm}^{-3}} \quad \ldots (2.10)$$

Similarly for the base B, we have

$B + H_2O \rightleftharpoons BH^+ + OH^-$

and $K = \frac{[BH^+][OH^-]}{[H_2O][B]}$

Now, $K_b = K[H_2O]$

$$\boxed{K_b = \frac{[BH^+][OH^-]}{[B]} \text{ mol dm}^{-3}} \quad \ldots (2.11)$$

where K_b is the **base dissociation constant.**

Similar to the hydrogen ion concentration and pH, K_a, K_b and pK_a, pK_b values are also used to express relative strength of acids and bases. Examples of K_a, pK_a, K_b and pK_b values for aqueous solutions are given in Table 2.2. We observe from the values of K_a or K_b, that smaller the extent of ionisation the weaker is acid or the base. On the other hand, smaller the value of pK_a or pK_b, the stronger is the acid or base.

Table 2.2 : K_a, pK_a, K_b and pK_b values of some substances in aqueous solution (mainly at 298 K)

	K_a	pK_a
Phenol	1.0×10^{-10}	10.0
p-Aminobenzoic acid	1.2×10^{-5}	4.92
Acetic acid	1.8×10^{-5}	4.74
Benzoic acid	6.46×10^{-5}	4.19
Lactic acid (2-Hydroxypropanoic acid)	1.4×10^{-4}	3.85
Nitrous acid	4.6×10^{-4}	3.34 (285.5 K)
2, 2-Dichloroacetic acid	3.32×10^{-2}	1.48
	K_b	pK_b
Pyridine	1.48×10^{-9}	8.83
Ammonia solution (aqueous)	1.77×10^{-5}	4.75
Carbonate ion ($CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$)	2.1×10^{-4}	3.68

Using Eq. 2.10 and 2.11, we can calculate equilibrium constant if pH of a solution of a given concentration of an acid or a base is known. If K_a or K_b is known, pH or pOH can be calculated for the given concentration of the acid or base.

With this background we will discuss the theory of acid-base titrations in the next section.

SAQ 2

(a) A sample of rain water from Delhi was recently found to have a pH of 4

(i) Is this sample acidic or basic?

(ii) Determine the $[H^+]$ and $[OH^-]$ of the sample.

.....

.....

.....

(b) K_a values of some acids are given below. Rank these acids in terms of strength and also calculate their corresponding pK_a values.

HCOOH (1.8×10^{-4}), NH_4^+ (5.7×10^{-10})

HCN (4.9×10^{-10}) and CH_3COOH (1.8×10^{-5})

.....

.....

.....

2.3 THEORY OF ACID-BASE TITRATIONS

In acid-base titrations, as discussed earlier, a standard solution of an acid can be used for quantitative determination of bases (**acidimetry**), or a standard solution of a base can be used for quantitative determination of acids (**alkalimetry**). We generally use standard solution of a strong acid such as hydrochloric acid for acidimetry and that of a strong base such as sodium hydroxide for alkalimetry. But, these substances are not primary standards and, therefore, their standard solutions cannot be prepared from exact weights diluted to definite volumes; they must be standardised by titration. For standardising hydrochloric acid, we commonly use sodium carbonate and for standardising sodium hydroxide we use oxalic acid or potassium hydrogenphthalate. The preparation of standard solutions and the method of standardisation will be discussed in the experimental part.

In titrations by the acid-base method, the titrant should be a strong acid or a strong base as an accurate end point can not be detected by indicator method if both the titrant and the titrand are weak acid or weak bases, and *vice versa*.

In an acid-base titration, if a solution of an acid is titrated with a solution of a base, the OH^- ions of the latter combine with the H^+ ions of the acid.

$$H^+ + OH^- \longrightarrow H_2O$$

So, the concentration of the latter gradually decreases while the solution pH increases. At a certain definite pH value, the equivalence point is reached, i.e. the number of moles of OH^- added is just enough to react completely with all the H^+ ions originally present. On the other hand, when a base is titrated with an acid solution, the OH^- ions are removed by the H^+ ions and the concentration of the latter gradually increases while the solution pH decreases. At a certain definite pH value the equivalence point is reached.

The pH value at the equivalence point depends on the nature of the reacting substances, acid and base. For example, in case of a strong acid and a strong base, the reaction is completed at pH 7, therefore, equivalence point should be at pH 7. However, in the case of titration of a weak acid and a strong base, due to the hydrolysis of the salt formed on the addition of the base, equivalence point is observed at $pH > 7$, and not at pH 7. For example, in the titration of acetic acid (0.1 mol dm^{-3}) with sodium hydroxide (0.1 mol dm^{-3}), the equivalence point is at pH = 8.72. In the case of the titration of a strong acid with a weak base, e.g., hydrochloric acid with sodium carbonate, the equivalence point will be at pH lower than 7. Thus, we can say, in different cases, titration will end at different pH values, depending on the nature and concentration of the reacting acid and base. The exact pH of the solution at the equivalence point in such titrations may be calculated from the ionisation constant of the weak acid (K_a) or the weak base (K_b) and the concentration (c) of the salt which is formed during the acid-base titration, using the following equations:

In the case of strong acids and bases equivalence point does not depend on concentration. In the case of weak acids or bases the equivalence point depends on the concentration of the weak acid/base.

If we titrate 0.1 mol dm^{-3} acetic acid, a weak acid, with 0.1 mol dm^{-3} sodium hydroxide, a strong base, at equivalence point we will obtain 0.05 mol dm^{-3} sodium acetate. Equation 2.12 then yields the pH at the equivalence point

pH = 7.0 + 2.37 − 0.65 = 8.72

Weak acid and strong base

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pc \qquad \ldots (2.12)$$

Weak base and strong acid

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b + \frac{1}{2} pc \qquad \ldots (2.13)$$

Weak acid and weak base

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b \quad \text{... (2.14)}$$

Titration curves can also be used to find out the pH at the equivalence point. These will be discussed in sub-section 2.3.2.

When we choose an indicator for a titration we want that the indicator end point (when the colour changes) and the titration equivalence point to be as close as possible.

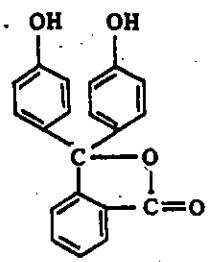
There are many methods available to detect equivalence point, experimentally, during titration. The most common method is the use of acid-base indicators. Indicators are organic dyes which change colour at or near the equivalence point to indicate the end of the reaction. In fact, the point at which indicator shows colour change is known as the **end point** of the titration. Of course, we choose the indicator to have the end point and the equivalence point as close as possible. But if we choose a wrong indicator and stop titrating when that indicator changes colour, we make a **titration error**. If V_{end} is the volume of titrant added at the end point, and V_{eq} is the volume required to reach the equivalence point, then by definition,

$$\frac{V_{end} - V_{eq}}{V_{eq}} \times 100 = \text{percent titration error}$$

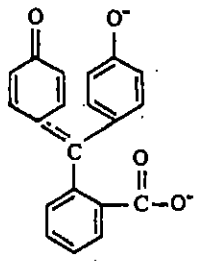
Other methods to detect equivalence point are pHmetry or potentiometry and conductometry. These methods will be discussed in detail along with Experiments 2 and 3. Now we will discuss the theory of acid-base indicator.

2.3.1 Acid-Base Indicators

As we have said already, acid-base indicators are organic dyes which change colour as pH changes. This is because the indicator has two forms, one in acidic and the other in basic medium. For example, phenolphthalein in acidic solutions exists in form (I) which is colourless. In basic solutions, it exists in form (II) which is pink.

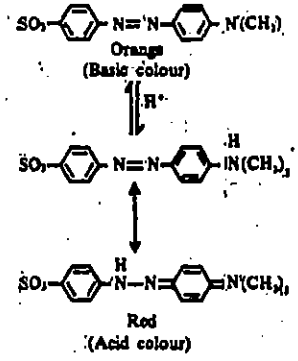


Colourless
(I)



Red
(II)

Phenolphthalein is an example of the weak acid type, whereas, as shown below, methyl orange of the weak base type of an indicator.



pH range 3.1 to 4.4

Acid-base indicators are weak acids or weak bases, therefore, in titrating an acid or a base, the indicator acts as a second acid or a second base. For example, in titrating an acid with sodium hydroxide, the indicator (the second acid) is weaker than the main acid and titrates after it. The indicator should have a very low concentration, otherwise, it will affect equivalence point by increasing or decreasing the pH of the solution.

In general we have two possible indicator reactions :

$$HIn \rightleftharpoons H^+ + In^- \quad (2.15)$$

Acid colour Basic colour
(weak acid)

$$In^- + H_2O \rightleftharpoons InH^+ + OH^- \quad (2.16)$$

Basic colour Acid colour
(weak base)

Concentration and the degree of ionisation are the two main factors which determine the colour of the indicators. Equilibrium expressions for Eq. 2.15 and 2.16 are,

$$K_a = \frac{[H^+][In^-]}{[HIn]} \quad (2.17)$$

and $K_b = \dfrac{[InH^+][OH^-]}{[In]}$ (2.18)

Experimental observations have shown that to see the colour of one form over the other, the concentration of the first should be 10 times the second. Thus, to see the colour of the acidic from , $[In^-]/[H\,In]$ must be 1/10 and to see the basic colour $[In^-]/[H\,In]$ must be 10/1. The contrast between the two colours is also important, but in general, the ten fold relationship will apply.

If these two concentration ratios are substituted into the equilibrium expression for the indicator (Eq. 2.17), the dependence of colour change of the indicator on hydrogen ion concentration, is demonstrated. For the acid colour, the expression simplifies to

$$\frac{[H^+]1}{10} = K_a,\ [H^+] = 10\,K_a \text{ and } pH = pK_a - 1$$

and for the basic colour

$$\frac{[H^+]10}{1} = K_a,\ [H^+] = \frac{K_a}{10} \text{ and } pH = pK_a + 1$$

The difference in pH between the acidic and the basic form of indicator transition is

$$pH_{basic} - pH_{acidic} = (pK_a + 1) - (pK_a - 1) = 2$$

We see, therefore, that the change of concentration ratio from 1 : 10 to 10 : 1 corresponds to colour change of the indicator over a 2 unit change of pH, i.e. a hundred-fold change in $[H^+]$. In general, pH range at which indicator shows colour changes is given by the equation,

$$pH \text{ range} = pK_a \pm 1$$

The pH range is termed as the colour-change interval of the indicator. The position of the colour-change interval in the pH scale varies widely with different indicators. For most acid-base titrations, we can, therefore, select an indicator which exhibits a distinct colour change at a pH close to that obtained at the equivalence point. Table 2.2, summarises the details of some useful acid-base indicators and also pH range in which the indicator will appear to change from one colour to the other.

Table 2.3 : Colour changes and pH ranges of acid-base indicators

Indicator	Acid colour	pH Range	Basic colour
Cresol red	red	0.2 — 1.8	yellow
Thymol blue	red	1.2 — 2.8	yellow
Bromophenol blue	yellow	3.0 — 4.6	blue
Methyl orange	red	3.1 — 4.4	orange/yellow
Methyl red	red	4.2 — 6.3	yellow
Bromothymol blue	yellow	6.0 — 7.6	blue
Phenol red	yellow	6.8 — 8.4	red
Thymol blue	yellow	8.0 — 9.6	blue
Phenolphthalein	colourless	8.3 — 10.0	red/pink
Thymolphthalein	colourless	9.3 — 10.5	blue

To select an indicator for an acid-base titration, it is necessary to know the pH of the equivalence point before using Table 2.2. The equivalence point pH may be calculated using Eq. 2.12, 2.13 or 2.14. Alternatively, an experimentally determined titration-curve may be used, which we will discuss in the next sub-section.

2.3.2 Acid-Base Titration Curves

If the pH of the titrand is monitored during a titration, a graph of pH against the amount of titrant added can be plotted. The curve so obtained is called the **acid-base titration curve** or **neutralisation curve**. The characteristics of this curve are important in equivalence point detection and in the selection of suitable titration conditions and indicators. For the purpose

of illustration, let us first consider titration of a strong acid with a strong base. For example, we titrate 100 cm^3 of 1*M* hydrochloric acid with 1*M* sodium hydroxide. During titration sodium hydroxide is added in small portions, pH changes with each addition. The pH at various stages during titration is determined by a pH meter or by the calculations. Table 2.4

Table 2.4 : Titration of 100 cm^3 of 1*M* HCl with 1*M* NaOH

NaOH added (cm^3)	pH	NaOH added (cm^3)	pH
0	0.0	100.1	10.7
50	0.5	100.2	11.0
75	0.8	100.5	11.4
90	1.3	101	11.7
98	2.0	102	12.0
99	2.3	110	12.7
99.5	2.6	125	13.0
99.8	3.0	150	13.3
99.9	3.3	200	13.5
100.0	7.0		

gives the pH of the solution with addition of different volumes of sodium hydroxide; the data is presented graphically in Fig. 2.1. The significant feature of this curve is the very sharp and sudden change in pH near the equivalence point. This is where the stoichiometric balance of the reaction is reached. As you can see in this curve, the equivalence point in this case is at pH 7.

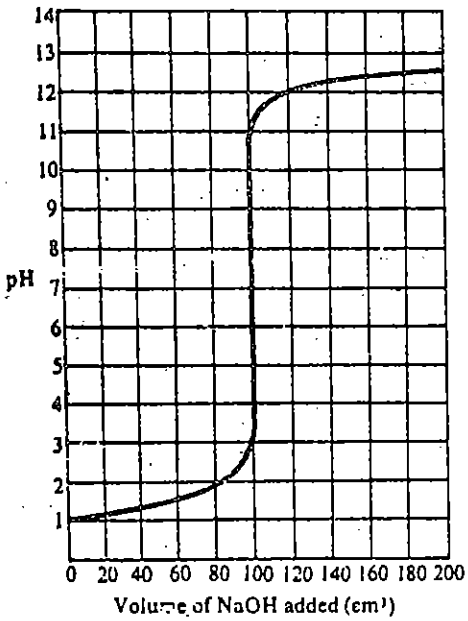


Fig. 2.1 : Strong acid-strong base titration curve

The influence of concentration is shown in Fig. 2.2. Curves I, II and III are for the titration of 1*M*, 0.1*M*, .01*M* concentrations of hydrochloric acid with 1*M*, 0.1*M* and 0.01*M* sodium

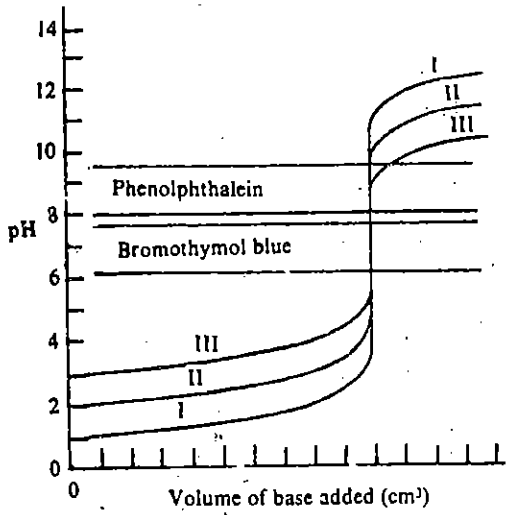


Fig. 2.2 : Titration curves for strong acid against strong base at three different concentrations

hydroxide, respectively. You can see that the equivalence point in all three cases is still at pH 7, though there is a less marked change in pH before and after the equivalence point as the solution becomes dilute. The change in pH at the equivalence point is about 8 pH units in I, down to about 4 pH units in III, with ranges of pH change 3-11 and 5-9, respectively. When we look at our indicator ranges we find that methyl orange, methyl red, bromothymol blue, and phenolphthalein all fit comfortably for curve I, whereas the choice of indicator is more restricted for curve III and bromothymol blue alone would do.

We now turn to titration of weak acids with strong bases. Suppose that 100 cm^3 of 0.1*M* acetic acid solution is titrated with 0.1*M* sodium hydroxide solution. The results obtained, in this case, are summarisd in Table 2.5 and are depicted graphically in Fig. 2.3.

Table 2.5 : Titration of 100 cm^3 of 0.1*M* acetic acid with 0.1*M* sodium hydroxide

NaOH added (cm^3)	pH	NaOH added (cm^3)	pH
0	2.9	99.9	7.7
10	3.8	100.0	8.7
25	4.3	100.2	10.0
50	4.7	100.5	10.4
90	5.7	101	11.7
99.0	6.7	125	12.0
99.5	7.0	150	12.3
99.8	7.7	200	12.5

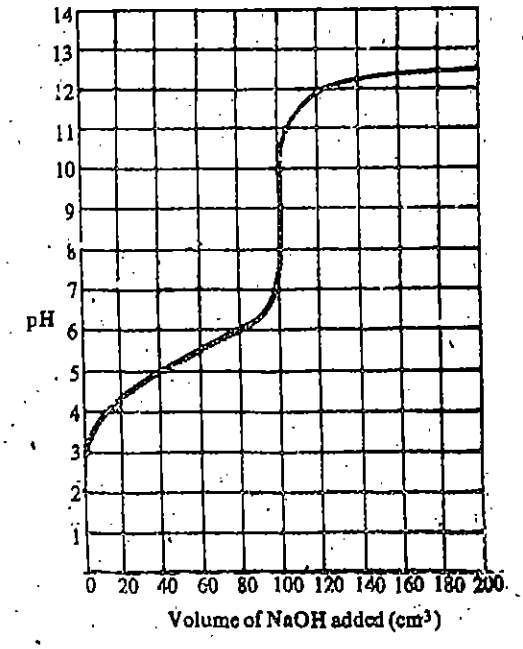


Fig. 2.3 : Titration curve for a weak acid with a strong base

The equivalence point in this case is at pH 8.7, and it is necessary to use an indicator with a pH range on the slightly alkaline side, such as phenolphthalein (pH range, 8.3-10).

As you know a solution containing a substantial amount of both a weak acid and its conjugate weak base, resistant to pH change on a slight addition of an acid or a base, is a buffer solution. Notice (Table 2.5) that during the addition of 25 cm^3 to 90 cm^3 of NaOH, the solution contains substantial amounts of both undissociated acetic acid (weak acid) and acetate ion (conjugate weak base). The solution, therefore, gets buffered in this region of the curve as shown in Fig. 2.3. The pH does not change very much as the volume of base added increases from 25 cm^3 to 90 cm^3.

The slowly rising flattered regi... before the equivalence point is c... led the buffer region.

The influence of the strength of the acid or base, i.e., K_a or K_b on the pH change near the equivalence point is summarised in Figs. 2.4 and 2.5, respectively.

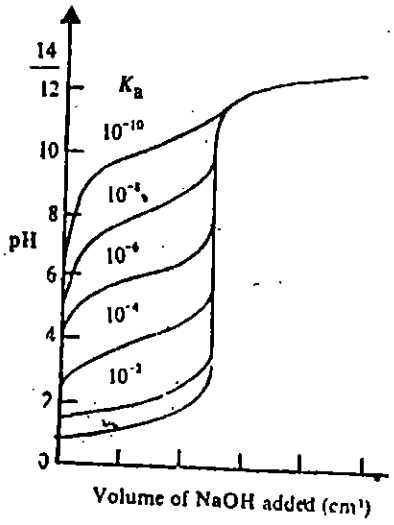


Fig. 2.4 : The effect of K_a on the titration curves for weak acid with a strong base

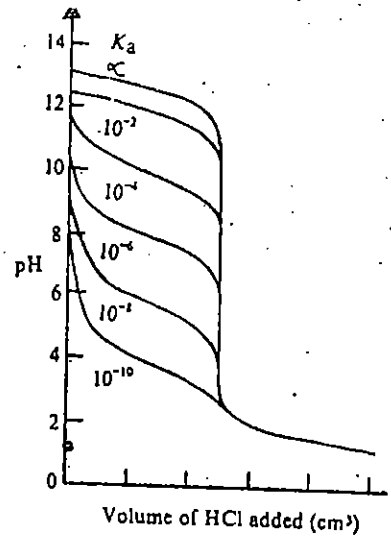


Fig. 2.5 : The effect of K_b on the titration curves for weak bases with a strong acid

From the above we can conclude that different shapes of titration curves are obtained for different concentrations and strengths of acids or bases. Shape of the curve tells us about the position of the equivalence point and helps in the choice of acid-base indicator.

In the next part we shall try to put together the theoretical knowledge gained on acid-base titration and the practical aspects. This would enable you to understand acid-base titrations more clearly.

SAQ 3

For the titration curve given in Fig. 2.6, choose the most appropriate indicator.

Indicator	pH Range
(a) Methyl orange	3.1 — 4.4
(b) Bromothymol blue	6.0 — 7.6
(c) Phenolphthalein	8.3 — 10.0

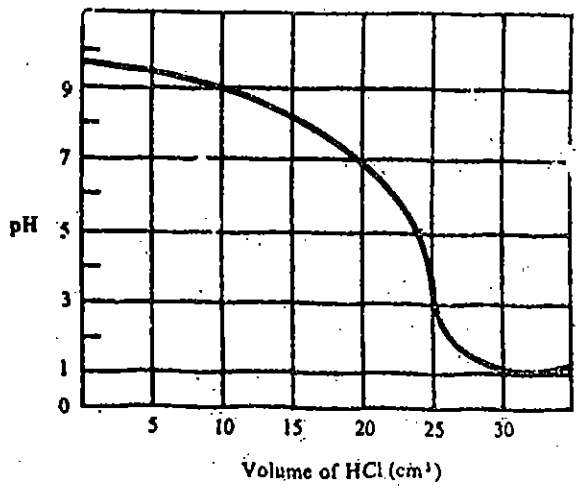


Fig. 2.6 : Acid-base titration curve; pH against volume of HCl

SAQ 4

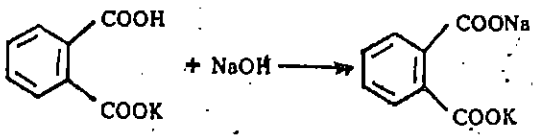
Indicate the buffer region in the titration curve given in Fig 2.3.

2.4 EXPERIMENT 1 : ESTIMATION OF ACETIC ACID IN VINEGAR BY ACID-BASE INDICATOR METHOD

Acetic acid is a weak acid having a K_a of 1.8×10^{-5}. It is widely used in industrial chemistry as glacial acetic acid. In the food industry it is used as vinegar, a dilute solution of glacial acetic acid. Vinegar usually contains 4-5 per cent acetic acid. Let us first understand the principle on which this experiment is based.

2.4.1 Principle

In this experiment we are titrating vinegar, a weak acid, with a standard solution of a strong base, sodium hydroxide. Sodium hydroxide is not a primary standard, therefore, before using it for the estimation of acetic acid, it should be standardised with a suitable primary standard such as potassium hydrogen phthalate or oxalic acid. The reaction between potassium hydrogen phthalate and NaOH is



... (2.19)

From Eq. 2.19, we can see that potassium hydrogen phthalate and sodium hydroxide react in the ratio 1 : 1 and hence, substituting the values of p and q in Eq. 1.8,

$$\frac{M_1V_1}{M_2V_2} = \frac{1}{2}, \text{ i.e., } M_1V_1 = M_2V_2 \qquad \text{... (2.20)}$$

where M_1 = Molarity of potassium hydrogen phthalate, M_2 = Molarity of sodium hydroxide, V_1 = Volume of potassium hydrogen phthalate, V_2 = Volume of sodium hydroxide.

In this titration phenolphthalein is used as indicator.

According to the theory of acid-base titrations discussed earlier, the end point in the titration of vinegar with sodium hydroxide will be observed between pH 8 and 10, therefore, here also phenolphthalein is a suitable indicator.

The stoichiometry of the titration is given by,

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O \qquad \text{... (2.21)}$$

From Eq. 2.21, we can see that one mole of acetic acid reacts with one mole of sodium hydroxide. Therefore, substituting the values of p and q in Eq. 1.8, the molarities are related as per the following equation;

$$\frac{M_3V_3}{M_4V_4} = \frac{1}{1}, \text{ i.e., } M_4V_4 = M_3V_3 \qquad \text{... (2.22)}$$

where M_3 = Molarity of sodium hydroxide, M_4 = Molarity of acetic acid (vinegar), V_3 = Volume of sodium hydroxide, V_4 = Volume of acetic acid (vinegar).

2.4.2 Requirements

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 1
Weighing bottle – 1

Chemicals

Vinegar
Potassium hydrogen phthalate

Volumetric flask (100 cm^3) – 1
Volumetric flask (250 cm^3) – 1
Funnel-1
Burette stand with clamp-1

Solutions provided

Indicator solution : Prepared by dissolving 0.4 g of phenolphthalein in 500 cm^3 of ethanol with addition of 500 cm^3 of water by constantly stirring and filtering if there is any precipitate.

0.1 *M* Sodium Hydroxide solution : Prepared by dissolving 4 g NaOH in 1 dm^3 of distilled water.

2.4.3 Procedure

i) **Preparation of standard potassium hydrogen phthalate solution** : Take already dried potassium hydrogen phthalate from the counsellor. Carefully weigh the weighing bottle with about 5.4 g potassium hydrogen phthalate. Transfer this sample to a 250 cm^3 volumetric flask through a glass funnel. Weigh the weighing bottle again and find the exact mass of potassium hydrogen phthalate transferred, by difference. Dissolve it in 40-50 cm^3 of distilled water, make the solution up to the mark, and shake well to make it homogeneous.

ii) **Standardisation of sodium hydroxide solution** : First collect the solution of sodium hydroxide in a 250 cm^3 bottle from your counsellor. Rinse the burette and fill it up with this solution. Note the initial reading of the burette and record it in the observation Table I under the 'initial reading' column. Pipette out 20 cm^3 of standard potassium hydrogen phthalate solution into a 250 cm^3 conical flask. Add one or two drops of phenolphthalein indicator. Titrate this solution by slowly adding small amounts of sodium hydroxide solution and continuously shaking the conical flask. Continue the titration until a permanent pink colour appears. This indicates the end point of the titration. Note the burette reading and record it in the observation Table I under the 'final reading' column. The difference of the two readings gives the volume of NaOH used.

Repeat the titration to get at least two concordant readings to ensure a correct and exact measurement.

iii) **Titration of vinegar solution with sodium hydroxide Solution** : Pipette out a 20 cm^3 aliquot of commercial vinegar carefully into a 100 cm^3 volumetric flask and dilute to the volume with distilled water. Transfer a 20 cm^3 aliquot from this solution into a 250 cm^3 conical flask by a pipette. Add approximately, 40 cm^3 of distilled water and two drops of phenolphthalein indicator. Take the initial reading of the burette and record it in the observation Table II. Titrate the above mixture carefully with the standardised sodium hydroxide solution until a faint pink colour of the indicator persists. Record the final reading in the observation Table II. Difference of the two readings gives the volume of NaOH required to titrate 20 cm^3 vinegar solution.

Repeat the titration to get at least two concordant readings. Do not throw the remaining NaOH solution. You will use it for Expt. 2 and Expt. 3.

2.4.4 Observations

Approximate mass of the weighing bottle = m_1 = ... g
Mass of the weighing bottle + potassium hydrogen phthalate = m_2 = ... g
Mass of the bottle after transferring the salt = m_3 = ... g
Mass of potassium hydrogen phthalate = $m_2 - m_3 = m$ = ... g
Molar mass (M_m) of potassium hydrogen phthalate = 204.2 g mol^{-1}
Volume of potassium hydrogen phthalate solution prepared = 250 cm^3
Molarity of potassium hydrogen phthalate (M_1),

$$M_1 = \frac{m \times 1000}{M_m \times 250} = \frac{m \times 4}{204.2} = \text{.....} \text{ mol dm}$$

Observation Table I
Potassium hydrogen phthalate vs. sodium hydroxide solution

Sl. No.	Volume of potassium hydrogen phthalate in cm^3	Burette Reading		Volume of NaOH in cm^3 (Final-initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Vinegar solution vs. sodium hydroxide solution

Sl. No.	Volume of vinegar solution in cm^3	Burette Reading		Volume of NaOH in cm^3 (Final-initial)
		Initial	Final	
1	20.			
2	20			
3	20			

2.4.5 Calculations

(a) Determination of the strength of sodium hydroxide solution

Molarity of potassium hydrogen phthalate = M_1 = ... mol dm^{-3}
Volume of potassium hydrogen phthalate solution = V_1 = 20 cm^3
Volume of NaOH solution used (from Table I) = V_2 = ... cm^3
Molarity of NaOH solution = M_2 = ?
Using Eq. 2.20,

$M_1V_1 = M_2V_2$

Molarity of NaOH solution = $M_2 = \frac{M_1V_1}{V_2}$

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

(b) Estimation of the strength of vinegar solution

Molarity of NaOH solution = $M_3 = M_2$ = ... mol dm^{-3}
Volume of NaOH solution used (from Table II) = V_3 = ... cm^3
Volume of vinegar solution = V_4 = 20 cm^3
Molarity of vinegar solution = M_4 = ?
Using Eq. 2.22,

$M_4V_4 = M_3V_3$

Molarity of vinegar solution = $M_4 = \frac{M_3V_3}{V_4}$ = ... mol dm^{-3}

Since 20 cm^3 of vinegar got diluted to 100 cm^3, the molarity of commercial vinegar sample

$= \frac{M_4 \times 100}{20} = 5M_4$ = ... mol dm^{-3}

Strength of commercial vinegar = $5M_4 \times$ Molar mass

= $5M_4 \times 60$ = ... g dm^{-3}

2.4.6 Result

Molarity of vinegar solution = ... mol dm^{-3}
Molarity of commercial vinegar = ... mol dm^{-3}
Strength of commercial vinegar = ... g dm^{-3}

Compare the calculated molarity and strength of the commercial vinegar with the correct values, which you can get from your counsellor.

2.5 EXPERIMENT 2 : ESTIMATION OF ACETIC ACID IN VINEGAR BY POTENTIOMETRY

In the previous experiment, we estimated acetic acid in vinegar using an acid-base indicator. We also observed that there were some conditions necessary for a satisfactory indicator

titration. We may summarise them as :

i) There has to be a region of sharp pH change with a small added volume of the titrant.

ii) The pH range of indicator has to lie within this pH change.

iii) The indicator volume should be minimal.

iv) The colour should be clear and sharp.

v) The sample should be colourless.

vi) The sample must not be too dilute.

From this you can infer that coloured solutions, very dilute solutions of weak acids and weak bases cannot be titrated accurately using acid-base indicators. To overcome most of these problems we use potentiometric titrations. In the next section we will give you a brief description of the principle of potentiometry.

2.5.1 Principle

In a potentiometric titration, the equivalence point is detected by measuring the potential change during the titration. Fig. 2.7 shows the usual apparatus for a potentiometric titration.

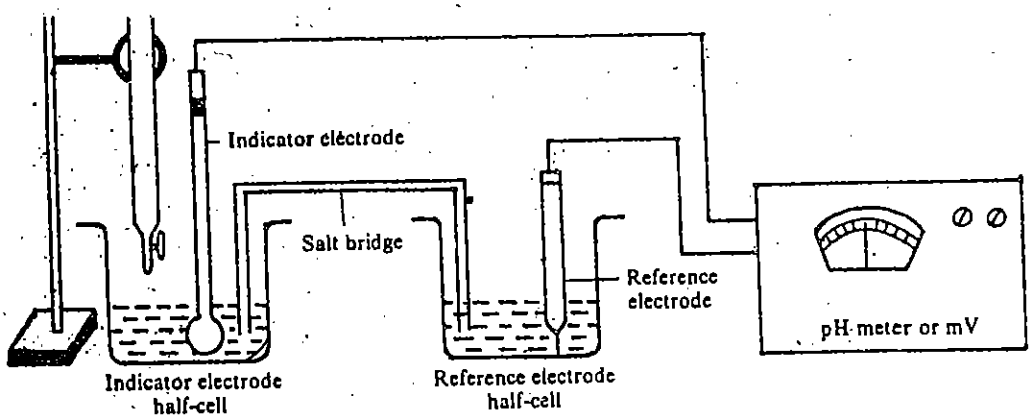


Fig. 2.7 : Apparatus for potentiometric titration.

Half-cell reactions : Oxidation or reduction reaction occurring at an electrode.

Electric potential (E) is measured in volts (V). The smaller unit of potential is millivolt (mV).
$1mV = 10^{-3}V$

The potential between the reference electrode half-cell (whose potential is known) and the indicator electrode half-cell (whose potential varies with concentration of the solution) is measured at the start and after the addition of small amounts of titrant, say each cm^3, and more closely near the equivalence point, when readings start to change by larger values. After each addition the solution is stirred well and the reading is allowed to become steady.

For detecting the equivalence point in a potentiometric titration, a graph is plotted between the potential and the volume of the titrant to give a titration curve such as shown in Fig. 2.8 (a).

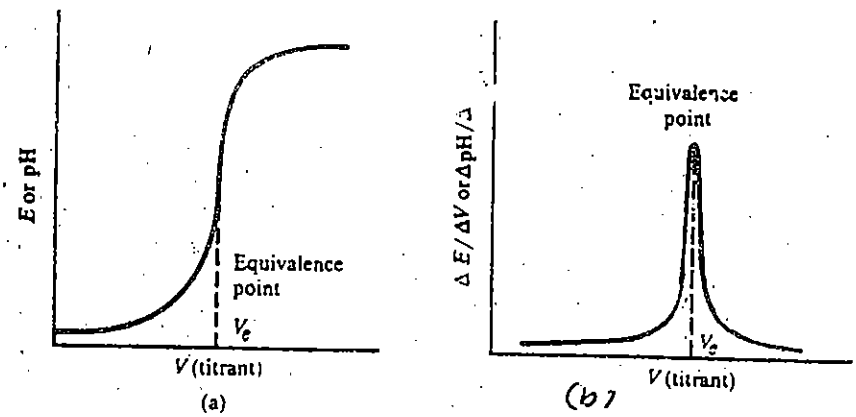


Fig. 2.8 : Methods of equivalence point determination (a) Normal plot (b) first derivative

Once the titration curve is at hand, we must determine where the curve is steepest, normally by some sort of inspection. We may draw a vertical line through the steep portion of the curve and find the intersection of this line with the volume axis. To overcome the

uncertainty in this procedure, we plot another graph as shown in Fig. 2.6 (b). This is a plot of the slope of a titration curve, that is, the change in potential with change in volume ($\Delta E/\Delta V$) against volume of the titrant. The resulting curve rises to a maximum height at the equivalence point. The volume at the equivalence point (V_e) is determined by drawing a vertical line from the peak to the volume axis.

Now, the question arises as to why there are potential changes during a titration. At a given temperature, let us say 298 K, the potential at the electrodes of a cell depends upon two factors :

i) Nature of the reaction of the solution in which electrodes are dipped.

ii) Concentration of the species taking part in the reaction.

While the first factor, specific for a particular reaction, is reflected in the reduction potentials of different substances, the second factor is responsible for the potential change during a titration. To understand the effect of concentration on potential, we have to consider **Nernst equation.** For a general redox reaction,

$$aA + bB \longrightarrow cC + dD$$

At 298 K, Nernst equation has the form,

$$E = E^\circ - \frac{0.0591}{n} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

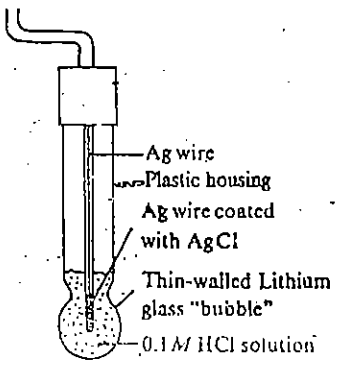
In the above equation, E is the electrode potential at a given concentration, E° is the standard electrode potential, i.e., at 1M concentration for a solution or 1 atm. for a gas, n is the number of moles of electrons transferred in the reaction and A, B, C and D are the species whose concentration is being varied. The small letters, a, b, c and d refer to coefficients in the balanced equation.

An important application of the Nernst equation is its use in determining the concentration of hydrogen ions or pH from the experimentally measured voltage of a carefully designed cell. In the potentiometric determination of pH, first a cell is assembled in which the indicator electrode is reversible to hydrogen ions and dips in the solution whose pH is to be determined, while the reference electrode is usually the calomel electrode whose potential is known. Junction between the two is made either through a salt bridge or by immersing the reference electrode directly into the solution. By measuring the voltage of the cell formed by the reference electrode and the indicator electrode, pH is calculated using the Nernst equation.

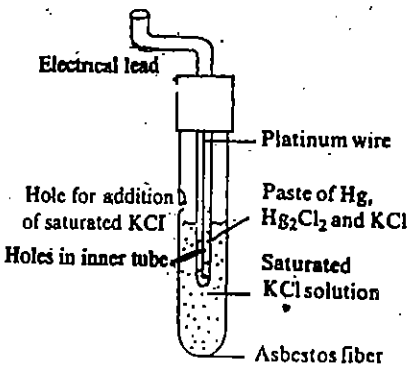
There are several electrode systems available for potentiometric pH determination. We are listing some of them in Table 2.6.

Table 2.6 : Electrode systems for hydrogen ion or pH measurement

Indicator electrode	Reference electrode
Hydrogen	Calomel/silver—silver chloride
Antimony	—do—
Quinhydrone	—do—
Glass	—do—



Glass electrode



Calomel electrode

In glass electrode, the inner and the outer glass surfaces are bound to generate different potentials. We get a junction potential which is asymmetric and depends on the type of glass, age and usage of the electrode.

Quinhydrone is a 1 : 1 mixture of p-quinone and hydroquinone.

For the glass electrode, the Nernst equation has the following form :
$E = k + 0.0591$ pH, or
$E = k - 0.0591 \log [H^+]$
where k is the asymmetry junction potential, approximately a constant factor for an individual glass electrode.

For the quinhydrone electrode, Nernst equation has the following form :
$E = 0.700 + 0.0591 \log [H^+]$
or $E = 0.700 - 0.0591$ pH

From these equations it would be possible to record the actual pH by calibration. In a pH meter, the meter is directly calibrated in pH units. In everyday use we check the instrument against buffer solution of known pH, and adjustments are made for errors.

For detecting the equivalence point in a pH metric titration, graphs similar to Fig. 2.8(a) and (b) are plotted.

So far we have discussed the basic principle of potentiometry and pH meter. Now, we will consider the basic features and the operational parts of a pHmeter.

Before that, try to answer the following SAQ.

SAQ 5
Give two advantages of potentiometric method of titration.

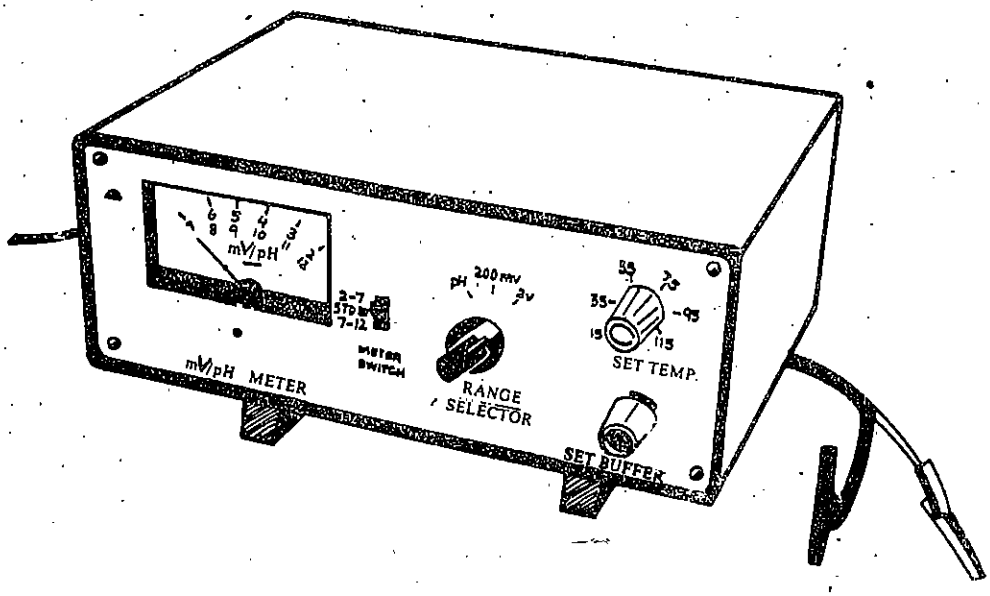
.....

.....

.....

2.5.2 pH Meter

The pH meter on which you are going to perform your experiment is shown in Fig. 2.9.



Description of Controls

Power Switch : This is located on the back panel of the instrument, which turns the instrument OFF/ON. If the instrument is plugged to a 220 V AC supply, the light emitting diode (LED) on the front panel will glow when the switch is in ON position.

Range Selector : This switch may be put on three positions marked pH, 200 mV and 2V. The selector brings into the circuit either the pH scale or 200 mV scale or 2V scale.

Meter Switch : This is a sliding switch with three positions. The middle position serves as a standby position. For pH measurement, the switch chooses the appropriate range (7 – 2 or 7 – 12).

Set Temperature : It is used to set the temperature of pH meter according to that of the solution.

Set Zero : For voltage measurement, this knob is used to null the meter reading. During pH measurement, this control should be used to set the meter at the pH of the solution in the indicator cell.

Set Slope : There are two such knobs on the back panel. The lower knob comes into the circuit for voltage measurement, i.e., when the selector is on 200 mV or 2V, while the upper knob becomes operational when the selector is on the pH mode. The use of these knobs is described under the operating procedure.

Cell Connection : There are two arrangements for connecting a voltage/pH source to the instrument. In one arrangement, two lead wires with black and red crocodile clips are provided for cells having carbon electrodes. For pH measurement, the black clip should be connected to the reference half-cell and the red clip to the indicator half-cell. In the other arrangement, a socket is fitted on the back panel for plugging a commercial glass electrode and a terminal is provided nearby for connecting a reference electrode, e.g., a calomel electrode.

Before using the pH meter it is necessary to calibrate it. We are discussing here only calibration for pH measurement. Calibration for potential (E) measurement can be read from the instruction manual of mV/pH meter.

2.5.3 Calibration of pH Meter for pH Measurement

Requirements

Apparatus	**Chemicals**
pH Meter with carbon electrodes	Quinhydrone
Beakers (100 cm^3) – 3	KCl (for salt bridge)

Solutions provided

Buffer solution of pH 4 : It is prepared by dissolving a buffer tablet of pH 4 in a 100 cm^3 volumetric flask diluting it up to the mark with distilled water or alternatively, it is prepared by dissolving 10.21 g of the potassium hydrogen phthalate in distilled water and diluting to 1 dm^3.

Buffer solution of pH 7 : It is prepared by dissolving a buffer tablet of pH 7 in a 100 cm^3 volumetric flask and diluting it up to the mark with distilled water or it may be prepared by dissolving 3.40 g of potassium dihydrogen phosphate (KH_2PO_4) and 3.55 g of disodium hydrogen phosphate (Na_2HPO_4) in distilled water and diluting to 1 dm^3.

Preparation of salt bridge : A suitable jelly is prepared by dissolving about 3 g of KCl and 0.3 g agar powder in 10 cm^3 of water. The contents are heated in a small beaker on a steam bath or water bath when a clean solution is obtained. It is sucked while hot into U tubes and is cooled under tap water. This mixture sets to a gel.

Salt bridge is a U-tube containing a high concentration of a salt, such as KCl, immobilised in gelatin. It connects the solution in the two beakers. Salt bridge serves to maintain electrical neutrality within the solution.

Procedure for Calibration of pH Meter

The procedure described below assumes that the reference half-cell and the indicator half-cell are both quinhydrone electrodes made from carbon rods and dipping into the solution to which quinhydrone has been added. This is undoubtedly the simplest and the cheapest method. However, the instrument can be used with any electrode system with a slight modification in the procedure. The various steps of the procedure in sequence are :

1. Take about 20 cm^3 of a buffer solution of pH 7.0 in two 100 cm^3 beakers.
2. Add sufficient quinhydrone in each of the beakers to saturate the two solutions.
3. Take an agar-agar salt bridge containing saturated KCl solution and place it in the two beakers. Alternatively, soak a 20 cm strip of folded filter paper in a saturated potassium chloride solution and use it as a salt bridge.
4. Insert a carbon electrode in each of the beakers. Stir the solutions for sometime. Connect the electrodes to the pH meter using the black crocodile clip for the reference half-cell and the red crocodile clip for the indicator half-cell.

5. Plug-in the instrument to 220 V, AC supply. Turn on the power switch on the back panel. The indicator LED should glow on the front panel.
6. Set the selector on the pH mode and the meter switch on 7 − 2 position.
7. Measure the temperature of the solution and rotate the Set Temperature Control to that temperature.
8. Use the Set Zero control to set the meter reading to 7.0.
9. Slide the meter switch to STD.BY position.

While using filter paper salt-bridge, ensure that it should not become dry.

10. Take out the indicator electrode and salt bridge from the beaker. Wash with distilled water. Replace the beaker by another 100 cm^3 beaker containing 20 cm^3 of pH 4.0 buffer solution. Add sufficient quinhydrone to saturate it. Stir the solution for sometime. Reinsert the carbon electrode in the solution and also put salt-bridge. If you are using filter paper as salf-bridge then replace it with a new one.
11. Set the meter switch-bridge to 7 − 2 position. The meter should read 4.0. If it does not, use the lower knob on the back panel to adjust it to 4.0.

In next part we will describe the experimental procedure for the estimation of acetic acid in vinegar.

2.5.4 Requirements

Apparatus
Burette (10 cm^3) − 1
Pipette (20 cm^3) − 1
Beaker (100 cm^3) − 2
Volumetric flask (100 cm^3) − 1
pH meter − 1
Carbon electrodes − 2
Burette stand with clamp − 1

Chemicals
Vinegar
Quinhydrone
Potassium chloride
(for making salt-bridge)

Solution provided

0.1 *M* **Sodium hydroxide solution** : You can use standardised sodium hydroxide solution of Experiment 1.

2.5.5 Procedure

1. Prepare vinegar solution by taking 3 cm^3 of vinegar in 100 cm^3 volumetric flask and dilute it with distilled water to the mark.
2. Calibrate the pH meter as mentioned earlier.
3. Pipette out 20 cm^3 of vinegar solution in a 100 cm^3 beaker. After calibration of the pH meter wash the indicator carbon electrode and salt bridge, then replace the buffer solution of pH 4 with vinegar solution. Insert the indicator electrode in this solution. Also, connect vinegar solution and buffer solution of pH 7 using a salt bridge. If you are using filter paper as salt bridge, use a new one after dipping it in a saturated solution of potassium chloride.
4. Slide the meter switch to 2-7 position. Read the pH of this solution and record it in observation Table I.

The concentration of the titrant is usually 5 to 10 times higher than that of the solution to be titrated. This is done so that the volume change is as small as possible.

5. Fill the 10 cm^3 burette with standardised sodium hydroxide solution (0.1 *M*), use the same solution which you have standardised for Experiment 1. Add NaOH from the burette in 0.1 cm^3 lots as given in observation Table I. After each addition stir the solution well and read the pH of the solution. Enter the pH values in observation Table I.
6. Plot pH vs. volume of NaOH on a graph sheet. Also plot $\Delta pH/\Delta V$ versus volume of NaOH.

2.5.6 Observations

Volume of vinegar solution taken $= V_2 = 20$ cm^3
Molarity of standardised NaOH solution (calculated from Experiment 1)
$= M_1$ ..... mol dm^{-3}

Observation Table I

Burette reading		Volume of NaOH (Final—initial) cm^3	pH	ΔV	ΔpH	$\frac{\Delta pH}{\Delta V}$
Initial	Final					
		0.0				
		0.1				
		0.2				
		0.3				
		0.4				
		0.5				
		0.6				
		0.7				
		0.8				
		0.9				
		1.0				
		1.1				
		1.2				
		1.3				
		1.4				
		1.5				
		1.6				
		1.7				
		1.8				
		1.9				
		2.0				
		2.1				
		2.2				
		2.3				
		2.4				

2.5.7 Calculations

Read the volume of NaOH required for the complete neutralisation of acetic acid in the vinegar solution from the graph. Let this volume be V_1. Calculate the molarity, M_2, of vinegar solution using the equation :

$M_1V_1 = M_2V_2$ (similar to Eq. 2.22)

$$M_2 = \frac{V_1 \times M_1}{V_2}$$

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

Since, 3 cm^3 of vinegar got diluted to 100 ml;
hence the molarity of commercial vinegar sample

$$= \frac{M_2 \times 100}{3}$$

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

$$\text{Strength of commercial vinegar} = \frac{M_2 \times 100}{3} \times \text{molar mass}$$

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

2.5.8 Result

The molarity of vinegar = ... mol dm^{-3}
The molarity of commercial vinegar solution = ... mol dm^{-3}
Strength of commercial vinegar = ... g dm^{-3}

Compare the above values of molarity and strength of the commercial vinegar with the correct values, which you can get from your counsellor.

2.6 EXPERIMENT 3 : ESTIMATION OF ACETIC ACID IN VINEGAR BY CONDUCTOMETRY

In the previous experiment we discussed potentiometry, which is one of the electrochemical methods for detection of the equivalence point. In this experiment we will discuss conductometry, another electrochemical method for detection of the equivalence point. In

this case, the rate of change of conductance as a function of added titrant is used to determine the equivalence point. Conductometric titrations are especially useful for very dilute solutions. Before going into the details of the experimental procedure, we would like to first discuss the basic principles of conductometry.

The reciprocal of resistance is termed as conductance. This is measured in reciprocal ohms (or Ω^{-1}), for which the term siemens (S) is used.

2.6.1 Principle

The electrical conductance of a solution is a measure of its current carrying capacity and is, therefore, determined by the total ionic strength and mobility of ions. In a conductometry titration, ionic species of interest are converted to non-ionic forms by neutralisation, as in acid-base titrations, precipitation titrations, etc. In conductometric titrations, we measure the conductance of an electrolyte solution using an AC source. An AC source of electric supply is used to prevent deposition of ionic species on the electrodes. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added. Look at the titration curve in Fig. 2.10 for a strong acid-strong base titration.

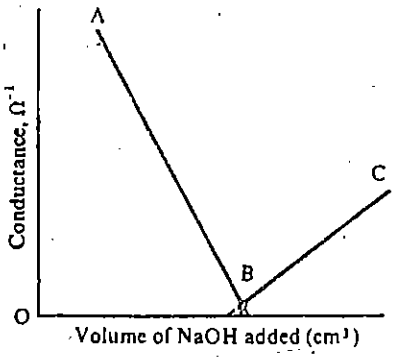


Fig. 2.10 : Conductometric titration curve for strong acid (HCl)—strong base (NaOH) titration

Molar conductivity is defined as the conductance of one meter cube of one molar concentration of a material. It has units $\Omega^{-1}\ m^2\ mol^{-1}$

In case of acid-base titration, H^+ and OH^- ions have very large molar conductivity. For this reason and because H_2O has a very low conductivity, acid-base titrations yield the most clearly defined equivalence points (see Fig. 2.10). To further illustrate, consider first the titration of a strong acid, like hydrochloric acid, with a strong base, like sodium hydroxide. In the initial stage, the conductance of hydrochloric acid is due to the presence of hydrogen and chloride ions. As alkali is added, gradually the hydrogen ions are replaced by slower moving sodium ions of low conductivity,

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + \underset{\text{(unionised)}}{H_2O}$$

Hence, on continued addition of sodium hydroxide, the conductance will go on decreasing, until the acid has been completely neutralised. After this point any subsequent addition of sodium hydroxide will result in introducing hydroxide ions of high conductivity. The conductance, therefore, after reaching a certain minimum value, will begin to increase. On plotting the conductance against the volume of alkali added on a graph paper, conductometric curve, similar to the one in Fig. 2.10, is obtained. In this figure, curve AB indicates decrease in conductivity and curve BC indicates increase in conductivity. The point of intersection, B, of these two curves indicates the equivalence point. A line drawn from 'B' to the axis indicating volume of NaOH (V_e) added to obtain equivalence point.

Now let us consider the case of our experiment, in which we are titrating acetic acid in vinegar with a strong base, sodium hydroxide. To begin with, the conductance of the solution will be low on account of the poor dissociation of the acid. On adding the base, highly ionised sodium acetate is formed and hence the conductance begins to increase.

$$\underset{\text{(poorly ionised)}}{CH_3COOH} + Na^+ + OH^- \longrightarrow \underset{\text{(ionised)}}{CH_3COO^-} + Na^+ + H_2O$$

When the acid is completely neutralised, further addition of the base introduces excess of hydroxide ions of high conductivity. The conductance of the solution, therefore, begins to increase even more sharply than before. On plotting a graph of the conductance against the volume of the base added, two curves are obtained and the point of their intersection gives the equivalence point (see Fig. 2.11).

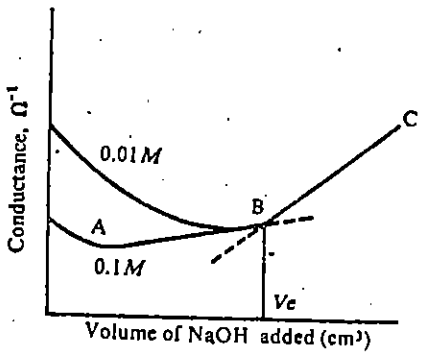


Fig. 2.11 : Titration of acetic aold against sodium hydroxide

Conductance of a solution is measured in millisiemens (mS) using a conductometer. Now, we will study the basic features of this instrument.

SAQ 6

Using Fig. 2.11, pick out the correct statements out of the following :

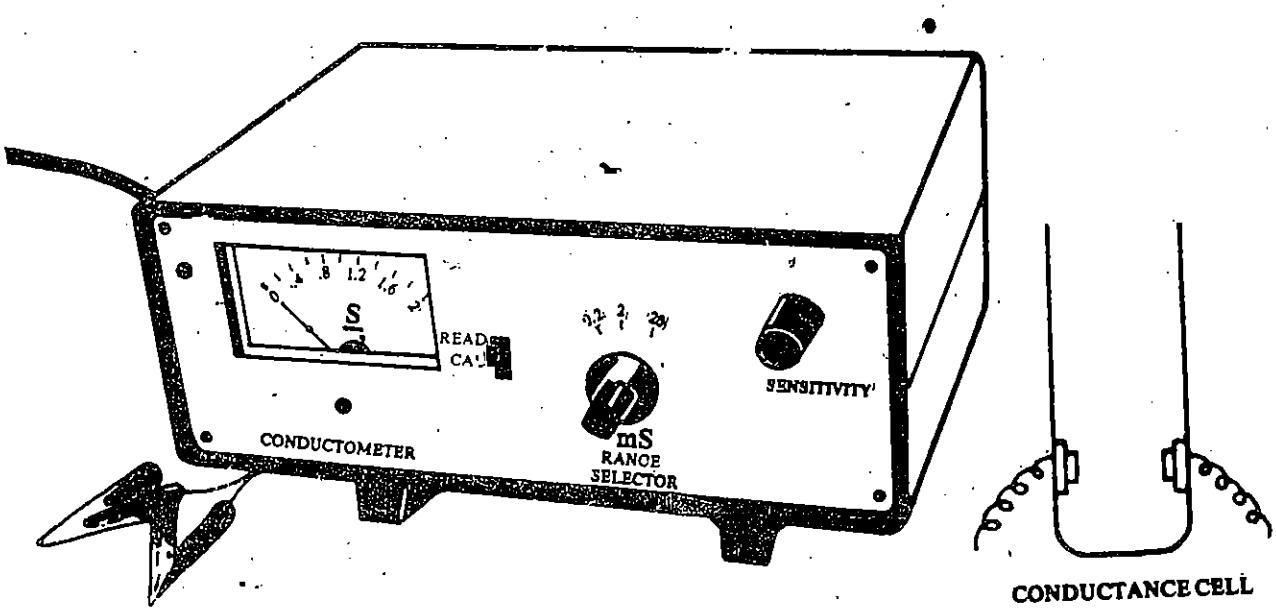
(a) Slope of curve AB depicts the increase of conductance due to the ionisation of sodium acetate formed.

(b) The increase of conductance shown by AB portion of the curve is due to the addition of hydroxide ions having high conductivity.

(c) The increase of conductance shown by BC portion of the curve is due to excess of hydroxide ions.

2.6.2 Conductometer

The conductometer, which you are going to use is shown in Fig. 2.12.



Description of Controls

Power Switch : This is located on the back panel of the instrument, which turns the instrument OFF/ON. When ON, the LED on the front panel will glow if the instrument is plugged to a 220 V, AC supply.

Range Selector : This is a rotational selector switch and it has three positions marked 0.2, 2 and 20 which refer to the full scale meter deflection in millisiemens (mS).

Mode Selector : This is a sliding selector switch used to set the instrument either in the calibrating mode or the read mode. The two positions are marked CAL and READ. In the CAL mode, the standard resistor, inside the instrument replaces the conductance cell.

Sensitivity : This knob is used to set the meter reading to the calibration mode.

2.6.3 Calibration of Conductometer

1. Plug in the instrument to the 220 V AC supply. Turn on the power switch on the back panel. The indicator LED should glow on the front panel.
2. Set the Mode Selector on CAL.
3. Set the Range Selector on the desired setting, i.e. 0.2, 2 or 20.
4. Set the meter reading to 1.0 with the help of the sensitivity knob.

When the range selector is switched to a new position, it is advisable to check the calibration again. Set the meter reading to 1.0 with the sensitivity knob, if any deviation is observed. In the next section we will describe the experimental procedure for the estimation of acetic acid in vinegar.

2.6.4 Requirements

Apparatus
Burette (10 cm^3) – 1
Pipette (20 cm^3) – 1
Conductometer – 1
Conductance Cell – 1
Glass Rod – 1
Burette stand with clamp – 1

Chemical
Vinegar

Solution provided

0.1 *M* **Sodium hydroxide solution** : You can use standardised sodium hydroxide solution of Experiment 1.

2.6.5 Procedure

1. Pipette out 20 cm^3 of vinegar solution (which you have already prepared for Experiment 2), in the conductance cell.
2. Take NaOH solution in the 10 cm^3 burette.
3. Connect the conductometer to the mains and to the conductance cell. Switch on the instrument keeping the meter switch at 'CAL'.
4. Calibrate the meter keeping the selector knob at '2*m*S' by rotating the 'sensitivity' knob till the meter reads 1.0.
5. Shift the meter switch to 'Read'. Read the conductance of the solution (keep the stirrer above the solution). Record this value in observation Table I.
6. Make additions of NaOH from the burette as given in observation Table I. After each addition, stir the solution well and read the conductance, keeping the stirrer above the solution. Enter all the conductance values in observation Table I.
7. Plot conductance versus volume of NaOH on a graph sheet.

2.6.6 Observations

Volume of vinegar solution taken = V_2 = 20 cm^3
Molarity of standardised NaOH solution (calculated from Experiment 1) = M_1
= ..... mol dm^{-3}

Observation Table I

Burette reading in cm^3		Volume of NaOH (Final – initial)	Conductance
Initial	Final		mS
		0.0	
		0.1	
		0.2	
		0.3	
		0.4	
		0.5	

		0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.4 2.6 2.8 3.0	

2.6.7 Calculations

Read the volume of NaOH required for the complete neutralisation of acetic acid in vinegar solution from the graph. Let this volume be V_1. We can calculate molarity of the vinegar solution, M_2, using the formula (Similar to Eq. 2.22).

$M_2 V_2 = M_1 V_1$

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

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

Since, we have diluted 3 cm^3 vinegar to 100 cm^3 solution. Hence, the molarity of commercial vinegar,

$$= \frac{M_2 \times 100}{3}$$

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

$$\text{Strength of commercial vinegar} = \frac{M_2 \times 100 \times \text{Molar mass}}{3}$$

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

2.6.8 Result

Molarity of the vinegar solution = ... mol dm^{-3}
Molarity of the commercial vinegar sample given = ... mol dm^{-3}
Strength of commercial vinegar = ... mol dm^{-3}

Compare the calculated molarity and strength of the commercial vinegar with correct values, which you can get from your counsellor.

In all the three experiments of this unit, you have titrated vinegar solution using three different titrimetric methods. Now put your results from all these experiments in the table given below :

	Experiment 1	Experiment 2	Experiment 3
Correct value of strength in g dm^{-3}			
Calculated strength in g dm^{-3}			

Give your comments in your practical note-book about the accuracy of the results, time factor and convenience of these experiments.

Based on what you have learnt, you can design experiments for analysis of some commercial products such as : estimation of citric acid in lemon juice, tartaric acid in wine, phosphoric acid in soft drinks, acetylsalicylic acid in aspirin, etc.

2.7 ANSWERS TO SAQs

1. a)

$$\underset{\text{Acid}_1}{HI} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{I^-}$$

conjugate pair: HI / I^-; conjugate pair: H_2O / H_3O^+

b)

$$\underset{\text{Acid}_1}{H_2O} + \underset{\text{Base}_2}{CO_3^{2-}} \rightleftharpoons \underset{\text{Acid}_2}{HCO_3^-} + \underset{\text{Base}_1}{OH^-}$$

conjugate pair: H_2O / OH^-; conjugate pair: CO_3^{2-} / HCO_3^-

c)

$$\underset{\text{Acid}_1}{CH_3COOH} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{CH_3COO^-}$$

conjugate pair: CH_3COOH / CH_3COO^-; conjugate pair: H_2O / H_3O^+

d)

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{NH_3} \rightleftharpoons \underset{\text{Acid}_2}{NH_4^+} + \underset{\text{Base}_1}{Cl^-}$$

conjugate pair: HCl / Cl^-; conjugate pair: NH_3 / NH_4^+

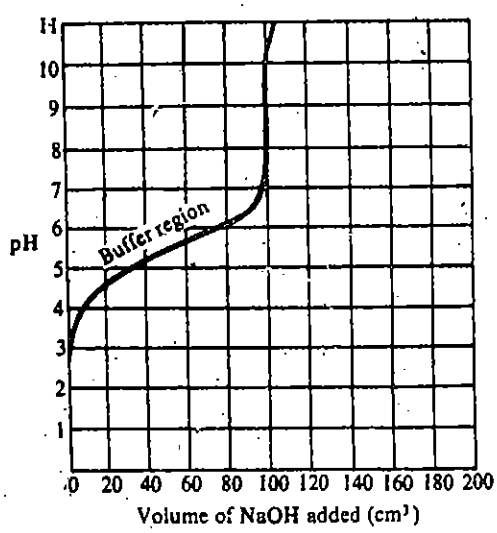
2. a) (i) Acidic (ii) $(H^+) = 1 \times 10^{-4}$ mol dm^{-3}, $(OH^-) = 1 \times 10^{-10}$ mol dm^{-3}

b) Increasing order of acid strength :
$HCN < NH_4^+ < CH_3COOH < HCOOH$

$$\begin{aligned} pK_a \text{ of HCOOH} &= -\log K_a \\ &= -\log 1.8 \times 10^{-4} \\ &= -(\log 1.8 + 10^{-4}) \\ &= -(0.2553 - 4) \\ &= 3.7 \end{aligned}$$

pK_a of HCN = 9.31, pK_a of NH_4^+ = 9.24, pK_a of CH_3COOH = 4.74.

3. Methyl orange
4. Buffer region in the titration curve of Fig. 2.3.



5. (i) Potentiometric titration gives very accurate results.
   (ii) Weak acid-weak base titration can be performed by potentiometry.
   (iii) Coloured solution can also be titrated for acid or base content.
6. a, c

UNIT 3 ACID-BASE TITRATIONS-II

Structure

3.1 INTRODUCTION

In Unit 2, we discussed the basic principle of acid-base titrations. Based on this, you performed three experiments for the analysis of acetic acid in vinegar using three different techniques. In this unit we are expanding acid-base titration method further for the analysis of a mixture of sodium carbonate and sodium hydroxide. This method of titration will help you in understanding the basic principle of some important industrial analyses such as that of soda ash, sodium bicarbonate, mixture of sodium carbonate—sodium bicarbonate, commercial caustic soda, washing soda, etc. The procedures, such as, conductometry, potentiometry or acid-base indicators can be used to analyse the above substances. Here we will discuss the acid-base indicator method only for the analysis of a mixture of sodium carbonate and sodium hydroxide.

Objectives

After performing this experiment you should be able to :

- state and explain the principle of acid-base titration with special reference to the titration of sodium carbonate and sodium hydroxide mixture,
- standardise the given solution of hydrochloric acid and use it in estimating basic solutions, and
- determine the strength of sodium carbonate and sodium hydroxide in a given solution.

3.2 EXPERIMENT 4 : DETERMINATION OF SODIUM CARBONATE AND SODIUM HYDROXIDE IN A MIXTURE BY INDICATOR METHOD

Titration of a mixture of sodium carbonate and sodium hydroxide is basically the same as the acid-base titration discussed in Unit 2, except that there will be more than one region in which the pH varies rapidly because such a titration has more than one equivalence point. Titration curve also shows more than one sharp pH breaks. First we will discuss the principle.

3.2.1 Principle

We observe two equivalence points in this titration. You may like to ask, why does a mixture of sodium carbonate and sodium hydroxide behave this way? To answer this question we should first study the behaviour of sodium carbonate solution and then the behaviour of a mixture of sodium carbonate and sodium hydroxide in acid-base titrations.

Sodium carbonate is a salt of a weak acid and a strong base; when such salts are dissolved in water, they behave as bases due to the basicity of the conjugate base CO_3^{2-} in this case. The equilibrium, which is often called hydrolysis, is given by the reaction:

$$\underset{\text{(carbonate ion)}}{CO_3^{2-}} + H_2O \rightleftharpoons \underset{\text{(bicarbonate ion)}}{HCO_3^-} + OH^- \quad \ldots (3.1)$$

The bicarbonate ion is further hydrolysed to carbonic acid :

$$HCO_3^- + H_2O \rightleftharpoons \underset{\text{(carbonic acid)}}{H_2CO_3} + OH^- \quad \text{... (3.2)}$$

The OH^- ions so produced in solution are responsible for the basic character of sodium carbonate.

When sodium carbonate is titrated with a strong acid, such as hydrochloric acid, the carbonate ions are first converted to the bicarbonate ions, and then to carbonic acid. This is due to the fact that a strong acid displaces a weak acid from the conjugate base of the latter.

$$\underset{(Na_2CO_3)}{CO_3^{2-}} + \underset{(HCl)}{H^+} \longrightarrow HCO_3^- \quad \text{... (3.3)}$$

$$HCO_3^- + \underset{(HCl)}{H^+} \longrightarrow H_2CO_3 \quad \text{... (3.4)}$$

Combining both the above equations we can write,

$$CO_3^{2-} + \underset{(HCl)}{2H^+} \longrightarrow H_2CO_3 \quad \text{... (3.5)}$$

From Eq. 3 5, we can see that $p = 1$ and $q = 2$, substituting these values in Eq. 1.8, we get

$$\frac{M_{Na_2CO_3}\, V_{Na_2CO_3}}{M_{HCl}\, V_{HCl}} = \frac{1}{2}$$

i e., $M_{HCl}\, V_{HCl} = 2M_{Na_2CO_3}\, V_{Na_2CO_3}$ ... (3.6)

Due to the neutralisation taking place in two steps as indicated by reactions in Eqs. 3.3 and 3.4, we observe two regions of sharp pH change in the titration curve (Fig. 3.1) and thus two equivalence points. Here up to the first equivalence point CO_3^{2-} is neutralised to HCO_3^- stage; and up to the second equivalence point HCO_3^- is neutralised to H_2CO_3 stage. In this experiment we will utilise this behaviour of sodium carbonate in the estimation of a mixture of sodium carbonate and sodium hydroxide.

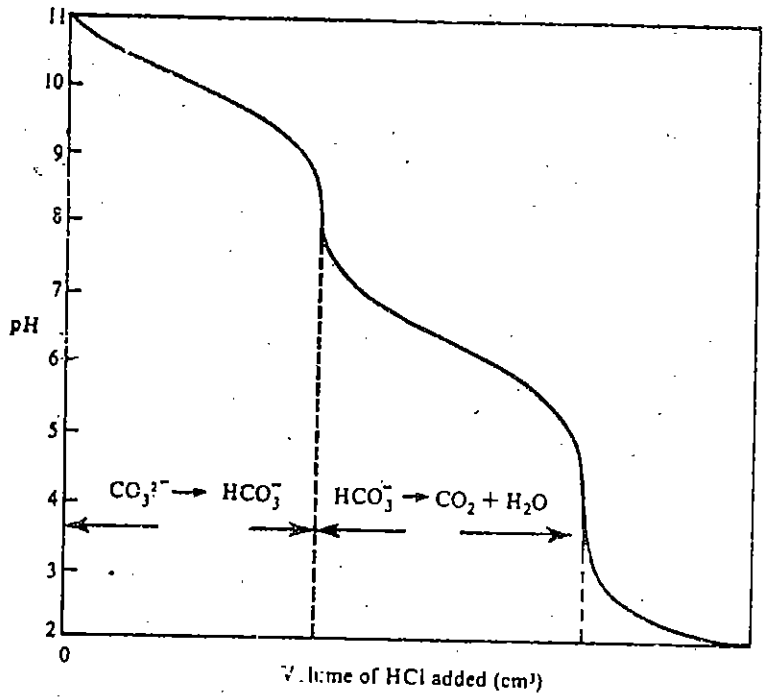


Fig. 3.1 : Titration curve for sodium carbonate titrated with hydrochloric acid.

The titration curve for a sodium carbonate and sodium hydroxide mixture is shown in Fig. 3.2. As you can see, it has two equivalence points. The first equivalence point indicates complete neutralisation of NaOH plus half neutralisation of the carbonate, i.e., its conversion to the bicarbonate (cf Eq. 3.3). The second equivalence point indicates neutralisation of the bicarbonate (cf Eq. 3.4).

From Fig. 3.2 and Table 2.3 you can see that for the detection of the first and the second end points, phenolphthalein and methyl orange, respectively, are the suitable indicators. Once these two end points are detected, volume of HCl used to titrate sodium hydroxide and sodium carbonate may be calculated. This can be further illustrated by considering Fig. 3.3.

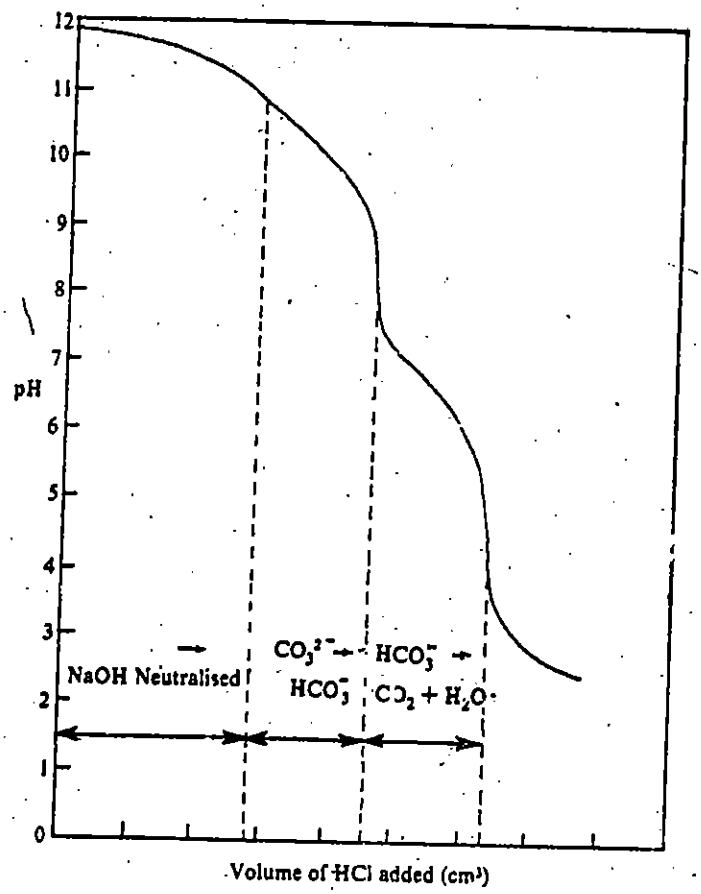


Fig. 3.2 : Titration curve for a mixture of sodium carbonate and sodium hydroxide titrated against acid.

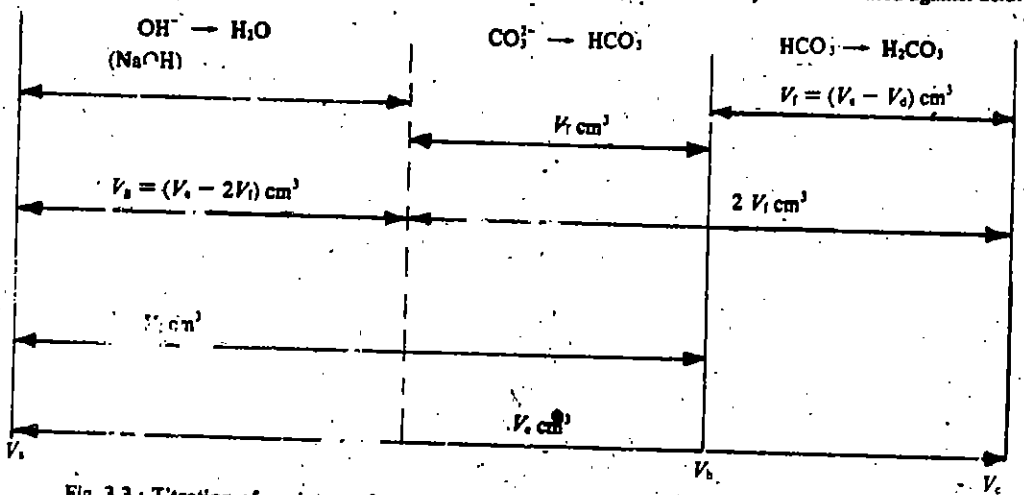


Fig. 3.3 : Titration of a mixture of sodium carbonate and sodium hydroxide with hydrochloric acid.

In this diagram V_s, V_b and V_c refer to burette readings—initial, at the end point with phenolphthalein and at the end point with methyl orange, respectively. The values of V_s, V_b and V_c are also used in observation Table II in calculating the volumes of HCl required for neutralising NaOH and Na_2CO_3 mixtures. Thus, for the first end point we need $V_b - V_s = V_d$ cm³ and for the second end point $V_c - V_s = V_c$ cm³ of hydrochloric acid, then the titration of HCO_3^- requires $V_c - V_d = V_f$ cm³ of HCl. An additional V_f cm³, therefore, is required to titrate the original CO_3^{2-} to HCO_3^-. Titration of the OH^- in the original sample needs $V_c - 2V_f = V_s$ cm³ of HCl.

The corresponding chemical reactions may be summarised as :

OH^- (NaOH) $+ H^+$ (HCl) $\longrightarrow H_2O$
CO_3^{2-} (Na_2CO_3) $+ H^+$ (HCl) $\longrightarrow HCO_3^-$

} end point with phenolphthalein; volume of HCl used $= V_d = V_b - V_s$

$HCO_3^- + H^+$ (HCl) $\longrightarrow H_2CO_3$

} end point with methyl orange; volume of HCl used $= V_f = V_c - V_d$

Before using hydrochloric acid for the titration it should be standardised with a suitable primary standard, preferably sodium carbonate. The reaction between sodium carbonate and hydrochloric acid is given in Eqs. 3.3–3.5 which we have already discussed. End point of the titration is detected with methyl orange indicator.

Before proceeding further, answer the following SAQs.

SAQ 1

Suggest whether aqueous solutions of the following substances are acidic, basic or neutral

a) NaCN b) NaCl c) CH_3COONa d) $NaHCO_3$ e) K_2CO_3

.....

.....

SAQ 2

Predict the number of pH breaks observed for the following titrations.

a) $CH_3COOH - NaOH$

b) $NaHCO_3 - HCl$

c) $K_2CO_3 - HCl$

.....

.....

SAQ 3

On the basis of Fig. 3.4 given below, suggest suitable indicators for the titration.

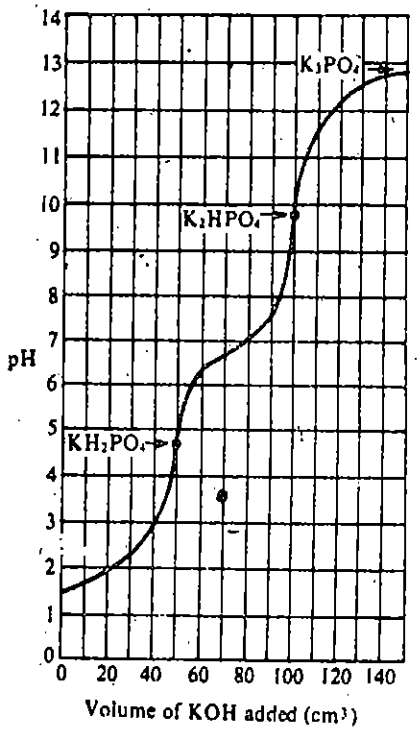


Fig. 3.4 : Titration of 50 cm³ of 0.1 *M* H_3PO_4 with 0.1 *M* KOH

3.2.2 Requirements

You will need the following apparatus and chemicals for this experiment.

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 1
Weighing bottle
Volumetric flasks (250 cm^3) – 2
Funnel – 1
Burette stand with clamp – 1

Chemicals

Sodium carbonate

Mixture of sodium carbonate and sodium hydroxide.

Phenolphthalein indicator solution : It is prepared by dissolving 5 g of the reagent in 500 cm^3 of ethanol and adding 500 cm^3 of water. If a precipitate is formed, it is filtered.

Methyl orange indicator solution : It is prepared by dissolving 5 g of free acid/sodium salt of the indicator in 1 dm^3 of water; 15.2 cm^3 of 0.1 *M* HCl is added to the sodium salt further, if necessary.

Hydrochloric acid solution (0.1 *M*) : This solution is prepared by taking 10 cm^3 conc. HCl in a 1 dm^3 volumetric flask and diluting the acid up to the mark with distilled water.

To obtain satisfactory results by double indicator method the solution titrated must be cold, and loss of carbon dioxide must be prevented as far as possible by keeping the tip of the burette immersed in the liquid.

3.2.3 Procedure

First collect 0.1 *M* hydrochloric acid in a 250 cm^3 bottle. Since hydrochloric acid is a secondary standard, you have to standardise it by titrating it against a primary standard, Na_2CO_3 in this case.

1) **Standardisation of hydrochloric acid** :
   i) Take approximate mass of a clean dry weighing bottle and then weigh the weighing bottle with about 1.35 – 1.40 g of dried sodium carbonate exactly. Transfer the sodium carbonate to a clean volumetric flask of 250 cm^3 capacity through a glass funnel. Weigh the weighing bottle again and find the exact mass of sodium carbonate transferred by subtracting this mass from the mass of the weighing bottle plus sodium carbonate. Dissolve sodium carbonate in volumetric flask and make up the volume to the mark with distilled water.
   ii) Fill up the burette with hydrochloric acid solution and mount it on a stand. Note the reading on the burette and record it in the observation Table I under the initial reading column.
   iii) Pipette out 20 cm^3 of the standard sodium carbonate solution, add two to three drops of methyl orange indicator. Titrate with constant swirling against a white back-ground till a red colour is obtained. Record your reading in the observation Table I under the final reading column. Repeat the titration to get at least two concordant readings.

2) **Titration of the mixture of sodium carbonate and sodium hydroxide against standardised hydrochloric acid** :
   i) Pipette out 20 cm^3 of the mixture solution in a conical flask. Add 1-2 drops of phenolphthalein to it; a pink colour will be obtained.
   ii) Note the initial reading of the burette in the observation Table II under the initial reading column. Run in standardised HCl from the burette slowly into flask until the pink colour is just discharged. Note the burette reading in the observation Table II under the 'reading with phenolphthalein' column.
   iii) Now, add a few drops of methyl orange to the solution in the conical flask; a yellow colour is obtained. Run in a further quantity of the acid until the yellow colour of the solution changes to red. Note the final burette reading in the observation Table II under the 'reading with methyl orange' column. Repeat both titrations with both the indicators to get two concordant sets of readings.

3.2.4 Observations

Mass of the weighing bottle = m_1 g = ... g
Mass of weighing bottle + sodium carbonate = m_2 g = ... g
Mass of weighing bottle (after transferring the salt) = m_3 g = ... g
Amount of sodium carbonate transferred = $m_2 - m_3 = m$ g = ... g
Molar mass (M_m) of sodium carbonate = 106 g mol^{-1}
Volume of sodium carbonate prepared = 250 cm^3
Molarity of sodium carbonate solution = M_1

$$= \frac{m \times 1000}{M_m \times 250} \text{ mol dm}^{-3}$$

$= \frac{m \times 4}{106}$ mol dm^{-3}

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

Observation Table I
Sodium carbonate solutions vs. hydrochloric acid solution

S. No.	Volume of Na_2CO_3 in cm^3	Burette reading Initial	Final	Volume of HCl in cm^3 (Final − Initial)
1	20			
2	20			
3	20			

Observation Table II
Hydrochloric acid solution vs. solution of a mixture of Na_2CO_3 and NaOH

S. No.	Volume of sodium carbonate and sodium hydroxide mixture solution in cm^3	Burette Reading: Initial V_a	with phenolphthalein V_b	with methyl orange V_c	Volume of HCl used in titration of NaOH + half of the Na_2CO_3 $V_d = (V_b - V_a)$ cm^3	Volume of HCl used in titration of NaOH + Na_2CO_3 $V_e = (V_c - V_a)$ cm^3	Volume of HCl used in titration of HCO_3^- $V_f = (V_e - V_d)$ cm^3	Volume of HCl used in titration of Na_2CO_3 $2V_f$ cm^3	Volume of HCl used in titration of NaOH $V_g = (V_e - 2V_f)$ cm^3
1	20								
2	20								
3	20								

3.2.5 Calculations

a) **Standardisation of hydrochloric acid solution :**
Molarity of sodium carbonate solution = M_1 ..... mol dm^{-3}
Volume of sodium carbonate solution = V_1 = 20 cm^3
Volume of hydrochloric acid (from observation Table I) = V_2 cm^3 = ... cm^3
Molarity of HCl solution = M_2 = ?
Using Eq. 3.6.
Molarity of HCl solution

$$M_2 = \frac{2M_1 V_1}{V_2}$$

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

b) **Estimation of sodium carbonate and sodium hydroxide in the mixture :** This can be done as follows :

i) **Estimation of sodium carbonate in the solution :** Volume of hydrochloric acid used in the titration of sodium carbonate in the given sample (from observation Table II) = $2V_f = V_3$ = ... cm^3
Molarity of hydrochloric acid solution = $M_3 = M_2$ = ... mol dm^{-3} (from standardisation of HCl solution)
Volume of HCl solution used = $2V_f = V_3$ = ... cm^3
Volume of sodium hydroxide and sodium carbonate solution = V_4 cm^3 = 20 cm^3
Molarity of Na_2CO_3 solution = M_4 = ?

Using Eq. 3.6,

$$2M_4V_4 = M_3V_3$$

$$M_4 = \frac{M_3 V_3}{2V_4}$$

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

Strength of sodium carbonate present in the given solution = M_4 × Molar mass
= ..... g dm^{-3}

ii) **Estimation of sodium hydroxide in the solution** : Volume of hydrochloric acid used in the titration of NaOH in the given sample (from observation Table II)
$= V_8 = V_5 =$ ..... cm^3
Molarity of hydrochloric acid solution $= M_5 = M_2 =$ ..... $mol\ dm^{-3}$
Volume of HCl solution used $= V_8 = V_5 =$ ..... cm^3
Volume of the solution containing sodium hydroxide and sodium carbonate $= V_6 = 20\ cm^3$
Molarity of sodium hydroxide solution $= M_6 = ?$
Using following molarity equation, (sodium hydroxide and hydrochloric acid react in equimolar ratio),

$$M_6 V_6 = M_5 V_5$$

$$M_6 = \frac{M_5 V_5}{V_6}$$

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

Strength of sodium hydroxide in the given solution
$= M_6 \times$ Molar mass $g\ dm^{-3}$
$=$ ..... $g\ dm^{-3}$

3.2.6 Results

i) Molarity of Na_2CO_3 in the given solution $=$ ..... $mol\ dm^{-3}$
Molarity of NaOH in the given solution $=$ ..... $mol\ dm^{-3}$

ii) Strength of Na_2CO_3 in the given solution $=$ .....
Strength of NaOH in the given solution $=$ .....

Compare these results with the correct values for the given solution of a mixture of sodium carbonate and sodium hydroxide.

Using the experimental technique mentioned above you can also design an experiment to determine the percentage purity of commercial caustic soda. As you know sodium hydroxide absorbs CO_2 from the air and gets converted into carbonate.

$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

Therefore, a solution of caustic soda always contains some Na_2CO_3.

3.3 ANSWERS TO SAQs

1. a) Basic
   b) Neutral
   c) Basic
   d) Basic
   e) Basic
2. a) One
   b) One
   c) Two

3. Phenolphthalein for the first pH break and methyl orange for second pH break (See Fig 3.5).

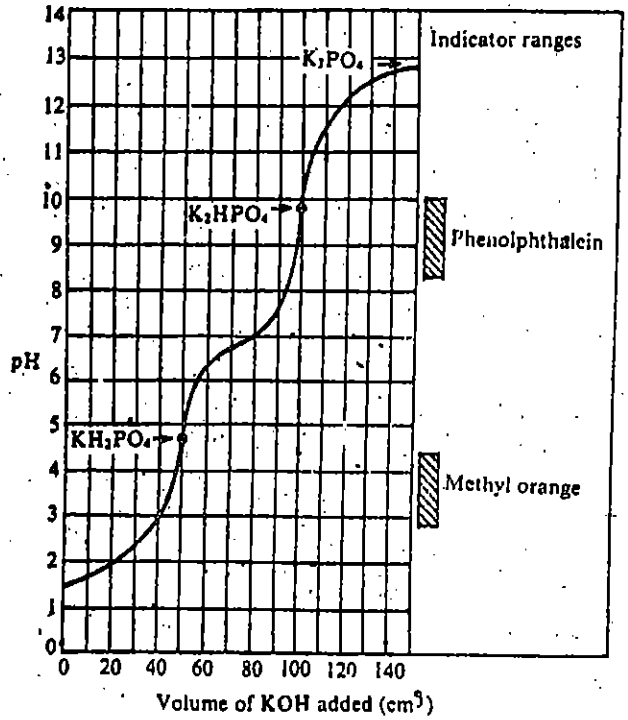


Fig. 3.5 : Titration 50 cm^3 of 0.1 *M* H_3PO_4 with 0.1 *M* KOH

NOTES

NOTES

UGCHE-L 6
Chemistry Lab - I

Block
2
QUANTITATIVE ANALYSIS-II

BLOCK INTRODUCTION

In the first block of this lab course, you studied some basic concepts which are important in titrimetric analysis. You learnt the principle involved in acid-base titrations and also carried out the experiments set in Unit 2 and Unit 3. We hope now you are familiar with the techniques used in these analyses.

In this block you would study, titrimetric and colorimetric methods for estimating a metal in a given sample, as well as complexometric and other methods for the analysis of water. As in Block 1, here also we have discussed the principle involved in each experiment along with the procedural details.

In Unit 4 you would learn to estimate ferrous iron using redox titration methods, namely, permanganatometry and chromatometry. In Unit 5, we have discussed another redox titration, i.e., iodometry to estimate copper. Besides this, you will also learn another method of copper estimation which is based on the principle of colorimetry. Unit 6, the last unit of this course discusses the analysis of water. Here you would learn to determine temporary, permanent and the total hardness of water, its alkalinity and dissolved oxygen in a water sample.

Objectives

After studying this block and performing the experiments set in it, you should be able to:

- explain the basic principle involved in redox titrations and in colorimetry,
- determine the percentage of iron by permanganatometry and chromatometry,
- determine the percentage of copper by iodometry and colorimetry,
- state and explain the principle of complexometry and apply this method to determine temporary, permanent and total hardness of water,
- determine the alkalinity of water using acid-base titration method, and
- state and explain the principle of Winkler's azide method and apply this method to estimate dissolved oxygen in a water sample.

UNIT 4 ESTIMATION OF IRON

Structure

4.1 INTRODUCTION

You have learnt about the theory and applications of acid-base titrations in Units 2 and 3. A large number of analytical determinations make use of another important kind of titration, namely, redox titration. As the name suggests these titrations are based on oxidation-reduction reactions. In contrast to acid-base titrations in which the titration reaction involves the formation of undissociated molecules of a weak electrolyte (water or a weak acid), a redox titration reaction is associated with the transfer of electrons. The electrons are transferred from a reducing agent to an oxidising agent. In this unit we will discuss such titrations. An attempt is made here to make you understand some fundamental concepts related to redox titrations and the theory behind the reactions involved. Analytical redox titrations involve the use of a variety of oxidising and reducing agents. Different types of redox titrations are named on the basis of oxidising/reducing agents involved. Of these, two types of titrations, namely, **permanganatometry** using potassium permanganate, $KMnO_4$ and **chromatometry** using potassium dichromate, $K_2Cr_2O_7$ would be the basis of the two experiments which you are going to do in this unit. In the next unit you will perform another type of redox titration, namely, **iodometry** using iodine.

Objectives

After reading this unit and performing the experiments you will be able to:

- define oxidation, reduction and redox titrations,
- explain the significance of redox potential in redox titrations,
- interpret redox titration curves,
- explain the use of various types of redox indicators,
- apply the redox titration methods, viz., permanganatometry and chromatometry, for estimating iron in the given solution,
- state and explain the principle involved in permanganatometry and chromatometry, and
- calculate the percentage of iron in the given solution by permanganatometric and chromatometric methods.

4.2 OXIDATION-REDUCTION: REDOX POTENTIAL

In this section we will briefly review the theory of oxidation and reduction reactions.

Oxidation is the process which results in the loss of one or more electrons by an atom or an ion, e.g.,

$$Fe^{++} \longrightarrow Fe^{+++} + e \qquad \ldots(4.1)$$

Reduction, on the other hand, is the process which results in the gain of one or more electrons by an atom or an ion, e.g.,

$$Cl_2 + 2e \longrightarrow 2Cl^- \qquad \ldots(4.2)$$

An oxidising agent is the one which gains electrons and gets reduced, e.g., Cl_2 in Eq. 4.2 and a reducing agent is the one which loses electrons and gets oxidised, e.g., Fe^{++} in Eq. 4.1.

Different oxidising/reducing agents differ from one another in their strength. An oxidising agent can behave as a reducing agent in the presence of a stronger oxidising agent. For a reaction of the type:

$$\underset{\text{agent}}{\text{Oxidising (I)}} + \underset{\text{agent}}{\text{Reducing (II)}} \longrightarrow \underset{\text{agent}}{\text{Reducing (I)}} + \underset{\text{agent}}{\text{Oxidising (II)}}$$

where we have a pair of oxidising-reducing agents such that either of the species can act as an oxidising or a reducing agent, the direction of the reaction is determined by comparing the **redox potential** of the oxidising/reducing agents. The redox potential is a quantitative characteristic of the oxidising/reducing power of a reagent. Let us try to understand the significance of redox potential.

In a system containing both an oxidising agent and its reduction product, there will be an equilibrium between them and the electrons. If an inert electrode, such as platinum, is placed in such a redox system, e.g., one containing Fe^{3+} and Fe^{2+} ions, it will assume a definite potential indicative of the position of equilibrium. If the system tends to act as an oxidising agent, then $Fe^{3+} \longrightarrow Fe^{2+}$ and it will take electrons from the platinum electrode leaving the latter positively charged, if, on the other hand, the system has reducing properties ($Fe^{2+} \longrightarrow Fe^{3+}$), electrons will be given up to the metal which will then acquire a negative charge. The magnitude of the potential will thus be a measure of the oxidising or reducing properties of the system. It is quite difficult to measure this potential between the metal and the solution or between different oxidation states of a metal. For this purpose, such a system is coupled with a standard hydrogen electrode (SHE), i.e., we make a galvanic cell and measure electromotive force (e.m.f.) of the cell. The e.m.f. of such a cell is the difference of potential of the given system and SHE, the potential of which is taken to be 0.01 *V*. This e.m.f. is referred to as the **redox potential.**

The potential of the standard hydrogen electrode is conventionally taken as zero, just as the temperature of melting ice is taken as zero in celsius scale.

It should be noted that a solution of a pure oxidising agent or a pure reducing agent always contains the products of their reduction or oxidation, respectively. For example, reductant Fe^{2+} always contains some Fe^{3+} and the oxidant MnO_4^- always contains Mn^{2+} ions. That is why it is more correct to speak of the redox potentials of oxidation-reduction couples such as Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+}, etc., rather than of the individual oxidant or reductant potentials.

For a simple reduction reaction,

$$\text{Ox. form} + ne \longrightarrow \text{Red. form}$$

Here, Ox. form = Oxidised form
Red. form = Reduced form

the reduction potential, E, is given by Nernst Equation:

$$E = E^\circ + \frac{RT}{nF} \log \frac{[\text{Ox}]}{[\text{Red}]} \qquad \ldots(4.3)$$

where R = Gas constant (= 8.314 J $mol^{-1}K^{-1}$)
T = Absolute temperature (K)
F = Faraday's constant (= 96,500 C)
E° = Standard redox potential
n = number of electrons gained or lost

When [Ox] = [Red], the log term in Eq. 4.3 becomes zero, then the potential of the system is called **standard potential.** It is a characteristic of a given system.

At 300 K, substituting the values of R, T and F in Eq. 4.3,

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{[Ox]}{[Red]} \quad \ldots (4.4)$$

Knowing the chemical reaction involved and the potential of the solution, we can use the Nernst equation to evaluate the relative concentrations of oxidised and reduced forms. The solution potential can also be calculated if we know the concentrations of the two forms.

SAQ 1

Write equations for the following half reactions:

i) Oxidation of hydrogen molecule to form hydrogen ions:

.....

ii) Oxidation of sulphide ions to form sulphur:

.....

iii) Reduction of chlorine molecule to form chloride ions:

.....

iv) Oxidation of cuprous ions to form cupric ions:

.....

v) Reduction of oxygen molecule to form oxide ions:

.....

4.3 REDOX TITRATIONS

You know, a redox titration is based upon the oxidation-reduction reaction between a titrand and a titrant. Here the end point can be detected either by the colour change of a redox indicator or by plotting data taken by using a potentiometer. In this section we first discuss the redox titration curves and then the redox indicators. These concepts will tell you how redox indicator and potentiometric detection procedures work.

4.3.1 Redox Titration Curves

We can see from Eq. 4.4 that the potential of a given reaction depends upon the relative concentrations of oxidised/reduced forms. In the course of a redox titration, the solution potential also changes, since the concentration of oxidised and reduced forms goes on changing. At one stage when either of the forms gets exhausted, i.e., at the end point, there is a sharp change in otherwise gradually varying potential. You may recall here what you studied in acid-base titrations, where either the pH or the conductance shows a sharp change at the end point. We shall theoretically try to see the variation of potential during the course of titration which is called redox titration curve. Let us illustrate this by taking an example of the titration between ferrous iron and potassium permanganate solution which incidentally is also the first experiment in this unit.

Redox titration curve for ferrous sulphate-potassium permanganate titration

In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium, the permanganate ions oxidise ferrous ions to ferric ions and get reduced to divalent manganese ions. The ionic reactions involved are as follows:

$$[Fe^{2+} \rightleftharpoons Fe^{3+} + e] \times 5 \quad \ldots (4.5)$$

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \quad \ldots (4.6)$$

Adding Eq. 4.5 and Eq. 4.6,

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \quad \text{... (4.7}$$

The system contains two redox couples, viz., Fe^{2+}/Fe^{3+} and MnO_4^-/Mn^{2+}. Since both the reactions are in equilibrium, at any stage of titration, the solution contains all the species. To calculate the potential of the solution theoretically at any instance of titration, we can make use of Nernst equation using the standard redox potentials for the two couples, and substituting the values of R, T and n in Eq. 4.3. The values of n can be obtained from Eq. 4.5 and Eq. 4.6.

Thus:

$$E = 0.77 + \frac{0.059}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad \text{... (4.8}$$

$$E = 1.51 + \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]} \quad \text{... (4.9}$$

However, it is simpler to use Fe^{2+}/Fe^{3+} couple in the region before the equivalence point and MnO_4^-/Mn^{2+} couple after it. This is because it is easier to calculate the amounts of the corresponding ions under such conditions.

Before we start the titration we have only ferrous ions in solution. When we add $KMnO_4$, MnO_4^- ions oxidise some of the ferrous ions to ferric ions and a potential is developed, point A in Fig. 4.1, between Fe^{2+} and Fe^{3+} ions. As we go on adding more and more of permanganate, the amount of Fe^{3+} ions goes on increasing and that of Fe^{2+} goes on decreasing whereby the potential (cf. Eq. 4.8) also goes on increasing gradually. At a stage just before the equivalence point, say about 0.1 cm³ less than that required for the end point, almost all the ferrous ions are oxidised and the potential is approximately equal to the maximum for Fe^{2+}/Fe^{3+} system under given conditions, point B in Fig. 4.1.

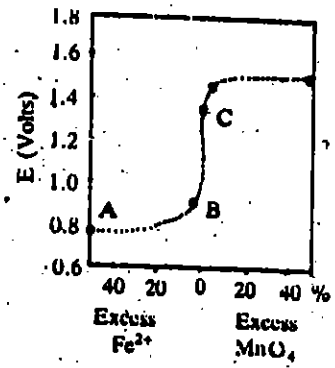


Fig. 4.1: Redox titration curve for ferrous sulphate-potassium permanganate titration.

At equivalence point, point C in Fig. 4.1, the potential is given by the following general equation:

$$E = \frac{bE^{\circ} + aE^{\circ}}{a + b} \quad \text{... (4.10)}$$

where E° and E° are the standard potentials of the oxidising and the reducing agent, respectively and a and b are the corresponding stoichiometric coefficients. In the present case $E^{\circ} = 0.77$, $E^{\circ} = 1.51$, $b = 1$, $a = 5$ and $E = 1.387$ V.

Immediately after the equivalence point the amount of Fe^{2+} is negligibly small and is difficult to calculate. The potential can be calculated by making use of MnO_4^-/Mn^{2+} couple as, at this stage it becomes easier to evaluate the amount of MnO_4^- and Mn^{2+} ions. The potential now corresponds to the minimum for the MnO_4^-/Mn^{2+} couple, point D in Fig. 4.1. Beyond this, further addition of MnO_4^- merely alters the relative amounts of MnO_4^- and Mn^{2+} and there is a gradual variation in the potential of the solution. The calculated redox potential during the titration of 100 cm³ of $FeSO_4$ solution at $[H^+] = 1M$ with permanganate solution of the same molarity is given in Table 4.1. You would notice that Eq. 4.9 for determining the potential of MnO_4^-/Mn^{2+} couple contains $[H^+]$ term. The concentration of $[H^+]$ is kept $1M$ so that in the effective equation we need only the amounts of MnO_4^- and Mn^{2+}. However, it may be mentioned here that the hydrogen ion concentration has an enormous effect upon the oxidation potential of the oxidising agent, MnO_4^- in this case. At a pH of 6, e.g., it is found that the oxidation potential of permanganate is about 0.6 volt lower than with $1M$ acid solution, where pH = 0. Use is made of this fact, e.g., in the fractional oxidation of halides to the corresponding halogen. At a pH of 5 or 6, iodide is oxidised to I_2 by permanganate, whereas bromide and chloride are not affected. At a pH of about 3 (acetic acid), bromide is oxidised, but chloride is still unaffected. The latter is oxidised only at a much higher hydrogen ion concentration.

able 4.1: Variations of the redox potential during titration of 100 cm³ of 0.1*M* $FeSO_4$ solution with 0.02*M* $KMnO_4$ solution at $[H^+] = 1M$

MnO_4 dded, cm³	Excess cm³ $FeSO_4$	Excess cm³ $KMnO_4$	$\frac{[Fe^{+++}]}{[Fe^{++}]}$	$\frac{[MnO_4^-]}{[Mn^{++}]}$	Calculation	Oxidation potential *E*, V
50	50	—	50:50=1	—	$E=0.77+0.059 \log 1$	0.770
91	9	—	91:9≃10	—	$E=0.77+0.059 \log 10$	0.829
99	1	—	99:1≃100	—	$E=0.77+0.059 \log 100$	0.888
99.9	0.1	—	99.9:0.1 ≃1,000	—	$E=0.77+0.059 \log 1,000$	0.947
100 (equiv. pt.)	—	—	—	— =	$E=\frac{0.77+5\times1.51}{5+1}$	1.387*
100.1	—	0.1	—	0.1:100=0.001	$E=1.51+\frac{0.059}{5} \log 0.001$	1.475
101.0	—	1.0	—	1:100=0.01	$E=1.51+\frac{0.059}{5} \log 0.01$	1.487
110.0	—	10	—	10:100=0.1	$E=1.51+\frac{0.059}{5} \log 0.1$	1.498
150	—	50	—	50:100=0.5	$E=1.51+\frac{0.059}{5} \log 0.5$	1.507

hese figures show that the equivalence point is not in the middle of the break, as was the case in tration curves by the neutralisation method.

dox potential of a redox system remains unaffected by dilution, this is because ution affects both the oxidised and the reduced species equally. This is justified cause in the Nernst equation also, the relative concentrations and not the absolute ncentrations of the two forms are required. On the other hand, in the region yond the equivalence point, the actual potential would be slightly different from calculated one, since $[H^+]$ ions are involved in the calculations and their ncentration does depend upon dilution. This error, however, does not affect the neral conclusions and can, therefore, be neglected.

e above description of redox titration curves is given to make you aware of the nges in potential taking place during the reaction. Since you are going to use only indicator method to detect the end point, you would not be required to draw h curves. However, these titrations can also be followed by actually measuring the ential of the solution with the help of a potentiometer (pH meter). In such cases, has to plot these curves and determine the equivalence point by using derivative ves as was done in case of acid-base titrations.

.2 Redox Indicators

have seen how the potential varies during the titration and also that at the ivalence point there is a sharp change in the potential. As said before, this change milar to the sharp change observed in the pH during acid-base titrations. As you d an acid-base indicator which changes colour in the pH range corresponding to sharp change in pH at the end point, here we need a chemical species which can nge colour in the potential range corresponding to the sharp change at the end t. A chemical substance which changes colour when the potential of the solution hes a definite value is termed an **oxidation-reduction or redox indicator.**

Redox indicators are substances which can be reversibly oxidised or reduced and have different colours in oxidised and reduced forms.

edox titrations, indicators are used in three different ways. These have already n discussed briefly in Unit 1. Let us recall it here. In certain titrations, e.g., those lving $KMnO_4$, one of the reacting species itself changes colour at the equivalence nt and is called a **self indicator.** In some cases the indicator needs to be added to solution, as phenolphthalein or methyl orange in the case of acid-base titrations, diphenylamine in case of chromatography. Such indicators are called **internal cators.** In yet some other cases, redox indicator may be replaced by a reagent ch is used as a spot test reagent for the ion being determined. Such indicators are added into the solution but are used externally. At various stages of the titration, op of the reaction mixture is taken out and tested for the ion by mixing with the cator on a porcelain plate. Potassium ferricyanide, $K_3[Fe(CN)_6]$, is an example of

an **external indicator** which is used in the titration of Fe^{2+} ions with dichromate. Having learnt about oxidation/reduction reactions, redox potential and redox indicators, let us now actually do a redox titration.

4.4 EXPERIMENT 5: DETERMINATION OF PERCENTAGE OF IRON IN THE GIVEN IRON FILINGS SOLUTION BY PERMANGANATOMETRY

As said before, potassium permanganate is a good oxidising agent. It is used in a number of titrimetric determinations where the method is known as permanganatometry. One of the most important determinations by this method is titrimetric determination of ferrous iron. A ferrous salt when titrated with $KMnO_4$ is oxidised to a ferric salt. The amount of iron in the unknown solution is easily calculated from the volume of the $KMnO_4$ solution needed for the titration and its molarity. In the next experiment you will use $K_2Cr_2O_7$ for the same purpose.

4.4.1 Principle

Potassium permanganate is an oxidising agent and gets reduced in the presence of a suitable reducing agent as, for example, Fe^{++} in the present case. Its reduction can be brought about in acidic, neutral or alkaline medium. The permanganate ion, MnO_4^-, gets reduced to Mn^{2+} ion in acidic medium as shown in Eq. 4.6, and to MnO_2 in neutral and alkaline media, as shown in Eq. 4.11.

$$\underset{+7 \text{ state}}{MnO_4^-} + 8H^+ + 5e \rightleftharpoons \underset{+2 \text{ state}}{Mn^{2+}} + 4H_2O, E^\circ = 1.51 \text{ V} \quad \ldots (4.6)$$

$$\underset{+7 \text{ state}}{MnO_4^-} + 2H_2O + 3e \rightleftharpoons \underset{+4 \text{ state}}{MnO_2} + 4OH^-, E^\circ = 0.57 \text{ V} \quad \ldots (4.11)$$

The oxidising power of permanganate ion is medium dependent; it is related to the change in the oxidation state of manganese in a particular medium.

Usually titrations involving potassium permanganate are carried out in acidic medium. This is due to the higher oxidising power of permanganate ion in acidic medium than in neutral or alkaline medium; secondly, the formation of brown coloured MnO_2 in alkaline medium interferes with the detection of the end point.

While permanganate ion gets reduced, ferrous ion, Fe^{2+} gets oxidised to the ferric ion, Fe^{3+}

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e \quad \ldots (4.5)$$

The overall ionic equation for the titration in acidic medium can be obtained by adding Eq. 4.5 and Eq 4.6 after balancing the number of electrons between them as follows:

$$[Fe^{2+} \rightleftharpoons Fe^{3+} + e] \times 5 \quad \ldots (4.5)$$

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \quad \ldots (4.6)$$

$$MnO_4^- + 5Fe^{2+}\ 8H \rightleftharpoons 5Fe^{3+} + Mn^{2+} + 4H_2O \quad \ldots (4.7)$$

We see from Eq. 4.7, that one mole of potassium permanganate reacts with 5 moles of ferrous ions. Therefore, substituting the values of p and q in Eq. 1.8, the molarities are related as per the following equation:

$$\frac{M_{KMnO4}\ V_{KMnO4}}{M_{FeSO4}\ V_{FeSO4}} = \frac{1}{5} \Longrightarrow, \text{ i.e., } 5\ M_{KMnO4}\ V_{KMnO4} = V_{FeSO4}\ M_{FeSO4} \quad \ldots (4.12)$$

A slight excess of $KMnO_4$ at the end point imparts a distinct pink colour to the solution and, therefore, acts as a self indicator. The solution of $KMnO_4$ is not stable.

its strength changes on storage. It is, therefore, a secondary standard. You have to standardise it by titrating against a suitable primary standard. A number of primary standards can be used for this purpose. Here you would be using a standard solution of ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4.6H_2O$ or Mohr's salt. Mohr's salt is preferred to ferrous sulphate because it has better shelf-life. However, the ionic equations are the same as given for ferrous iron solution, viz., Eq. 4.7. You can use Eq. 4.12 as the molarity equation to find out the molarity of the given $KMnO_4$ solution.

Permanganatometry finds its use also in the estimation of hydrogen peroxide, nitrites and persulphates, etc.

SAQ 2

Write the chemical reaction involving a titration of $KMnO_4$ and $FeSO_4$ solution in presence of dilute H_2SO_4.
[Hint: Two steps are involved in the reaction]

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SAQ 3

Why $KMnO_4$ cannot be taken as a primary standard?

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4.4.2 Requirements

Apparatus

Burette (50 cm^3)	– 1
Pipette (20 cm^3)	– 1
Conical flasks (250 cm^3	– 2
Test tube	– 1
Volumetric flask (250 cm^3)	– 1
Beaker (250 cm^3)	– 1
Weighing bottle	– 1
Funnel (small)	– 1
Wash bottle for distilled water	– 1
Burette stand	– 1

Chemicals

Ferrous ammonium sulphate $FeSO_4.(NH_4)_2SO_4.6H_2O$, FAS also known as **Mohr's salt.**

Sulphuric acid (1 *M*)

Solutions Provided

Iron filings solution: It is prepared by dissolving 1.2 g of iron filings in about 20 cm^3 of dilute sulphuric acid. A piece of zinc is added to this solution to prevent aerial oxidation of Fe^{2+} to Fe^{3+}. The solution is then transferred to a 1000 cm^3 volumetric flask and made up to the mark by adding distilled water carefully.

Approximately *M*/250 solution of potassium permanganate, prepared by dissolving 0.79 g of potassium permanganate in distilled water and making up the solution to 250 cm^3. It is then stored in a dark place preferably in an amber coloured bottle for a few days. Potassium permanganate solution is stored in dark because light accelerates decomposition of $KMnO_4$ by the reaction given below:

$$4KMnO_4 + 2H_2O \longrightarrow 4MnO_2\downarrow + 4KOH + 3O_2\uparrow$$

Indicator

$KMnO_4$ acts as a self indicator, so no other indicator is required.

4.4.3 Procedure

As indicated above, you are provided with approximately *M*/250 potassium permanganate solution and a solution of ferrous sulphate (prepared from iron filings) which is to be estimated.

You can start your experiment with the standardisation of $KMnO_4$ solution with standard ferrous ammonium sulphate solution.

Preparation of standard ferrous ammonium sulphate solution (concentration = $M/50$).

Take approximate mass of a glass weighing bottle. Then weigh it accurately with about 1.956 g of Mohr's salt. Transfer the salt to a clean and dry volumetric flask of 250 cm^3 capacity through a glass funnel. Find out the accurate mass of the bottle after transferring Mohr's salt. The difference between the two masses gives the actual amount of Mohr's salt transferred. Record these values in your observation note book. To the contents of the volumetric flask add about 10 cm^3 of dilute H_2SO_4 ($1M$) and about 50 cm^3 of distilled water, dissolve the salt completely; add more water, if necessary. Finally, make the volume upto the mark by adding distilled water carefully.

Caution: If the solution turns brownish, then the amount of acid added is not sufficient. Discard this solution. Do the whole exercise again using more H_2SO_4.

Titrations

In case of potassium permanganate it is convenient to use the upper meniscus.

Standardisation of potassium permanganate solution: Fill up the burette with the given $KMnO_4$ solution and mount the burette on a stand; also insert a parallex card. Note the reading in the burette and record it in the observation Table I. Pipette out 20 cm^3 of standard ferrous ammonium sulphate solution into a 250 cm^3 conical flask. Add approximately 10-15 cm^3 of dilute H_2SO_4($1M$) to the solution. **For this purpose take a test tube and fill it a little more than half with H_2SO_4 and mark its level so that you add the same amount of H_2SO_4 in every titration.**

Titrate ferrous ammonium sulphate solution by slowly adding small amounts of potassium permanganate solution and continuously shaking the conial flask. The pink colour, obtained on addition of $KMnO_4$ solution, disappears on shaking. Continue the titration until a permanent pale pink colour appears. This indicates the end point of the titration. Note the burette reading and record it in observation Table I. The difference of two readings gives a rough estimate of the volume of $KMnO_4$ required.

Repeat the titration to get at least two concordant readings to ensure a correct and exact measurement.

Do not throw the FAS solution left. You will use this for Experiment 6.

Titration of given iron filing's solution against standardised $KMnO_4$ solution: Perform this titration in exactly the same manner as given above by taking the solution prepared from iron filings in place of Mohr's salt solution. Record the readings in observation Table II.

SAQ 4

Can HCl or HNO_3 be used in place of H_2SO_4 for making the medium acidic in a redox titration where $KMnO_4$ is used as an oxidant? Justify your answer.

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4.4.4 Observations

Approximate mass of the weighing bottle = m_1 = ... g
Mass of bottle + ferrous ammonium sulphate (before transferring the salt) = m_2 = ... g
Mass of bottle (after transferring the salt) = m_3 = ... g
Mass of ferrous ammonium sulphate transferred = $m_2 - m_3$ = m = ... g
Molar mass of ferrous ammonium sulphate = 392.15 g mol^{-1}
Volume of ferrous ammonium sulphate solution prepared (V) = 250 cm^3

Molarity of ferrous ammonium sulphate solution (M_1)

$= \frac{m \times 1000}{\text{Molar mass} \times 250}$ mol dm^{-3}

$= \frac{m \times 4}{392.15}$ mol dm^{-3}

..... mol dm^{-3}

Observation Table I
Ferrous ammonium sulphate solution vs. potassium permanganate solution

Sl. No.	Volume of FAS solution in cm^3	Burette reading		Volume of $KMnO_4$ in cm^3 (Final – Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Ferrous iron solution prepared from iron filings vs. potassium permanganate solution

Sl. No.	Volume of Ferrous iron solution in cm^3	Burette reading		Volume of $KMnO_4$ in cm^3 (Final – Initial)
		Initial	Final	
1	20			
2	20			
3	20			

4.4.5 Calculations

Estimation of the strength of potassium permanganate

Molarity of FAS solution = M_1 = ...mol dm^{-3}
Vol. of FAS solution used = V_1 = 20 cm^3
Vol. of $KMnO_4$ solution used (from Table I) = V_2 = ... cm^3
Molarity of $KMnO_4$ solution = M_2 = ?
Using the molarity equation (Eq. 4.12),
$M_1 V_1 = 5M_2 V_2$

Molarity of $KMnO_4$ solution (M_2)

$= \frac{M_1 V_1}{5V_2}$,

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

Estimation of strength of ferrous iron solution prepared from iron filings
Molarity of $KMnO_4$ = M_3 = M_2 = ... mol dm^{-3}
Vol. of $KMnO_4$ solution used = V_3 = ... cm^3
Vol. of Fe^{++} solution taken = V_4 = 20 cm^3
Molarity of ferrous iron solution = M_4 = ?

Using the molarity equation,
$M_4 V_4 = 5M_3 V_3$

Molarity of ferrous iron solution

$M_4 = \frac{5M_3 V_3}{V_4}$

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

Determination of percentage of iron in iron filings
Mass of iron in 1000 cm^3 of the solution prepared from the iron filings = Molarity of the solution × Molar mass of iron

= $M_4 \times 55.85$ g
= m_4 = ... g

Percentage of Fe in iron filings = $\frac{\text{Estimated mass of iron in iron filings}}{\text{Mass of iron filings}} \times 100$

$$= \frac{m_4}{1.2} \times 100$$

= ..... %

4.4.6 Result

The percentage of iron in the sample of iron filings used for preparing the solution = ... %.

The above value can be compared with the actual one which you can get from your counsellor.

4.5 EXPERIMENT 6: DETERMINATION OF THE PERCENTAGE OF IRON IN THE GIVEN IRON FILINGS SOLUTION BY CHROMATOMETRY

In permanganatometry you used potassium permanganate as the oxidising agent to estimate Fe^{2+} ions in the given solution. In chromatometry, potassium dichromate is used for the same purpose. Dichromate acts as an oxidising agent only in the acidic medium. The general theory behind chromatometry is the same as for permanganatometry. The only difference being that while $KMnO_4$ acts as a self indicator, an indicator has to be used in chromatometry. The relevant equations along with the potentials are given below as well as the chemistry involved in the colour changes that the indicator undergoes.

4.5.1 Principle

Potassium dichromate is an oxidising agent and in acidic medium reacts according to the following half-reaction to give chromium (III) as the reduction product.

$$\underset{\text{(Cr in +6 state)}}{Cr_2O_7^{2-}} + 14H^+ + 6e \rightleftharpoons \underset{\text{(Cr in +3 state)}}{2Cr^{3+}} + 7H_2O \quad (E^\circ = 1.33\ V) \qquad \ldots (4.13)$$

Fe^{2+} when titrated with dichromate gets oxidised to Fe^{3+} as per the following equation:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e \quad (E^\circ = 0.77\ V) \qquad \ldots (4.5)$$

The overall ionic equation of the titration can be obtained by adding Eq. 4.12 and Eq. 4.5 after balancing the number of electrons between them as follows:

$$[Fe^{2+} \rightleftharpoons Fe^{3+} + e] \times 6 \qquad \ldots (4.5)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad \ldots (4.13)$$

$$\boxed{Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 6Fe^{3+}\ 2Cr^{3+} + 7H_2O} \qquad \ldots (4.14)$$

We see from Eq. 4.14, that one mole of potassium dichromate reacts with 6 moles of iron (II) in solution. Therefore, substituting the values of p and q in Eq. 1.8, the molarities are related by the following equation:

$$\frac{M_1 V_1}{M_2 V_2} = \frac{6}{1}$$

or $M_1 V_1 = 6 M_2 V_2$ ...(4.15)

Where M_1 and M_2 represent the molarities of iron (II) and potassium dichromate solutions, then V_1 and V_2 represent their volumes, respectively.

As you know, the factor 6 signifies that each mole of potassium dichromate reacts quantitatively with 6 moles of iron (II).
1 mole $K_2Cr_2O_7$ = 6 moles Fe(II)

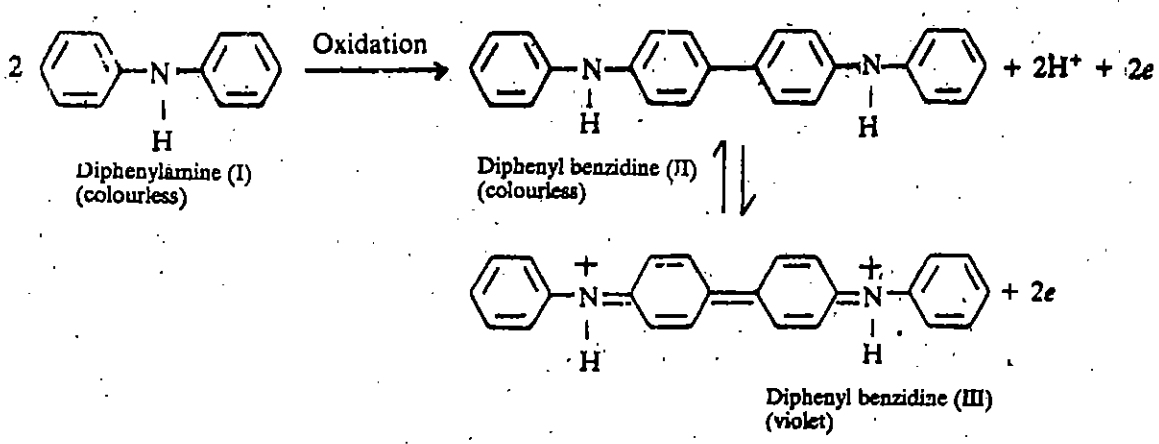
Potassium dichromate does not oxidise HCl, whereas $KMnO_4$ oxidises it to Cl_2. Hence, $KMnO_4$ cannot be used as an oxidising agent in estimating metal ions where the solution is made using HCl, whereas $K_2Cr_2O_7$ can be used in such cases too. Since metals are leached out from their minerals with HCl in many cases, chromatometry is the preferred technique of estimation in such cases.

Indicator

A dilute solution of $K_2Cr_2O_7$ has a faint orange colour and chromium (III) obtained as the reduction product is green in colour. So, a drop of $K_2Cr_2O_7$ in excess at the end point, unlike $KMnO_4$, is not sufficient to give a distinct colour to the solution. Further, the green colour of chromium (III) ions produced also interferes, therefore, $K_2Cr_2O_7$ cannot be used as a self indicator.

A redox indicator must, therefore, be used. Diphenylamine was one of the first internal redox-indicators used in this titration. However, as it is sparingly soluble in water, sodium salt of diphenylamine sulphonic acid can be used instead, as it is water soluble. These indicators are colourless in the reduced form and become intensely coloured on oxidation (deep blue-violet with diphenylamine; red-violet with sodium diphenylamine sulphonate).

At potentials lower than 0.73 V, iron is in +2 state and the indicator is present in form I which is colourless. In the course of the titration, when Fe^{2+} gets converted to Fe^{3+}, the potential increases gradually (cf. Eq. 4.8). At equivalence point all the ferrous ions are oxidised and as discussed earlier, at this stage there is a jump in the potential. This increase in the redox potential of the solution is sufficient to cause the oxidation of the indicator to form II. Form II gets readily converted into form III, which has a distinct colour and marks the end point. The above description about the indicator can be represented as shown below:



SAQ 5

a) Write the chemical reaction involving a titration of $K_2Cr_2O_7$ and $FeSO_4$ solution in presence of dilute H_2SO_4.
[Hint: The reaction involves two steps]

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b) Explain why $K_2Cr_2O_7$ reacts as an oxidising agent only in the acidic medium.

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SAQ 6

In the following tick √ on the correct and × on the wrong statements.
$K_2Cr_2O_7$ is superior to $KMnO_4$ because:

$K_2Cr_2O_7$ is more stable than $KMnO_4$ both in the dry state as well as in solution.

ii) A solution of $K_2Cr_2O_7$ is not intensely coloured.

iii) $K_2Cr_2O_7$ is not reduced by cold HCl if acid concentration does not exceed 1 or 2 *M*.

iv) $K_2Cr_2O_7$ can be easily weighed.

4.5.2 Requirements

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 1
Beaker (250 cm^3) – 1
Weighing bottle – 1
Funnel (small) – 1
Volumetric flask (250 cm^3) – 1
Wash bottle for distilled water – 1
Burette stand – 1

Chemicals

Ferrous ammonium sulphate, FAS (Mohr's salt)
Sulphuric acid, dilute (1*M*)
Phosphoric acid (85%)

Solutions Provided

Iron filings solution: As for the previous experiment, it is prepared by dissolving 1.2 g of iron filings in about 20 cm^3 of dilute H_2SO_4. A piece of zinc is added to this solution to prevent aerial oxidation of Fe^{2+} to Fe^{3+}. The solution is then transferred to a 1000 cm^3 volumetric flask and made up to the mark by adding distilled water carefully.

Approximately *M*/300 solution of potassium dichromate, prepared by dissolving 0.245 g of potassium dichromate in distilled water and making up the volume to 250 cm^3.

Diphenylamine (1%) solution in concentrated sulphuric acid or sodium diphenylamine sulphonate (0.2% aqueous solution).

4.5.3 Procedure

Potassium dichromate, as mentioned earlier, can be used as a primary standard which means that a standard solution of dichromate can be made by weighing an exact amount of the substance, dissolving it in water and making up to the known volume with distilled water. However, in this particular experiment, we are provided with solution of $K_2Cr_2O_7$, the molarity of which has to be found by titrating with a standard ferrous ammonium sulphate salt solution.

Standard ferrous ammonium sulphate solution (concentration = *M*/50) prepared in the previous experiment can be used here.

Titrations

Standardisation of potassium dichromate solution: Pipette out 20 cm^3 aliquot of standard ferrous ammonium sulphate solution into a 250 cm^3 conical flask. Add approximately 20 cm^3 of dilute sulphuric acid (1*M*), 5 cm^3 of phosphoric acid and 5 to 10 drops of the indicator solution. Titrate this with the dichromate solution. As the titration proceeds, the colour changes to a pale green, then to a greyish blue-green and with one drop to a persistent deep blue-violet colour of the indicator in the oxidised form. Record the volume of the titrant accurately.

Phosphoric acid combines with yellow Fe^{3+} ions to form $[Fe(HPO_4)]^+$ rendering the end point more visible.

Repeat the titration to get at least two concordant readings to ensure a correct and exact measurement. Record the observations in observation Table I.

Titration of the given iron (II) solution against standardised $K_2Cr_2O_7$ solution: Perform this titration exactly in the same manner as in the above experiment by taking the given iron (II) solution instead of ferrous ammonium sulphate solution. Record the observations in observation Table II.

4.5.4 Observations

Molarity of ferrous ammonium sulphate solution (M_1) as calculated in Exp. 5 = ... mol dm^{-3}

Observation Table I
Ferrous ammonium sulphate solution vs potassium dichromate solution

Sl. No.	Volume of FAS in cm^3	Burette reading		Volume of $K_2Cr_2Cr_2O_7$ in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Given Iron (II) solution prepared from iron filings vs potassium dichromate solution

Sl. No.	Volume of Ferrous iron solution in cm^3	Burette reading		Volume of $K_2Cr_2O_7$ in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

4.5.5 Calculations

Estimation of strength of $K_2Cr_2O_7$

Molarity of FAS solution = M_1 = ... mol dm^{-3}
Volume of FAS solution used = V_1 = 20 cm^3
Volume of $K_2Cr_2O_7$ solution used (from Table I) = V_2 = ... cm^3
Molarity of $K_2Cr_2O_7$ solution = M_2 = ?
Using the molarity equation,

$$M_1 V_1 = 6 M_2 V_2$$

Molarity of $K_2Cr_2O_7$

$$M_2 = \frac{M_1 V_1}{6 V_2}$$

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

Estimation of strength of Iron (II) solution prepared from iron filings

Molarity of $K_2Cr_2O_7$ solution = M_3 = M_2 = ... mol dm^{-3}
Volume of $K_2Cr_2O_7$ solution used = V_3 = ... cm^3
Volume of iron (II) solution taken = V_4 = 20 cm^3
Molarity of iron (II) solution = M_4 = ?

Using the molarity equation

$$M_4 = \frac{6 M_3 V_3}{V_4}$$

Molarity of Fe(II)

M_4 = ... mol dm^{-3}

Determination of percentage of iron in iron filings

Mass of iron in 1000 cm^3 (1 dm^3) = Molarity of the solution × Molar mass of iron of the solution prepared from iron filings

= $M_4 \times 55.85 = m_4$
= ..... g

$$\text{Percentage of iron in iron filings} = \frac{\text{Estimated mass of iron filings}}{\text{Mass of iron filings}} \times 100$$

$$= \frac{m_4}{1.2} \times 100$$

= ..... %..

4.5.6 Result

The percentage of iron in the sample of iron filings used for preparing the solution = ... %.

The above value can be compared with the actual one which you can get from your counsellor. Since in both permanganatometry and chromatometry experiments, you have used the same iron solution, compare the difference in two results obtained. The two results should be almost the same if the weighing is accurate and the titration error is not much. If the difference is more, then discuss the reasons for the difference with your counsellor.

4.6 ANSWERS TO SAQs

1) i) $H_2 \longrightarrow 2H^+ + 2e$
   ii) $S^{2-} \longrightarrow S + 2e$
   iii) $Cl_2 + 2e \longrightarrow 2Cl^-$
   iv) $Cu^+ \longrightarrow Cu^{2+} + e$
   v) $O_2 + 2e \longrightarrow 2O^{2-}$

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

$$\frac{[2FeSO_4 + H_2SO_4 + (O) \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5}{2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O}$$

3) $KMnO_4$ is not pure and always contains some of its reduction products such as MnO_2; also it is easily decomposed by reducing agents present in H_2O.

4) HCl acts as a reducing agent, itself getting oxidised to Cl_2; and HNO_3 acts as an oxidising agent again competing with the action of $KMnO_4$. Therefore, neither of these can replace H_2SO_4.

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

$$\frac{[2FeSO_4 + H_2SO_4 + (O) \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3}{K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O}$$

   b) In presence of an alkali, potassium dichromate reacts to give chromate salt and cannot act as an oxidising agent.

6) i) ✓
   ii) ×
   iii) ✓
   iv) ×

UNIT 5 ESTIMATION OF COPPER

Structure

5.1 INTRODUCTION

In the previous unit, you have estimated the amount of ferrous iron, Fe^{2+}, in a sample of iron filings by using two redox titrations, namely, permanganatometry and chromatometry. In this unit, we would estimate the amount of copper in a given sample. Here too, you would perform two experiments, one of which is based on a redox reaction, iodometry, while the other is based on colorimetric determination. Iodometric titrations make use of I_2/I^- redox reaction and the end point is detected by using starch as an indicator. Colorimetry, on the other hand, is a method of analysis based on comparing the colour intensity of an unknown with that of a standard solution, i.e., the solution of a definite known concentration. The theory behind iodometric and colorimetric determination of cupric ions, Cu^{2+} is given along with the procedural details of the experiments.

Objectives

After studying this unit and performing the experiments, you will be able to:

- define and differentiate between iodometry and iodimetry,
- explain the redox reactions involved in iodometry,
- explain the use of indicator in iodometry and standardise the given sodium thiosulphate solution,
- use the iodometric method in estimating Cu^{2+} ions,
- state Beer-Lambert law,
- explain the principle of colorimetry,
- describe the colorimeter and its calibration, and
- use the colorimetric method in estimating Cu^{2+} ions.

5.2 IODIMETRY AND IODOMETRY

Iodine is a mild oxidising agent and in the presence of a suitable reducing agent, gets reduced to iodide ions, I^-, according to the following equation:

$$I_2 + 2e \rightleftharpoons 2I^-, \quad E^0 = 0.54\,V \qquad \ldots(5.1)$$

Iodimetric titrations are used for estimating reducing agents while iodometric titrations are used for oxidising agents.

On the other hand, a variety of oxidising agents can oxidise I^- ions into I_2. In fact, both these reactions are made use of in analytical chemistry. Titrations involving the use of I_2 as a titrant to estimate the reducing agents are termed as **iodimetric titrations**. Iodine, being a much weaker oxidising agent than potassium permanganate and potassium dichromate, has limited applicability. Moreover, it is very volatile in nature and also has poor solubility.

Iodimetry: Titration with iodine
Iodometry: Titration of iodine produced by a chemical reaction

In certain cases, the oxidising agent to be determined is mixed with an excess of potassium iodide, KI, and kept for some time. The iodine, liberated during the reaction, is titrated against a standard solution of a reducing agent, e.g., sodium thiosulphate, $Na_2S_2O_3$. These titrations are referred to as **iodometric titrations**. Since Cu^{2+} ions, can behave as an oxidising agent by getting reduced to Cu^+ ions, we can use iodometric method for their determination.

Ideally an iodometric titration should be a titration using KI as a titrant to titrate the oxidising agent. In such a reaction, more and more of iodine is liberated from iodide ions as the titration proceeds. The end point of such a titration would be a stage where the liberation of iodine ceases. It is impossible to detect this end point with the help of an indicator. Starch can be used to detect the 'just appearance' or the 'just disappearance' of iodine but not the cessation of I_2 formation.

An indirect method of end point determination becomes essential in such cases. A known amount of the solution of the oxidising agent (to be determined) is measured and mixed with an excess of a solution of KI and acid. The solution is then left for about five minutes in the dark for the reaction to complete and the liberated iodine is titrated with a standardised solution of sodium thiosulphate using starch as the indicator. The following reaction takes place:

$$I_2 + 2Na_2S_2O_3 \rightleftharpoons 2NaI + Na_2S_4O_6 \qquad ...(5.2)$$

An excess of KI is used because iodine has got very poor solubility in water. Iodine forms an unstable complex, KI_3, with KI which is readily soluble in H_2O.

$$KI + I_2 \rightleftharpoons K[I_3]$$

In fact, iodine in an aqueous solution containing KI exists mainly as the triiodide ion, I_3^- and there is an equilibrium between I_3^- ion and I_2. In the course of the titration, as I_2 is consumed, more and more of I_3^- ions dissociate to give I_2 which reacts with thiosulphate. Further, such a titration should be carried out in cold, as I_2 is volatile and also the indicator, starch, loses its sensitivity at high temperatures.

SAQ 1

Give two limitations of I_2 as a titrant.

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5.2.1 Indicator

In principle, iodine can be used as a self indicator like $KMnO_4$, as a drop of iodine can impart a pale yellow colour to a solution. Since the colour imparted by iodine is quite faint, in practice, it becomes difficult to use this as an indication of the end point. Iodine is known to form a blue coloured adsorption complex with starch. This property of starch is exploited in using it as an indicator for titrations involving iodine.

The use of starch enhances the sensitivity of the determination of the end point.

In an iodometric determination, we titrate I_2 with $S_2O_3^{2-}$ ions and at the end point, addition of one drop of $S_2O_3^{2-}$ ions should just decolourise the blue colour of starch-iodine complex. In such titrations, starch should be added just before the end point, when a very little amount of I_2 remains and the solution being titrated has a faint straw yellow colour. If starch is added earlier, i.e., when a large amount of iodine is present, a large amount of starch-iodine complex is formed. This complex reacts quite slowly with $S_2O_3^{2-}$ and it is likely that the solution is over titrated.

5.2.2 Standardisation of Thiosulphate

As said above, in iodometry we titrate the liberated iodine with a standardised solution of sodium thiosulphate. Though sodium thiosulphate, $Na_2S_2O_3.5H_2O$, can be obtained chemically pure, a standard solution of thiosulphate cannot be made by exact weighing. This is because thiosulphate reacts with atmospheric O_2 and also the CO_2 dissolved in water. More so, even some microorganisms decompose thiosulphate.

A number of oxidising agents are available for the standardisation of $Na_2S_2O_3$. Potassium dichromate is normally used for the purpose.

In acidic medium $Cr_2O_7^{2-}$ ion gets reduced to Cr (III) as shown in the following equation :

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \quad ...(5.3)$$

and iodide ions from KI get oxidised to I_2;

$$2I^- \rightleftharpoons I_2 + 2e$$

To maintain electron balance, multiplying the above equation by 3, we get,

$$6I^- \rightleftharpoons 3I_2 + 6e \quad ...(5.4)$$

The overall ionic equation for the titration can be obtained by adding Eq.5.3 and Eq. 5.4,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O \quad ...(5.5)$$

We see from Eq. 5.5 that one mole of potassium dichromate reacts with 6 moles of potassium iodide liberating 3 moles of iodine.

The liberated iodine, in turn, reacts with sodium thiosulphate solution as,

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e \quad ...(5.6)$$

$$I_2 + 2e \rightleftharpoons 2I^- \quad ...(5.1)$$

Since three moles of I_2 are liberated by $Cr_2O_7^{2-}$,

$$3I_2 + 6e \rightleftharpoons 6I^- \quad ...(5.7)$$

The overall ionic equation for the titration of liberated I_2 with sodium thiosulphate can be obtained by adding Eq. 5.6 and Eq. 5.7,

$$[2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e] \times 3 \quad ...(5.6)$$

$$3I_2 + 6e \rightleftharpoons 6I^- \quad ...(5.7)$$

$$3I_2 + 6S_2O_3^{2-} \longrightarrow 6I^- + 3S_4O_6^{2-} \quad ...(5.8)$$

The net chemical reaction involving a titration of potassium dichromate and sodium thiosulphate in the presence of excess potassium iodide can be written by combining Eq. 5.5 and Eq. 5.8,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O \quad ...(5.5)$$

$$3I_2 + 6S_2O_3^{2-} \longrightarrow 6I^- + 3S_4O_6^{2-} \quad ...(5.8)$$

$$Cr_2O_7^{2-} + 14H^+ + 6S_2O_3^{2-} \longrightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O \quad ...(5.9)$$

We see from Eq. 5.9 that one mole of potassium dichromate is equivalent to 6 moles of sodium thiosulphate. Therefore, substituting the values of p and q in Eq.1.8, the molarities are related by the following relationship.

$$\frac{M_1 V_1}{M_2 V_2} = \frac{6}{1}$$

or $M_1 V_1 = 6M_2V_2$

Factor '6' here signifies that one mole of $K_2Cr_2O_7$ liberates 3 moles of I_2 which is equivalent to 6 moles of sodium thiosulphate.

where M_1 and M_2 represent the molarities of sodium thiosulphate and potassium dichromate solutions and V_1 and V_2 represent the volumes of sodium thiosulphate and potassium dichromate solutions, respectively.

5.3 EXPERIMENT 7 : DETERMINATION OF PERCENTAGE OF COPPER IN THE GIVEN SOLUTION BY IODOMETRIC METHOD

Many a time, an analytical chemist is confronted with the problem of finding out the amounts of some metals, e.g., Fe, Cu, etc. in a given sample. The sample may be of an ore or an alloy. Let us see how we carry out such an estimation for Cu in a given sample. We can do this by iodometric titrations. As said before, like permanganatometry and chromatometry, this titration is also based on a redox reaction.

To determine the amount of Cu in a given sample, a known mass of it is dissolved by suitable chemical treatment giving a solution of Cu^{2+} ions. This solution is titrated against a standard solution of sodium thiosulphate in the presence of an excess of KI. The Cu^{2+} ions on reacting with KI get reduced to Cu^{+} ions and liberate an equivalent amount of I_2 by oxidising I^- ions. This liberated iodine then reacts quantitatively with $S_2O_3^{2-}$ ions, and in turn, gets reduced to I^- ions. The principle and the equations involved are given in the next sub-section.

5.3.1 Principle

The reaction between Cu^{2+} and $Na_2S_2O_3$ in acidic medium, in the presence of excess of KI, involves oxidation of $S_2O_3^{2-}$ to $S_4O_6^{2-}$, tetrathionate ion, and reduction of Cu^{2+} to Cu^{+}. The reaction between Cu^{2+} and KI is given as,

$$2I^- \rightleftharpoons I_2 + 2e \quad \text{...(5.10)}$$
$$Cu^{2+} + e \rightleftharpoons Cu^{+} \quad \text{...(5.11)}$$

Balancing the reaction between Cu^{2+} and potassium iodide by combining Eq. 5.10 and Eq. 5.11, we get,

$$2I^- \rightleftharpoons I_2 + 2e \quad \text{...(5.10)}$$
$$[Cu^{2+} + e \rightleftharpoons Cu^{+}] \times 2 \quad \text{...(5.11)}$$
$$2Cu^{2+} + 2I^- \longrightarrow 2Cu^{+} + I_2 \quad \text{...(5.12)}$$

We see that two moles of Cu^{2+} react with two moles of potassium iodide and the liberated iodine reacts with sodium thiosulphate, shown earlier also, in the following manner:

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e \quad \text{...(5.6)}$$
$$I_2 + 2e \rightleftharpoons 2I^- \quad \text{...(5.7)}$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \quad \text{...(5.8)}$$

The net chemical reaction involving a titration of copper (II) and sodium thiosulphate in the presence of excess potassium iodide can be written by combining Eq. 5.12 and Eq. 5.8.

$$2Cu^{2+} + 2I^- \longrightarrow 2Cu^{+} + I_2 \quad \text{...(5.12)}$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \quad \text{...(5.8)}$$
$$2Cu^{2+} + 2S_2O_3^{2-} \longrightarrow 2Cu^{+} + S_4O_6^{2-} \quad \text{...(5.13)}$$

We see from Eq. 5.13, that two moles of copper (II) are equivalent to two moles of sodium thiosulphate. In other words one mole of copper (II) is equivalent to one mole of sodium thiosulphate.

Therefore, substituting the values of p and q in Eq. 1.8, the molarities are related by the following relationship :

$$\frac{M_3 V_3}{M_4 V_4} = \frac{1}{1}$$

or $M_3 V_3 = M_4 V_4$

where M_3 and M_4 represent the molarities of sodium thiosulphate and copper (II) solutions, and V_3 and V_4, the volumes of sodium thiosulphate and copper (II) solutions, respectively.

According to the above discussion, the iodometric determination of Cu^{2+} ions is based on the following reaction :

$$2Cu^{2+} + KI \longrightarrow 2CuI + 4K^+ + I_2 \quad \text{...(5.14)}$$
(excess)

where cupric ions are reduced to cuprous ions and iodide ions are oxidised to iodine. A look at the standard reduction potentials of Cu^{2+}/Cu^+ and I_2/I^- couples :

$$Cu^{2+} + e \rightleftharpoons Cu^+ \qquad E^0 = 0.17\ V \quad \text{...(5.15)}$$

$$I_2 + 2e \rightleftharpoons 2I^- \qquad E^0 = 0.54\ V \quad \text{...(5.1)}$$

suggests that the reaction represented by Eq. 5.14 should proceed in the reverse direction, i.e. iodine should oxidise Cu^+ to Cu^{2+}, but actually the reaction occurs as given in Eq. 5.14. The CuI formed during the reaction has a very low solubility in water, therefore, the concentration of the reduced form, Cu^+, is greatly reduced and the potential of Cu^{2+}/Cu^+ couple becomes greater than that of $I_2/2I^-$. This explains the actual course of reaction.

SAQ 2

Write the chemical equations involving a titration of copper (II) with thiosulphate in presence of excess KI.

[Hint : It involves two steps]

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5.3.2 Requirements

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flasks (250 cm^3) – 1
Beaker (250 cm^3) – 2
Funnel (small) – 1
Volumetric flask (250 cm^3) – 1
Measuring cylinder (10 cm^3) – 1
Test Tube – 1
Wash bottle for distilled water – 1
Weighing bottle – 1
Volumetric flask (1000 cm^3) – 1
Burette stand – 1

Chemicals

Potassium dichromate
Dilute sulphuric acid
Potassium iodide
Glacial acetic acid
Potassium thiocyanate
Distilled water

Solutions Provided

Procedures for the preparation of these solutions are given for the sake of information. These solutions would be prepared for you by the counsellor.

Preparation of solution of Cu^{2+} ions from Cu wire

Some clean copper wire is taken. If tarnished, it is cleaned first with fine emery cloth, or rinsed with dilute sulphuric acid, washed well with water, and dried before weighing. An amount of 1.5 g of the wire is weighed and placed in a 250 cm^3 conical flask. Then 5-10 cm^3 of 6*M* nitric acid is added. If the reaction is slow to start, a few drops of concentrated nitric acid are added. If the reaction goes too fast, a small watch glass is put over the top of the flask to catch the spray. The copper wire is dissolved by warming the solution on a water bath over a low flame. When all the copper has dissolved, the solution is diluted with about 50 cm^3 water and boiled gently for 10 minutes to remove oxides of nitrogen. Then 1 g of urea is added and the solution boiled for five minutes. The solution is cooled to room temperature and neutralised with 1:3 ammonia solution adding ammonia carefully, mixing well, until a faint permanent light blue precipitate of $Cu(OH)_2$ appears. In case the solution becomes deep blue on addition of ammonia, the latter is boiled off. Then glacial acetic acid is added a drop at a time, until the precipitate is dissolved and the solution is clear. The solution is transferred to a 1000 cm^3 volumetric flask, made up to the mark with distilled water, and shaken well to get a homogeneous solution.

Sodium thiosulphate solution (approx. *M*/50)

About 5g of sodium thiosulphate crystals are dissolved in 1dm^3 of water that has

been recently boiled and cooled. An amount of 0.2 g of sodium bicarbonate is added as a preservative and the solution stored in a clean bottle. Sodium thiosulphate solutions are somewhat unstable. Apart from oxygen and dissolved CO_2 they are easily attacked by air-borne bacteria with the liberation of sulphur. In case any turbidity is observed, the solution should be discarded.

Starch Solution: About 150 cm^3 distilled water is heated to boiling in a beaker. While this is being heated, 0.5 g to 1 g of soluble starch is stirred with about 10 cm^3 of distilled water to give a paste. The paste is stirred into the boiling water and boiled gently for a few minutes and cooled. The solution should be almost clear. It is kept in a stoppered bottle. (Starch solution should be freshly prepared before use).

Potassium Iodide Solution: Prepared by dissolving 5.0 g KI in 100 cm^3 of distilled water.

5.3.3 Procedure

Preparation of standard potassium dichromate solution: Prepare this solution using the same procedure as given in Experiment 6.

Standardisation of sodium thiosulphate solution

Pipette 20 cm^3 of potassium dichromate solution in a 250 cm^3 conical flask, add 10 cm^3 of dilute sulphuric acid and 1 g sodium hydrogen carbonate with gentle swirling to liberate carbon dioxide. Sodium hydrogen carbonate maintains an atmosphere of CO_2 in the solution which displaces the air and prevents the oxidation of iodide from air. The reaction $4I^- + O_2 + 4H^+ \rightleftharpoons 2I_2 + 2H_2O$ is catalysed by light, heat and acids. Then add 0.5 g potassium iodide or 10 cm^3 of 5% KI solution, swirl, cover the flask with a watch glass and allow the solution to stand for 5 minutes in a dark place. Titrate against sodium thiosulphate solution from the burette until a light pale yellow colour of iodine appears. Then add 2 cm^3 starch solution and continue to titrate until the blue colour of starch-iodine complex disappears on addition of a drop of the titrant. The final solution will be green coloured because of the presence of chromium (III) ions. Record the burette readings before and after the titration in observation Table I. Repeat the same exercise to get at least two concordant readings.

Titration of Copper (II) Solution

After standardising sodium thiosulphate solution, you can titrate the solution containing Cu^{2+} ions. For this, pipette out 20 cm^3 aliquot into a 250 cm^3 conical flask, and add 0.5 g solid potassium iodide or 10 cm^3 of 5% KI solution, swirl it to dissolve; then titrate with the standardised sodium thiosulphate which is taken in a burette. When the brown colour of iodine becomes pale yellow, add 2 cm^3 of fresh starch solution. The colour of the solution at this stage is deep blue. Swirl the flask for about 15 seconds and complete the titration adding sodium thiosulphate solution dropwise. During the titration, as CuI is formed, it absorbs I_3^- on the surface, as a result the reaction of I_2 with $Na_2S_2O_3$ titrant is very slow. Therefore, very close to the end point, when the colour is very light blue, add 1 g potassium thiocyanate, KSCN. Thiocyanate added at this stage reacts with CuI and forms CuSCN displacing iodine from the surface, making it available for the reaction.

$$CuI + SCN^- \rightleftharpoons CuSCN + I^-$$

However, if thiocyanate is added earlier during the titration, it will be slowly oxidised to sulphate by iodine. At the end point, the blue colour of the solution disappears and the precipitate appears white, or slightly grey, when allowed to settle. After standing for a couple of minutes at the end point, the precipitate should become pure white. Record the burette readings in observation Table II. Repeat the same exercise to get at least two concordant readings.

SAQ 3

During iodometric titrations, starch is added only towards the end of the titration. Why?

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SAQ 4

Why is sodium hydrogen carbonate or sodium bicarbonate added in the standardisation of sodium thiosulphate using potassium dichromate as titrand?

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5.3.4 Observations

Mass of the weighing bottle = m_1 = ... g
Mass of bottle + potassium dichromate crystals = m_2 = ... g
Mass of the bottle (after transferring $K_2Cr_2O_7$) = m_3 = ... g
Mass of potassium dichromate transferred = $m_2 - m_3 = m$ = ... g

Molar mass of potassium dichromate = 294.19 g mol^{-1}
Volume of $K_2Cr_2O_7$ prepared (V) = 250 cm^3
Molarity of $K_2Cr_2O_7$ solution = M_1

$$= \frac{m \times 4}{\text{Molar mass}} \text{ mol dm}^{-3}$$

$$= \frac{m \times 4}{294.19}$$

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

Observation Table I
Potassium dichromate solution vs. sodium thiosulphate solution

Sl. No.	Volume of $K_2Cr_2O_7$ solution in cm^3	Burette reading		Volume of $Na_2S_2O_3$ solution in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Sodium thiosulphate solution vs. copper (II) solution prepared from copper wire

Sl. No.	Volume of Copper (II) solution in cm^3	Burette reading		Volume of $Na_2S_2O_3$ solution in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

5.3.5 Calculations

Estimation of the strength of sodium thiosulphate solution

Molarity of $K_2Cr_2O_7$ solution = M_1 = ... mol dm^{-3}
Volume of $K_2Cr_2O_7$ solution = V_1 = 20 cm^3
Volume of $Na_2S_2O_3$ solution used = V_2 = ... cm^3
(From Table I)
Molarity of $Na_2S_2O_3$ solution = M_2 = ?
Using the molarity equation,

$$M_1V_1 = M_2V_2$$

Molarity of $Na_2S_2O_3$ solution = $M_2 = \frac{M_1V_1}{V_2}$

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

Estimation of the strength of Copper (II) solution prepared from copper wire

Molarity of $Na_2S_2O_3$ solution = $M_3 = M_2$ = ... mol dm^{-3}
Volume of $Na_2S_2O_3$ solution used = V_3 = ... cm^3
Volume of copper (II) solution taken = V_4 = 20 cm^3

Molarity of copper (II) solution = M_4 = ?
Using molarity equation $M_4V_4 = M_3V_3$,

$$\text{Molarity of copper (II) solution} = M_4 = \frac{M_3V_3}{V_4}$$

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

Determination of the amount of copper present in copper wire

Mass of copper present in 1 dm^3 of the solution prepared from copper wire = Molarity of the solution × atomic mass of copper

$$= M_4 \times 63.5 = m_4 = \text{.....} \ gdm^{-3}$$

$$\% \text{ of Cu} = \frac{m_4}{1.5} \times 100$$

= ..... %

5.3.6 Result

The percentage of copper in the given copper wire = ...%. You can compare the above value with the actual one which you can get from your counsellor.

5.4 COLORIMETRY

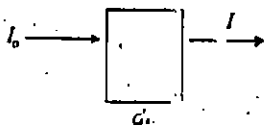
Colorimetry is based on the measurement of the intensity of colour to find the concentration of a given solution. Intensity of the colour depends on the concentration of the species which may be ions, molecules or a complex causing it. The species to be determined may possess an intrinsic capacity to impart colour to the solution or it may give a distinct colour on being complexed with a suitable reagent.

When light of an appropriate wavelength is passed through a coloured solution contained in a cell, a fraction of the light is absorbed depending on the concentration of the absorbing species and the thickness of the absorbing medium, and the rest of the light is transmitted. Though some light is reflected back from the solution, its amount is negligibly small and is eliminated by using a control. For all practical purposes we may say,

$I_0 = I_a + I_t$

where,

I_0 = Intensity of incident light
I_a = Intensity of light absorbed
I_t = Intensity of transmitted light.



The relationship between the intensity of incident radiation and that of the transmitted one is best given by **Lambert's** and **Beer's** laws which correlate I_a with the thickness and concentration of the medium, respectively. Let us understand these two laws first.

Lambert's Law

According to this law, when a light beam passes through a medium/solution, equal fractions of the incident light are absorbed by layers of equal thickness or we may say that the differential decrease in intensity with thickness of the absorbing medium is proportional to the intensity of the incident light. Mathematically,

$$-\frac{dI}{dl} = kI$$

where,

k = proportionality constant
l = thickness

Rearranging, we get,

$$-\frac{dI}{I} = kdl$$

Integrating and taking the condition that, when $l = 0$, $I = I_o$, we get,

$$\log_e \frac{I}{I_o} = -kl$$

or

$$\log_{10} \frac{I_o}{I} = \frac{kl}{2.303}$$

$$\frac{k}{2.303} = K$$

$\log_{10} \frac{I_o}{I}$ is called **'absorbance'** while K (k/2.303) is referred to as the **absorption coefficient.**

Beer's law

This law states that the intensity of a beam of light decreases exponentially as the concentration of the medium decreases arithmetically. We may say that the differential decrease in the intensity of light as a function of concentration is directly proportional to the intensity of the incident light.

$$\frac{-dI}{dc} = kI$$

Rearranging, we get,

$$\frac{-dI}{I} = kdc$$

Integrating and putting the condition that when $c = 0$, $I = I_o$, we get,

$$\log_e I/I_o = -kc$$

$$\text{or } \log_{10} I_o/I = \frac{kc}{2.303} = Kc$$

$\log I_o/I = A$, i.e., **absorbance**

K = **absorption coefficient**

As you can see $K = K$

5.4.1 Beer-Lambert Law

The two laws explained above are combined to give the commonly known Beer-Lambert law which states that the fraction of light absorbed by a given absorbing medium is directly proportional to the thickness of the medium and the concentration of the absorbing species. Solving the mathematical expression similar to the one in Lambert's law and Beer's law, we get,

$$\boxed{A = \varepsilon cl} \qquad \text{...(5.16)}$$

where,

l = thickness of the medium

c = concentration in mol dm^{-3}

ε = molar absorption coefficient

ε the **molar absorption coefficient** is the absorbance of a solution having unit concentration, 1M, placed in a cell of unit thickness, 1 cm. Absorbance is also called **optical density (OD).**

According to Eq. 5.16, the absorbance or OD of a solution in a container of fixed path length is directly proportional to the concentration. A plot between absorbance and concentration is expected to be linear and a solution showing such a behaviour is said to obey Beer-Lambert law. Dilute solutions obey the law over a considerable concentration range, the upper limit varies from system to system. At higher concentrations discrepancies are found which are attributed to the changes occurring in the coloured solute, which may undergo association at higher concentration. It is, therefore, advisable to prepare a calibration curve using a series of standards of known concentration.

There are a number of instruments in which a colorimetric determination can be made. We will make use of a simple instrument called colorimeter. The details of the instrument and the instructions for its use are discussed in the instruction manual. Further, the use of the instrument would also be explained by your counsellor. The basic principle on which the instrument is based is briefly given here. Before going over to that try the following SAQ.

SAQ 5

Tick ✓ in front of the right statements and put × in front of the wrong statements given below :

i) Transmittance of a sample increases with a decrease in absorbance.
ii) Absorbance of a sample decreases with an increase in its concentration.
iii) Absorbance of a sample is independent of its length.
iv) An air bubble in the sample will not affect the value of absorbance.

5.4.2 Principle of Colorimeter

Generally one determines the intensity of a given colour by the use of one's eyes, i.e. we have a visual estimate of the colour. We can compare two colours and within the limits of human error we may differentiate between the deeper and the lighter colour. But it is difficult to quantify colour **VISUALLY**. For this we need the help of a measuring device. A photoelectric colorimeter is such a device. This, too, gives an indirect estimate. It does not measure the colour, rather it measures the amount of light which comes out after passing through the solution. Knowing the initial intensity of light, we can work out the amount of light absorbed.

A colorimeter consists essentially of a light source, a cell/cuvette for holding the solution, a photoelectric cell to capture the radiation transmitted by the solution and a measuring device to detect the response of a photocell.

A schematic diagram is given in Fig. 5.1. There are three light emitting diodes (LEDs) in the colorimeter which you are going to use. These emit light of different colours. You would be using one of them depending on the colour of absorbing medium. The light from the source is made to pass through a slit so that we get a thin ray, which falls on the cell containing the solution. Some of the light is absorbed and the rest is transmitted. The transmitted light falls on the photocell where a current is generated, whose magnitude is proportional to the intensity of the light falling on it. This current signal is suitably amplified and then measured by the help of an ammeter. The deflection on the meter is proportional to the light intensity. The intensity of incident light is measured by putting only distilled water in the cuvette, when no light is absorbed and the whole of it falls on the photocell. In case the solution is made in a solvent other than water, the reference sample taken as the pure solvent. The difference of the two readings gives the amount of light absorbed.

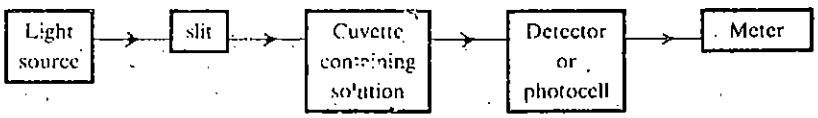


Fig.5.1 : Schematic diagram of a colorimeter

5.5 EXPERIMENT 8: DETERMINATION OF PERCENTAGE OF COPPER IN THE GIVEN SOLUTION USING COLORIMETRIC METHOD

In the previous experiment, you estimated copper using an indicator titrimetric method. In this experiment, you will use the instrument, colorimeter, for the same.

Colorimetric determinations are possible only when the colours of the solutions are not too intense. Extremely dilute solutions can be used for such determinations when volumetric methods do not work. These methods are also used widely because of their high speed. You will know the advantages of colorimetry when you do this experiment. You have already read the Beer-Lambert law on which colorimetric determinations are based. Now you will read and learn the principle on which this experiment is based, and about the instrument and its calibration, procedural details and plotting a calibration curve in the following subsections.

5.5.1 Principle

The colorimetric determination of copper in a given solution is based on a simple principle. As you know, the blue colour of copper salts is due to hydrated Cu^{2+} ions. The intensity of the colour can be used as a measure of concentration of Cu^{2+} ions in the solution. Here you will prepare a number of solutions containing known but variable amounts of Cu^{2+} ions and measure their absorbance in the colorimeter to make a concentration-absorbance calibration curve. The concentration of the unknown solution is determined by the help of this calibration curve.

5 5.2 Colorimeter

The colorimeter on which you will perform your experiment is shown in Fig. 5.2.

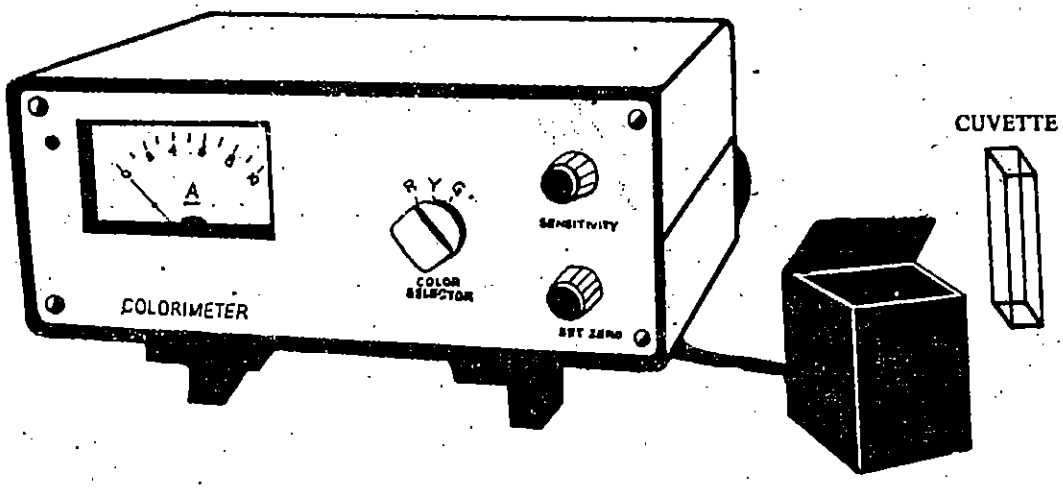


Fig. 5.2 : Colorimeter

Description of Controls

Power Switch: This is a SPST toggle switch, located on the back panel of the instrument, which turns the instrument OFF/ON. When ON, the LED on the front panel will glow if the instrument is plugged to a 220 V supply.

Colour Selector: This is a 2 pole 3 way rotary selector switch used to switch on a particular LED in the cell holder and also to bring into the amplifier circuit a particular parallel resistor. It has three positions R, Y, and G signifying red, yellow and green colours.

Set Zero: This knob is used to set the meter reading to zero when the reference solution is introduced in the cell holder.

Sensitivity: This knob is used to adjust the meter sensitivity.

Six pin plug: This is located at the right hand side of the back panel. The six pin socket from the cell holder is inserted in this plug. (Wires from the LEDs and the LDR are connected to the socket).

Before using the colorimeter, you will have to calibrate it by the procedure given below and plotting a graph to check the linearity.

5.5.3 Calibration of Colorimeter for Colorimetric Measurement

Requirements

Apparatus		Chemicals
Colorimeter with cuvettes		$CuSO_4 \cdot 5H_2O$
Burette	– 1	
Test tubes	– 10	
Test tube stand	– 1	

Caution: Do not use a plastic cuvette for organic solvents like chloroform, acetone, etc.

- Take a clear dry cuvette and fill it with distilled water or the reference solution. Note that the cuvette has two plane sides and two striated sides. Mark one of the plane sides with a pen and insert the cuvette in the cell holder with the marked side facing the LEDs inside the holder.
- **Always insert the cuvette the same way.** Close the lid of the cell holder.
- Use the **Set Zero** knob to adjust the meter reading to zero.
- Remove the cuvette, pour off the reference solution, rinse and dry it.
- Prepare 100 cm^3 of 8% copper sulphate stock solution. Fill the cuvette with the stock solution. Insert the cuvette in the cell holder in the **same orientation** as in Step 1. Close the lid of the cell holder.
- Set the **Selector** on **R.** (A copper sulphate solution has an absorption maximum in the red region. For an unknown solution, choose the LED which gives the highest meter reading, i.e. the largest absorbance.) Use the **Sensitivity** knob to adjust the meter reading near to the end of the scale (say 0.9).
- Repeat Steps 1 and 2 for setting the zero with distilled water (or the reference solution.)

Linearity Check

- Take ten clean, dry test tubes and add 10.0 cm^3, 9.0 cm^3, 8.0 cm^3, 7.0 cm^3, 6.0 cm^3, 5.0 cm^3, 4.0 cm^3, 3.0 cm^3, 2.0 cm^3 and 1.0 cm^3 of the $CuSO_4 \cdot 5H_2O$ stock solution in them respectively. Dilute each with distilled water to make 10.0 cm^3 of total volume.
- Take the same cuvette as used for calibration. Measure the meter reading, which is proportional to absorbance, for each of the solutions making sure that the cuvette is rinsed properly before pouring the solution. Also make sure that the **set zero** and **sensitivity** knobs are not disturbed throughout this set of measurements.
- Plot the meter readings against the volume of stock solution taken in each of the test tubes. A linear graph is expected as $CuSO_4$ solution is known to obey the Beer-Lambert law in this concentration range. (A linear graph also shows that the vlaue of parallel resistor for red LED is correct.)

5.5.4 Requirements

Apparatus

Colorimeter – 1
Volumetric flask (100 cm^3) – 1
Test tubes – 15
Test tube stand – 1
Measuring cylinder – 1
Beaker – 2
Burette (50 cm^3) – 1
Burette stand – 1

Solutions Provided

Cu^{2+} ion solution, prepared from copper wire using the same procedure as in the iodometry experiment. However, here the mass of Cu wire taken is 1.7 g, and the volume of solution prepared is 100 cm^3.

Stock solution of copper nitrate (10% *m/v*), prepared by dissolving 10 g of $Cu(NO_3)_2 \cdot 3H_2O$ in water and making the volume upto 100 cm^3.

5.5.5 Procedure

Before starting the experiment you will have to prepare copper nitrate solution of varying concentrations as you did for the linearity check of the instrument.

For this purpose take six test tubes and label them 1 to 6. Put $Cu(NO_3)_2 \cdot 3H_2O$ stock solution and water in the marked test tubes with the help of a burette as given in the following table :

S. No.	Volume of $Cu(NO_3)_2 \cdot 3H_2O$ stock solution	Volume of distilled water	% $Cu(NO_3)_2 \cdot 3H_2O$
1	0	10	0
2	2	8	2
3	4	6	4
4	6	4	6
5	8	2	8
6	10	0	10

Thus, you will get six solutions where the concentration of $Cu(NO_3)_2 \cdot 3H_2O$ varies from 0 – 10% as given in the table.

Before estimating Cu^{2+} ions in an unknown solution, a calibration curve will have to be plotted between the concentration and the meter response in the instrument. For this, clean the cuvette thoroughly and fill it with solution no. 1, after rinsing it with the same solution. Place the cuvette in the cuvette holder in the instrument and record the response in the meter in observation Table I. Then remove the solution and rinse the cuvette with solution no.2, fill it with the solution and once again note and record the meter response in the table. Repeat the same procedure with the rest of the solutions too. Plot the calibration curve in the graph sheet.

Wash the cuvette again and fill it with the solution whose concentration has to be determined. Place the cuvette in the cuvette holder and note the meter response. Using the calibration curve, measure the concentration corresponding to this reading.

5.5.6 Observations

Observation Table I
Meter response as a function of concentration of copper nitrate

Sl.No.	Strength of $Cu(NO_3)_2 \cdot 3H_2O$ in % *m/v*	Meter Response
1	0	
2	2	
3	4	
4	6	
5	8	
6	10	
Unknown	.....	

5.5.7 Calibration Curve

A sample reading, Table II, and a calibration curve, reproduced from the readings is shown in the graph given in Fig. 5.3 for your guidance. See it carefully, it will help you to plot the one with the readings you have noted.

Table II
Meter response as a function of concentration of copper sulphate

Sl. No.	Strength of $CuSO_4$ $5H_2O$ in % *m/v*	Meter response
1	2	1.8
2	4	3.9
3	6	6.10
4	8	8.05

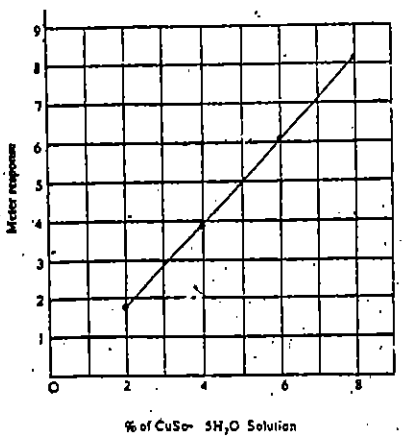


Fig. 5.3: Sample calibration curve drawn from the readings given in Table II

Now plot the observations recorded in Table I in a graph.

5.5.8 Calculations

From the graph, the % of copper nitrate solution is x% = ... %

$\Rightarrow \frac{x \times 63.5}{187.5}$ = z g of Cu/100 cm^3

mass of copper wire taken = 1.7 g/100 cm^3

% of Cu = $\frac{z}{1.7} \times 100$ = p%

= ..... %

5.5.9 Result

The percentage of copper in the given copper solution = ...%. You can compare the above value with the correct value which you can get from your counsellor.

In this unit you have used two methods for the determination of percentage of copper in a given solution. As you know, one of these methods is titrimetric indicator method, the other colorimetric which is an instrumental method. You can very well compare the two methods after having used them. The comparison can be made in terms of:

a) accuracy : Which method is more accurate? Generally the instrumental methods are more accurate because of the very obvious errors which we can make in titrimetric methods, e.g., errors of distinguishing a colour change and thus the end point, etc.

b) facility : Instrumental method is more facile.

c) time : This you can judge yourself and we are sure that you will find that the instrumental method has taken lesser time.

d) cost : For this particular experiment, KI is so expensive that one will like to avoid its use. Instead of this, you are using a low cost instrument so in terms of cost, again, instrumental method is supposed to be better.

You can discuss these experiments in the light of above points with your counsellor.

5.6 ANSWERS TO SAQs

1) i) I_2 is almost insoluble in water.
ii) I_2 is volatile in nature and is lost from an open container in a short period. It requires standardisation every few days.

2) $2CuSO_4 + 4KI \longrightarrow 2CuI + 2K_2SO_4 + I_2$
$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

$2CuSO_4 + 4KI + 2Na_2S_2O_3 \longrightarrow 2CuI + 2K_2SO_4 + 2NaI + Na_2S_4O_6$

3) The iodine-starch complex is only slightly dissociated and a diffuse end point will result if large amount of iodine were absorbed on starch.

4) Sodium bicarbonate produces CO_2 in a solution containing KI, $K_2Cr_2O_7$ and acid and displaces the air present in it. Air present in the solution, otherwise, would oxidise iodide to iodine and cause an error in the titration.

5) i) ✓ ii) × iii) × iv) ✓

UNIT 6 ANALYSIS OF WATER

Structure

6.1 INTRODUCTION

In the previous unit you were introduced to the iodometric and colorimetric methods for determining copper. In this unit you will first analyse a sample of water for hardness and alkalinity, and then for dissolved oxygen (DO).

As you know water is one of the most important substances used for life. It is indispensable to every form of life. Apart from being essential for agriculture, water has numerous industrial uses. The rapidly expanding needs for pure and clean water for drinking and recreation purposes, in the face of dwindling sources of fresh water, have raised concern among the environmentalists.

Municipal water supplies are derived from two main sources—surface water from rivers, lakes, etc. and ground water from wells, boreholes, etc., or a combination of both. Ground water is a better source of drinking water than surface waters, because most of the bacteria originally present in water are gradually filtered out as it percolates downwards through the soil.

Water, as it occurs in nature, contains organic and inorganic dissolved impurities as well as suspended solids and gases. The chemical and physical behaviour of the impurities present in water forms the basis for the procedures used in the analysis of water.

The dissolved inorganic impurities are mainly chlorides, sulphates, carbonates, and bicarbonates of sodium, potassium, calcium and magnesium. Besides these, natural water also contains dissolved oxygen and carbon dioxide.

Water containing salts of heavy metals, mainly calcium and magnesium is called **'hard water'**. Hard water is not desirable for use at home or in industry. Hardness of water precipitates soap, thus reducing its cleansing action. Dissolved solids precipitate on heating and thus clog boiler pipes and deposit on boiler plate when hard water is used for steam making. You may have noticed a similar hard white deposit called "scale" in the kettle used for boiling water for making tea.

It is important to find out the nature of the dissolved impurities present in water and also their concentration to judge whether a given sample of water is suitable for municipal or industrial use. For example, waters with high magnesium content are not suitable for drinking; similarly, waters with high iron content should not be used in paper or textile industry. High concentrations of carbon dioxide, dissolved oxygen and high salinity, if present in water, speed up corrosion.

In various water systems, the concentration of dissolved oxygen depends on various factors, such as, temperature, salinity and biological activity. Pollution by domestic sewage and industrial wastes can decrease the dissolved oxygen concentration in surface waters. Sewage contains large amounts of organic matter and also of nitrates and phosphates, which accelerate algal growth. Such growth has also been traced to excess amounts of carbon dioxide (CO_2) and carbonates (CO_3^{2-}). Bacteria decompose organic material in the sewage, and consequently use large amounts of oxygen, especially near the bottom. As a result, the large bottom fish which requires more oxygen for survival dies because of the lack of oxygen. The decrease in the amount of dissolved oxygen in water due to increased bacterial activity is called **eutrophication**. So, determination of dissolved oxygen in water is of prime importance in the study of natural waters.

There are different physical and chemical parameters like pH, conductivity, total hardness, temporary and permanent hardness, magnesium hardness, alkalinity, dissolved oxygen, chemical oxygen demand (COD) and biological oxygen demand (BOD), etc., which are used to assess the quality of water. It may not be possible for you to evaluate all these parameters. In this unit you would determine the following parameters in a water sample using chemical methods:

i) Total hardness
ii) Temporary and permanent hardness
iii) Alkalinity
iv) Dissolved oxygen

Objectives

After performing water analysis experiments, you should be able to:

- list different substances present in water obtained from natural sources,
- define total, temporary and permanent hardness,
- describe the formation of a complex of metal ions with ethylenediamine tetraacetic acid (EDTA),
- discuss the role of the buffer and the indicator in complexometric titrations,
- estimate total, temporary and permanent hardness in water by complexometric titration,
- define alkalinity of water,
- estimate total alkalinity or methyl orange alkalinity and phenolphthalein alkalinity,
- state the principle of Winkler's method for determination of dissolved oxygen in water, and
- estimate the dissolved oxygen in a sample of water by Winkler's method.

6.2 EXPERIMENT 9: DETERMINATION OF TOTAL HARDNESS OF WATER BY COMPLEXOMETRY

Determination of the hardness of water is necessary for determining the quality of water for household and industrial uses. As we have stated earlier that hardness of water is due to the presence of salts of calcium and magnesium in it. When we add simple soap (not a synthetic detergent) to hard water, an insoluble substance commonly known as "soap scum" is produced. Therefore, we also sometimes define

hardness as the soap consuming capacity of water. There are two types of hardness:

i) **Temporary hardness:** This is due to bicarbonates of calcium and magnesium. Temporary hardness gets removed on boiling water, when soluble bicarbonates decompose to give insoluble carbonates, however, $MgCO_3$ is partially soluble.

Hard water causes formation of deposits or scales inside the water pipes of boilers and other water conditioning equipment.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$
$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2$$
(partially soluble)

ii) **Permanent hardness:** It is so called because it does not get removed on boiling. Permanent hardness is due to chlorides and sulphates of calcium and magnesium. Total hardness is temporary and permanent hardness together.

$$\text{Total hardness} = \text{Temporary hardness} + \text{Permanent hardness}$$

It is necessary to know temporary and permanent hardness separately to devise a suitable treatment for water softening. Hardness of water is expressed in terms of mg of $CaCO_3$ per dm^3 of water or as ppm.

Hardness is expressed in ppm of $CaCO_3$ although in Experiment 9 the hardness may be due to magnesium or other cations.

Hardness of a water sample can be determined by titration with soap solution or by complexometric titration with EDTA (Ethylenediamine tetraacetic acid) or by conductometric methods. EDTA method is accurate, simple and fast. We shall first discuss the principle of complexometric titrations.

It is usual to know $CaCO_3$ equivalent to some common salts causing hardness. 100 parts of $CaCO_3$ are equivalent to:
162 parts $Ca(HCO_3)_2$
111 parts $CaCl_2$
95 parts $HgCl_2$
136 parts $CaSO_4$
120 parts $MgSO_4$

6.2.1 Principle

In complexometric titration we use, EDTA as complexing reagent, which forms soluble complexes with metal ions like Ca^{++} and Mg^{++}. **End point** in this titration is detected by colour change of eriochrome black T indicator. As the stability of the complex and colour change of the indicator are sensitive to pH changes, the solution to be titrated must be well buffered by ammonium hydroxide-ammonium chloride buffer solution of pH 10. Let us study complexation action of EDTA and the role of metal ion indicators in detail.

Complexation Reaction

A complexation reaction with a metal ion involves the replacement of one or more of the coordinated solvent molecules by other nucleophilic groups. The groups bound to the central ion are called **ligands**. In aqueous solution, the reaction can be represented by the following equation:

$$M(H_2O)_n + nL \longrightarrow ML_n + nH_2O$$

where, L = Ligand, e.g., NH_3, CN^-, EDTA

n = Coordination number of the metal ion and represents the maximum number of monodentate ligands that can be bound to it.

In this experiment EDTA is used as the ligand. The structure of EDTA is given in Fig. 6.1. EDTA has very wide general application in analysis because of its powerful complexing action and commercial availability.

Ligands may be classified according to the number of points of attachment to the central metal ions. Monodentate ligand—with one point of attachment, e.g., cyanide ions, halide ions, molecules of water and ammonia, Bidentate ligand—with two points of attachment, e.g., oxalic acid, Polydentate ligand—with more than two points of attachment, e.g., EDTA.

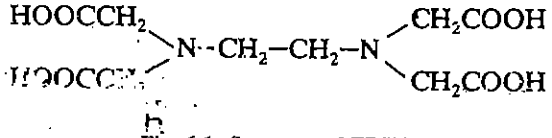


Fig. 6.1: Structure of EDTA

Abbreviation H_4Y is often employed in representing EDTA. The disodium salt of EDTA, Na_2H_2Y, also called sodium versenate, is generally used in EDTA titrations. The sodium salt is stable, can be obtained in high purity as a dihydrate and is soluble in water, whereas EDTA itself is quite insoluble. Na_2H_2Y undergoes extensive hydrolysis in solution giving H_2Y^{2-} ions. The disodium salt reacts with metal ions in 1 : 1 ratio. The reaction with cations, e.g., M^{2+}, may be written as,

$$M^{2+} + H_2Y^{2-} \longrightarrow MY^{2-} + 2H^+$$

It is apparent from the above equation that there is always a competition in the solution between the metal ions and hydrogen ions seeking the negative sites on EDTA. The equilibrium situation is determined by the strength of the bond between the metal ion and the ligand and the relative concentrations of metal ion versus hydrogen ion. In other words, we can say that the stability of a metal–EDTA complex will be governed by the hydrogen ion concentration or pH of the solution.

Table 6.1, gives minimum pH values for the stability of EDTA complexes of some selected metals.

Table 6.1: Stability with respect to pH of some metal-EDTA complexes

Minimum pH at which complex is stable	Selected Metals
1 – 3	Zr^{4+}, Hf^{4+}, Th^{4+}, Bi^{3+}
4 – 6	Pb^{2+}, Cu^{2+}, Zr^{2+}, Co^{2+}, Sb^{2+}, Mn^{2+}, Fe^{2+}
8 – 10	Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}

You can see that in general, EDTA complexes with alkaline earth metal ions are stable in alkaline solution, whilst complexes with tri- and tetravalent metal ions may exist in solution of much higher acidity. This is the reason why complexometric titrations for determining total hardness, i.e., Ca^{2+} and Mg^{2+}, are carried out at pH 10.

Metal Ion Indicators

We can titrate a metal-ion solution directly with standard EDTA solution. At the end point, the concentration of metal ion decreases abruptly. This is generally determined by change in the colour of a metal ion indicator which responds to change in metal ion concentration.

The end point may also be determined by conductometric, colorimetric, or in some cases, by potentiometric methods. Since in this experiment, we would be using metal ion indicators, we will briefly discuss them. A metal ion indicator forms a complex with a metal ion.

$$M^{2+} + HIn^{2-} \longrightarrow MIn^{-} + H^{+}$$

Where HIn^{2-} represents indicator form at a particular pH.

However, metal ion indicator complexes are generally less stable than the metal–EDTA complexes. The indicator releases the metal ions at the end point, and this shows a change in colour.

In the determination of the hardness of water, we use eriochrome black T or solochrome black as metal ion indicator. Eriochrome black T is sodium 1–(1–hydroxy–2–napthylazo)–6–nitro–2–napthol–4–sulphonate. Its structure is given in Fig. 6.2.

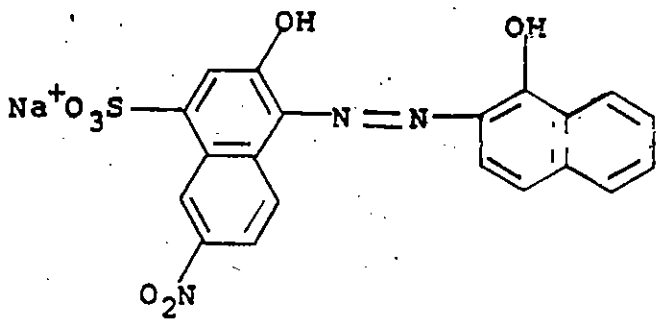


Fig. 6.2: Structure of eriochrome black-T.

e presence of metal ions, eriochrome black–T forms a wine red complex. The ır changes to blue of the free indicator when the metal ions are fully complexed EDTA at the end point in a titration.

$$MIn^- + H_2Y^{2-} \longrightarrow MY^{2-} + HIn^{2-} + H^+$$
(wine red) (colour-less) (blue)

ere H_2Y^{2-} represents disodium salt of EDTA and HIn^{2-} represents eriochrome k T in a buffer solution of pH 10.

he determination of the total hardness by EDTA titration, since Ca/Mg–EDTA ıplexes are stable at pH 8–10, the pH of the solution during the titration must be ntained at pH 10 by adding a suitable buffer like NH_4Cl/NH_4OH solution. In this ıtion, calcium ions do not form a sufficiently strong complex with eriochrome ck T, Mg–EDTA complex is added to the titration flask, if the sample either does contain sufficient magnesium ions or does not contain these ions at all to provide ıarp colour change at the end point.

Eriochrome black T has acid-base properties, which are summarised as follows,

$H_2In^- \underset{}{\overset{pH\ 8.1}{\rightleftharpoons}} HIn^{2-} \overset{pH\ 12.4}{\rightleftharpoons} In^{3-}$

(red) (blue) (orange)

Since it forms metal complexes with red form only, eriochrome black T is a useful metal-ion indicator only in the pH range 8.1 – 12.4.

emical changes during titration may be written as:

$$Ca^{2+} + H_2Y^{2-} \longrightarrow CaY^{2-} + 2H^+ \quad \ldots(6.1)$$
$$Mg^{2+} + H_2Y^{2-} \longrightarrow MgY^{2-} + 2H^+ \quad \ldots(6.2)$$
$$Mg^{2+} + HIn^{2-} \longrightarrow MgIn^- + H^+$$
$$MgIn^- + H_2Y^{2-} \longrightarrow MgY^{2-} + HIn^{2-} + H^+ \text{ (at the end point)}$$
Wine red Colourless Colourless Blue

om the Eq. 6.1 and Eq. 6.2, it is clear that one mole of the disodium salt of EDTA acts with one mole of Ca^{2+}/Mg^{2+} ions. Therefore, the molarities are related as per e following equation.

$$\frac{M_1V_1}{M_2V_2} = \frac{1}{1}$$
$$M_1V_1 = M_2V_2 \quad \ldots. (6.3)$$

Where M_1 and M_2 are the molarities of EDTA salt and metal-ion solutions, spectively. V_1 and V_2 are the volumes of EDTA salt and metal-ion solutions, spectively.

n the next section we are going to give you experimental details for determination of he total hardness of water and the method of calculation. Before that try the ollowing SAQs.

AQ 1

hy is water sample buffered at pH 10 before titration with EDTA?

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AQ 2

Explain why Mg^{2+} ion may be added when water sample is titrated with EDTA using riochrome black T as indicator.

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6.2.2 Requirements

You will need the following apparatus, chemicals and solutions for this experiment.

Apparatus
Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 2
Weighing bottle
Volumetric flask (250 cm^3) – 1
Funnel–1
Burette stand with clamp – 1

Chemicals
Disodium salt of EDTA

Solutions Provided
Water sample
NH_4OH–NH_4Cl Buffer solution, pH 10
It is prepared by dissolving 64g of NH_4Cl in distilled water, adding 570 cm^3 of ammonia solution (sp.gr. 0.88) and diluting to 1 dm^3 with distilled water.

Eriochrome black T (0.5% mass/volume)

0.50g indicator is weighed and dissolved in 100 cm^3 ethanol.

Mg–EDTA complex (0.005 *M*) solution
It is prepared by adding stoichiometric amounts of 0.01 *M* disodium salt of EDTA and 0.01 *M* $MgCl_2$. A portion of Mg–EDTA solution, when treated with a few drops of eriochrome black T at pH 10 should change to a wine red colour, which should change to pure blue on the addition of one drop of 0.01 *M* EDTA solution and wine red on addition of a single drop of 0.01 *M* $MgCl_2$ solution.

6.2.3 Procedure

The experimental procedure involves the following steps:

1) **Preparation of standard 0.01 *M* EDTA solution:** As said earlier, EDTA is available as its disodium dihydrate salt ($Na_2H_2Y.2H_2O$). First take already dried disodium salt of EDTA from the counsellor. Then take rough mass of a glass weighing bottle and transfer about 0.95 g of the salt to the weighing bottle and weigh accurately. Transfer the salt to a clean and dry volumetric flask of 250 cm^3 capacity through a glass funnel. Find out the accurate mass of the weighing bottle after transferring the salt. The difference between two masses gives the actual amount of EDTA salt taken. Record these values in your observation note book to calculate exact concentration according to the mass of the EDTA salt taken. Now, dissolve the salt in deionised or distilled water. Make up to the mark with distilled water and shake thoroughly to make a homogeneous solution.

2) **Titration of water sample**
   i) Fill the burette with the EDTA salt solution after rinsing it with this solution and mount the burette on a stand, also insert a parallex card. Note the reading in the burette and record it in the observation Table I under the 'Initial reading' column.
   ii) Pipette out 60 cm^3 of the water sample using a 20 cm^3 pipette in a 250 cm^3 conical flask, add 2 cm^3 of the buffer solution, 0.5 cm^3 of Mg–EDTA complex solution–mandatory , and five drops of eriochrome black T indicator. Colour of the mixture at this stage must be wine red.
   iii) Titrate with 0.01 *M* EDTA from the burette with constant swirling. End point is detected by the colour change from wine red through purple to a clear blue. The solution should be stirred thoroughly and the titrant added slowly near the end point.

A white crystalline precipitate of calcium carbonate may appear after the buffer is added, if the water is very hard. This should dissolve during the course of the titration. The precipitate may dissolve slowly, however, it must dissolve before the end point is reached.

In some cases, where the alkalinity of the water sample is very high, it is recommended to boil a known volume of the water sample with a few drops of HCl to remove CO_2. Cool, add a few drops of methyl red and neutralise with NaOH solution till the red colour is discharged.

iv) Note the burette reading and record in the observation Table I under the 'Final reading' column. The difference of the two readings gives the volume of EDTA salt solution used in the titration. Repeat the titration to get at least two concordant readings.

The volume of EDTA salt solution used for the titration should not be less than 10 cm^3. Adjust the volume of the water sample accordingly.

6.2.4 Observations

Approximate mass of the weighing bottle = m_1 = ...g

Mass of the weighing bottle + EDTA (before transferring the salt) = m_2 = ...g

Mass of the weighing bottle (after transferring the salt) = m_3 = ...g

Amount of EDTA salt transferred = $m_2 - m_3 = m$ = ...g

Molar mass (M_m) of sodium salt of EDTA = 372.3 g mol^{-1}

Volume of EDTA salt solution prepared = 250 cm^3

Molarity of EDTA salt solution

$$= M_1 = \frac{m \times 1000}{M_m \times 250} \text{ mol dm}^{-3}$$

$$= \frac{m \times 4}{372.31} \text{ mol dm}^{-3}$$

Observation Table I
Water sample vs EDTA salt solution

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of EDTA salt in cm^3 (Final − Initial)
		Initial	Final	
1	60			
2	60			
3	60			

6.2.5 Calculations

Estimation of total hardness of water sample

Molarity of EDTA salt solution = $M_1 = m \times 4/372.3$ = ... mol dm^{-3}

Volume of EDTA salt solution used (From Table I) = V_1 = ... cm^3

Volume of water sample = V_2 = 60 cm^3

Molarity of Ca^{2+}/Mg^{2+} in the water sample = M_2 = ?

Using Eq. 6.3,

$$M_1 V_1 = M_2 V_2$$

Molarity of Ca^{2+}/Mg^{2+} in water sample

$$M_2 = \frac{M_1 V_1}{V_2} \text{ mol dm}^{-3}$$

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

Total hardness of water sample in mg of $CaCO_3$ in one dm^3 of water

= M_2 × Molar mass of $CaCO_3$ × 1000

Molar mass of $CaCO_3$ = 100.09

For all the practical purposes this may be taken as 100.00 for the sake of convenience in calculations. Now, we have,

Total hardness of water sample = $M_2 \times 100 \times 1000$ = ... ppm of $CaCO_3$.

6.2.6 Result

Total hardness of the given sample of water = ... ppm of $CaCO_3$.

Hardness of more than 300-500 mg dm^{-3} of $CaCO_3$ is considered excessive for public water supply and results in high soap consumption as well as objectionable scale in heating vessels and pipes. Keeping these points in view, discuss the suitability of water sample given to you.

6.3 EXPERIMENT 10: DETERMINATION OF PERMANENT AND TEMPORARY HARDNESS OF WATER

In Experiment 9, you have determined the total hardness of water, i.e., temporary + permanent hardness. As we have discussed earlier if a water sample is boiled for sometime, bicarbonates of calcium and magnesium which cause temporary hardness are precipitated as carbonates and can be removed by filtration. If you now titrate the filtered water sample with EDTA salt, this gives you the permanent hardness only. Once permanent hardness is determined, you can easily calculate temporary hardness by subtracting the permanent hardness from the total hardness.

In this experiment, you will first remove the temporary hardness by boiling and then titrate water sample for permanent hardness. Finally you will calculate permanent and temporary hardness.

6.3.1 Principle

You are again going to use EDTA titration method, therefore, the principle involved is same as in the case of Experiment 9.

SAQ 3

Define permanent and temporary hardnesses of water and also list the compounds which are responsible for them.

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6.3.2 Requirements

You can use the apparatus, chemicals and solutions which you have prepared for Experiment 9, besides that you will need a 400 cm^3 beaker, a 250 cm^3 volumetric flask, burner, funnel and filter paper.

6.3.3 Procedure

1) First determine the total hardness of the water sample by performing Experiment 9. If you are using the same water sample, there is no need to repeat this experiment.
2) Measure 250 cm^3 of the same water sample with the help of a volumetric flask and transfer it to a 400 cm^3 beaker. Boil it for 30 minutes. Cool the sample and filter it through a filter paper, Whatman No. 1 into a 250 cm^3 volumetric flask. Magnesium and calcium carbonates, which are precipitated on boiling are filtered off. Make up the filtered sample to the mark by adding distilled or deionised water. Now, the temporary hardness has been removed and you can titrate the filtered sample with EDTA salt for permanent hardness.
3) Pipette out 60 cm^3 of the filtered sample using a 20 cm^3 pipette into a 250 cm^3 conical flask, add 2 cm^3 of buffer solution, 0.5 cm^3 of Mg – EDTA complex solution – mandatory, and five drops of eriochrome black T indicator. The colour at this stage must be wine red.
4) Fill the burette with the EDTA salt solution which is prepared for Experiment 9. Note its initial reading and record it in the observation Table I.
5) Titrate the contents of the conical flask with EDTA salt solution as directed under the procedure for total hardness and note the final reading in the observation Table I. The difference of the final and initial readings gives the

volume of EDTA salt solution used in the determination of permanent hardness. Repeat the titration to get at least two concordant readings.

6.3.4 Observation

Observation Table I
EDTA salt solution vs water sample (after boiling)

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of EDTA salt solution in cm^3 (Final − Initial)
		Initial	Final	
1	60			
2	60			
3	60			

6.3.5 Calculations

(a) **Permanent hardness of water sample**

Molarity of EDTA salt solution = M_1 = ... mol dm^{-3}
(From Experiment 9, if you are using the same EDTA solution).
Volume of EDTA solution = V_1 = ... cm^3
used (From Table I)
Volume of water sample = V_2 = 60 cm^3
Molarity of Ca^{2+}/Mg^{2+} in water sample = M_2 = ?
after boiling
Molarity of Ca^{2+}/Mg^{2+} in water sample
after boiling

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

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

Permanent hardness of water sample in mg of $CaCO_3$ in one dm^3 of water
= M_2 × Molar mass of $CaCO_3$ × 1000
= M_2 × 100 × 1000 = ... ppm of $CaCO_3$

(b) **Temporary hardness of water sample**

= Total hardness − Permanent hardness
(From Experiment 9) (From Experiment 10)
= ..... ppm of $CaCO_3$

6.3.6 Result

Permanent hardness of the given water sample = ... ppm of $CaCO_3$
Temporary hardness of the given water sample = ... ppm of $CaCO_3$

6.4 EXPERIMENT 11: DETERMINATION OF ALKALINITY OF WATER

In the previous two experiments you were introduced to the complexometric titration methods. Now, we are again going to discuss acid-base or neutralisation titration method to estimate alkalinity of water. As you may recollect neutralisation titration was discussed in Units 2 and 3.

The alkalinity of water is a measure of its quantitative capacity to neutralise a strong acid to a designated pH. The alkalinity of many surface waters is primarily due to carbonate, bicarbonate and hydroxide ions and less frequently borates, silicates and phosphates. It is, however, taken as an indication of the concentration of former.

Alkaline waters containing bicarbonates of calcium and magnesium when heated, form crust like scales in pipes thus restricting the flow of fluids. Carbon dioxide released in the reaction is corrosive.

Alkalinity values provide guidance in applying proper doses of chemicals in water and waste water treatment plants, particularly in coagulation, softening and operational control of anaerobic digestion. Alkalinity in excess of the permissible concentration is significant in determining the suitability of water for irrigation. High alkalinity in water can damage root hairs of plants.

6.4.1 Principle

As mentioned above, the primary species contributing to alkalinity are carbonate, bicarbonate and hydroxide ions. Alkalinity is determined by titration with standard solution of a strong acid using phenolphthalein and methyl orange indicators similar to Experiment 4. Besides bicarbonates, waters having a pH above 8.3 contain, normal carbonates and hydroxides also. Titration to an end point of pH 8.3 determines the alkalinity contributed by hydroxide and half that of the carbonate present as you know, at this pH carbonate gets converted to bicarbonate. This is obtained by using phenolphthalein as an indicator.

The alkalinity fraction equivalent to the amount of acid required to lower the pH of the water sample to 8.3 is called phenolphthalein alkalinity.

The amount of acid required to lower the pH to 4.5 of water sample determines the total alkalinity or methyl orange alkalinity.

The total alkalinity is determined by titration of the sample to the end point using a suitable indicator like methyl orange having a colour change at about pH 4.5.

The reactions which take place can be summed up as follows:

$$OH^- + H^+ \rightleftarrows H_2O$$
$$CO_3^{2-} + H^+ \rightleftarrows HCO_3^-$$

(end point with phenolphthalein (phenolphthalein alkalinity))

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

(end point with methyl orange (total or methyl orange alkalinity))

Alkalinity results are expressed in terms of concentration of $CaCO_3$. You know that one mole of $CaCO_3$ is neutralised by 2 moles of HCl as shown in the following equation:

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

Therefore, the molarity equation for the alkalinity can be written as,

$$M_{HCl}\ V_{HCl} = 2M_{CaCO_3}\ V_{CaCO_3} = 2M_{WS}\ V_{WS} \quad \text{..... (6.4)}$$

Where M_{WS} is the molarity of alkalinity in water sample in terms of $CaCO_3$ and V_{WS} is the volume of water sample.

We use above molarity equation to calculate phenolphthalein and methyl orange alkalinity.

Alkalinity is taken primarily as an indication of the concentration of carbonate, bicarbonate, and hydroxide ions. Presence of these ions is shown as follows,
i) Carbonate ion (CO_3^{2-}) is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.
ii) Hydroxide ion (OH^-) is present if phenolphthalein alkalinity is more than half the total alkalinity.
iii) Bicarbonate ion (HCO_3^-) is present if phenolphthalein alkalinity is less than half the total alkalinity.

A minimum quantity of 0.1 *M* sodium thiosulphate solution is added to the sample to remove traces of residual chlorine that would otherwise interfere in colour change in the determination of total alkalinity.

6.4.2 Requirements

You will need the following apparatus and chemicals for this experiment.

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 1
Weighing bottle
Volumetric flask (250 cm^3) – 1
Funnel – 1
Burette stand with clamp – 1

Chemicals

Sodium carbonate

Solutions Provided

Water sample

Hydrochloric acid (approximately *M*/50)

It is prepared by diluting 2 cm^3 of concentrated HCl to 1 dm^3 with distilled water to make an approximately *M*/50 solution.

Phenolphthalein indicator solution

It is prepared by dissolving 0.5 g of phenolphthalein in 50 cm^3 of ethanol and diluting to 100 cm^3 with distilled water.

Methyl orange indicator solution

0.1 g of methyl orange is dissolved in 200 cm^3 of distilled water.

Sodium thiosulphate (0.01 *M*)

2.48 g of $Na_2S_2O_3 \cdot 5H_2O$ is dissolved in distilled water and diluted to 100 cm^3.

Distilled water
Use distilled water having a pH higher than 6.0. If the water has a lower pH, it should be boiled for at least 15 minutes and allowed to cool to room temperature. This water should be used for the preparation of all standard solutions.

6.4.3 Procedure

As given above, you are provided with an approximate $M/50$ hydrochloric acid solution. The exact concentration of hydrochloric acid solution is determined by titrating against a standard solution of Na_2CO_3.

1) **Preparation of standard sodium carbonate solution ($M/100$):** Weigh accurately 0.26 – 0.27 g Na_2CO_3 (previously dried) in a weighing bottle. Transfer it to a clean 250 cm^3 volumetric flask. By weighing the weighing bottle again, find out by difference, the accurate mass of the salt transferred. Dissolve the salt in 100 cm^3 freshly boiled and cooled distilled water and make up the solution to the mark. Shake the solution till it is completely homogeneous.

2) **Standardisation of HCl solution:** Pipette out 20 cm^3 of the given Na_2CO_3 solution into a 250 cm^3 conical flask. Add 2–3 drops of methyl orange indicator. Your solution will turn yellow on the addition of this indicator. Titrate with HCl taken in the burette. Swirl the flask after each addition till a permanent red colour is obtained at the end point. Record your observations in observation Table I. Repeat the titration till you get two concordant readings.

3) **Titration of water sample with HCl solution**

i) Pipette 60 cm^3 of the water sample in a 250 cm^3 conical flask. Add a drop of 0.1 M sodium thiosulphate to the water sample to remove possible chlorine residues. Add 2-3 drops of phenolphthalein indicator and slowly titrate with HCl from the burette with constant swirling till the colour just disappears (pH 8.3). Record your observations in observation Table II. Repeat the titration to get at least two concordant readings.

Note: If no pink colour develops on addition of phenolphthalein to the water sample, do not titrate the sample for phenolphthalein alkalinity.

ii) Again take 60 cm^3 of the water sample as above and titrate with HCl using methyl orange indicator till a red colour is obtained (pH 4.5).

Record your observations in observation Table III. Repeat the titration to get at least two concordant readings. Adjust the volume of water sample so that the volume of HCl required is about 15 to 20 cm^3.

6.4.4 Observations

Mass of the weighing bottle	$= m_1 =$ ..... g
Mass of weighing bottle + Na_2CO_3 before transferring the salt)	$= m_2 =$ ..... g
Mass of the bottle after transferring the salt)	$= m_3 =$ ..... g
Amount of Na_2CO_3 transferred	$= m_2 - m_3 = m$ ..... g
Molar mass of Na_2CO_3	$= 106$ g mol^{-1}
Volume of Na_2CO_3 solution prepared	$= 250$ cm^3
Molarity of Na_2CO_3 solution	$= M_1$
	$= \frac{m \times 1000}{M_m \times 250}$
	$= \frac{m \times 4}{106}$
	= ..... mol dm^{-3}

Observation Table I
Na_2CO_3 solution vs HCl solution

Sl. No.	Volume of Na_2CO_3 sample in cm^3	Burette reading		Volume of HCl in cm^3 (Final – Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Water sample vs HCl solution (Phenolphthalein indicator)

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of HCl in cm^3 (Final – Initial)
		Initial	Final	
1	60			
2	60			
3	60			

Observation Table III
Water sample vs HCl solution (Methyl orange indicator)

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of HCl in cm^3 (Final – Initial)
		Initial	Final	
1	60			
2	60			
3	60			

6.4.5 Calculations

(a) Estimation of the strength of HCl solution

Morality of Na_2CO_3 solution = M_1 = $m \times 4/106$ = ... mo
Volume of Na_2CO_3 solution = V_1 = 20 cm^3
Volume of HCl solution (from Table I) = V_2 = ... cm^3
Molarity of HCl solution = M_2 = ?

Using Eq. 3.6 (Unit 3)

$$2M_1V_1 = M_2V_2$$

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

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

In this titration one mole of Na_2CO_3 reacts with two moles of HCl.

(b) Estimation of Phenolphthalein alkalinity of water sample

Molarity of HCl solution = M_3 = M_2 = ... mol dm^{-3}
Volume of HCl solution (From Table II) = V_3 = ... cm^3
Volume of water sample = V_4 = 60 cm^3
Molarity of phenolphthalein-alkalinity in water sample in terms of $CaCO_3$ = M_4 = ?

Using Eq. 6.4

$$M_3V_3 = 2M_4V_4$$

$$M_4 = \frac{M_3V_3}{2V_4}$$

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

Phenolphthalein alkalinity of water sample in mg of $CaCO_3$ in one dm^3 of wa
= M_4 × Molar mass of $CaCO_3$ × 1000
Molar mass of $CaCO_3$ = 100 g mol^{-1}

Phenolphthalein alkalinity of water sample
= $M_4 \times 100 \times 1000$ ppm $CaCO_3$
= ..... ppm $CaCO_3$

Simply, we can define phenolphthalein alkalinity as:

Phenolphthalein alkalinity

$$\text{mg of } CaCO_3 \text{ dm}^{-3} \text{ or ppm} = \frac{\left(\text{Volume of HCl (cm}^3\text{) to phenolphthalein end point}\right) \times M_{HCl} \times 100{,}000}{2 \times \text{Volume of water sample (cm}^3\text{)}}$$

(c) Estimation of methyl orange (total) alkalinity of water sample

Molarity of HCl $= M_5 = M_2 =$ ..... mol dm^{-3}
Volume of HCl $= V_5 =$ ..... cm^3
Volume of water sample $= V_6 = 60$ cm^3
Molarity of methyl orange-alkalinity in water sample in terms of $CaCO_3$ $= M_6 = ?$

Using Eq. 6.4
$M_5 V_5 = 2M_6 V_6$

$$M_6 = \frac{M_5 V_5}{2V_6}$$
$$= \text{.....} \text{ mol dm}^{-3}$$

Methyl orange alkalinity of water sample in mg of $CaCO_3$ dm^{-3}
$= M_6 \times$ Molar mass of $CaCO_3 \times 1000$
$= M_6 \times 100 \times 1000$
$=$ ..... ppm of $CaCO_3$

Simply, we can define methyl orange alkalinity as:

Total alkalinity or methyl orange alkalinity

$$\text{mg of } CaCO_3 \text{ dm}^{-3} \text{ or ppm} = \frac{\left(\text{Volume of HCl (cm}^3\text{) to methyl orange end point}\right) \times M_{HCl} \times 100{,}000}{2 \times \text{Volume of water sample (cm}^3\text{)}}$$

6.4.6 Result

Phenolphthalein alkalinity = ... ppm of $CaCO_3$
Methyl orange alkalinity = ... ppm of $CaCO_3$

6.5 EXPERIMENT 12: DETERMINATION OF THE DISSOLVED OXYGEN (DO) IN A GIVEN WATER SAMPLE

In the previous experiment, you have determined the alkalinity of a water sample. In this experiment you will be determining dissolved oxygen (DO) in a given water sample.

While oxygen itself is not a pollutant in water, its presence, particularly, its deficiency, is an indicator of several types of pollution in waters. Dissolved oxygen is necessary for life of fish and other aquatic organisms. When its concentration is less than 4 ppm, the fresh water systems are unsuitable for aquatic life, especially the game fish like trout. Oxygen is also needed to enable bacteria to oxidise organic matter present in water. Low concentration or absence of oxygen is an indicator of pollution in water. Further dissolved oxygen in boiler feed water causes corrosion of boiler plate. Its determination is, therefore, essential.

The rate at which oxygen is consumed by a sample of wat called the biochemical oxyger demand (BOD), which for polluted water is usually muc higher than for clean waters. is because of the large consumption of oxygen by bacteria as they decompose organic waste material in poll water. BOD is used to indica the amount of organic matter water.

Both chemical and instrumental methods are available for determination of dissolved oxygen. There are sensors available, which could be lowered into the water sample at any location and which would rapidly furnish a readout related to the *in situ* concentration of oxygen at that exact time and place. Oxygen electrode also has its limitations and is quite unselective for oxygen in the presence of other oxidants.

There are problems in sampling and storing water for chemical determination of dissolved oxygen, especially so if microflora remains active in the sample. Titrimetric procedure is also inconvenient for field work.

Winklers azide method for determination of dissolved oxygen in water is perhaps the most well-known of all the chemical methods used for estimation of dissolved oxygen in water. In this experiment, you will use this method to estimate dissolved oxygen in a water sample.

6.5.1 Principle

Winklers azide method of determining dissolved oxygen in water was developed in 1888 by Winkler. It involves introducing first a concentrated solution of manganese (II) sulphate, sodium hydroxide and potassium iodide — azide reagent into the water sample. The white precipitate of manganese (II) hydroxide $Mn(OH)_2$ is formed, and is oxidised by dissolved oxygen in the water sample to give a brown precipitate of manganese (III) hydroxide, $Mn(OH)_3$. The sample is then said to be fixed and can be stored in this condition indefinitely. In the presence of sulphuric acid, manganese (III) hydroxide dissolves and liberates free iodine from the potassium iodide added, in an amount exactly equivalent to the amount of dissolved oxygen in the water sample. In the presence of excess iodide ions, the liberated iodine (I_2) is present in the form of I_3^-. The amount of liberated iodine is then estimated by titrating against sodium thiosulphate using starch as an indicator.

The series of reactions which take place can be summarised by the following equations:

$$MnSO_4 + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4$$
$$4Mn(OH)_2 + O_2 + 2H_2O \longrightarrow 4Mn(OH)_3$$
$$Mn(OH)_3 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + O$$
$$2KI + H_2SO_4 + O \longrightarrow K_2SO_4 + H_2O + I_2$$
$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

The ratio between the moles of dissolved oxygen in the sample and the moles of thiosulphate needed to react with liberated I_2 can be deduced from the following:

$$4Mn(OH)_2 + O_2 + 2H_2O \longrightarrow 4Mn(OH)_3$$
$$4Mn(OH)_3 + 4I^- + 12H^+ \longrightarrow 4Mn^{2+} + 2I_2 + 12H_2O$$
$$2I_2 + 4S_2O_3^{2-} \longrightarrow 2S_4O_6^{2-} + 2I^-$$

From the above equations, it is clear, two moles of I_2 are liberated per mole of O_2 and since each I_2 reacts with two $S_2O_3^{2-}$, one mole of O_2 will be equivalent to four moles of sodium thiosulphate that the stoichiometric ratio between the moles of oxygen in the water sample and moles of thiosulphate used is 1 to 4, i.e.,

$$O_2 = 2I_2 = 4S_2O_3^{2-}$$

Therefore , if $M_{Na_2S_2O_3}$ is the molarity of sodium thiosulphate solution, M_{DO} is the molarity of dissolved oxygen in the water sample and $V_{Na_2S_2O_3}$ is the volume of sodium thiosulphate used for the titration of water sample and V_{DO} is the volume of water sample, respectively, substituting these values for p and q in Eq. 1.8 the molarities are related as per the following equation.

$$\frac{M_{Na_2S_2O_3}\, V_{Na_2S_2O_3}}{M_{DO}\, V_{DO}} = \frac{4}{1}$$

or $$M_{Na_2S_2O_3}\, V_{Na_2S_2O_3} = 4M_{DO}\, V_{DO} \qquad ...(6.5)$$

The main interference in this process is due to the presence of nitrites. These react with KI and liberate iodine according to the following equation,

$$2HNO_2 + H_2SO_4 + 2KI \longrightarrow 2NO + K_2SO_4 + 2H_2O + I_2$$

This liberated iodine will also use up thiosulphate. Sodium azide is, therefore, used in this process to take care of any nitrite present in the water sample, it distroys the nitrite when the sample is acidified,

$$2NaN_3 + H_2SO_4 \longrightarrow \underset{\text{(Hydrazoic acid)}}{2HN_3} + Na_2SO_4$$

$$HNO_2 + HN_3 \longrightarrow NO_2 + N_2 + H_2O$$

Standardisation of sodium thiosulphate solution

This method is based on the principle of iodometry, which has been discussed in Unit 5. In this case, potassium dichromate oxidises iodide to iodine in the acidic medium according to the reaction,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O \quad ...(6.6)$$

The librated iodine, similar to iodometric titration, is titrated with sodium thiosulphate solution according to the reaction,

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^- \quad ...(6.7)$$

On combining Eq. 6.6 and 6.7, we get,

$$Cr_2O_7^{2-} + 6S_2O_3^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O \quad ...(6.8)$$

We see from Eq. 6.8, that one mole of potassium dichromate reacts with 6 moles of sodium thiosulphate. Therefore, substituting the values for p and q in Eq. 1.8, the molarities are related as per the following equation:

$$\frac{M_{K_2Cr_2O_7}\, V_{K_2Cr_2O_7}}{M_{Na_2S_2O_3}\, V_{Na_2S_2O_3}} = \frac{1}{6}$$

$$6M_{K_2Cr_2O_7}\, V_{K_2Cr_2O_7} = M_{Na_2S_2O_3}\, V_{Na_2S_2O_3} \quad ...(6.9)$$

SAQ 4

Mark the following as true (T) or false (F).

a) Dissolved oxygen is necessary for life of fish and other aquatic organisms.
b) Concentration of dissolved oxygen less than 4 ppm is unsuitable for aquatic life.
c) Concentration of oxygen is a good indicator of polluted waters.
d) Dissolved oxygen is desirable for industrial water supply.

SAQ 5

What is the role of manganese (II) sulphate and alkaline potassium iodide solution in the detection of dissolved oxygen?

.....

.....

.....

.....

.....

.....

6.5.2 Requirements

Apparatus

Burette (50 cm³) – 1
Pipette (20 cm³) – 1
Conical flask (250 cm³) – 1
Weighing bottle
Volumetric flask – 1
Stoppered bottle (250 cm³) – 1
Dropper (2 cm³) – 1
Burette stand with clamp – 1

Chemicals

Sodium bicarbonate
Conc. sulphuric acid or
Phosphoric (V) acid

Potassium iodide

Solutions Provided

Water sample.

Manganese (II) sulphate solution: It is prepared by dissolving 50 g of manganese (II) sulphate pentahydrate in distilled water and making up to 100 cm³.

Alkaline iodide-azide solution: It is prepared from 40 g of sodium hydroxide, 20g of potassium iodide and 0.5g of reagent grade sodium azide (NaN_3) made up to 100 cm³ with water. Sodium azide is added to the cooled solution

Caution: Sodium azide is poisonous, it may also explode if exposed to heat. Handle with care.

Note: Both manganese (II) sulphate and alkaline iodide-azide solutions are added to the water sample just below the surface of water with the help of the jet arrangement attached to the burette (see Fig. 6.3).

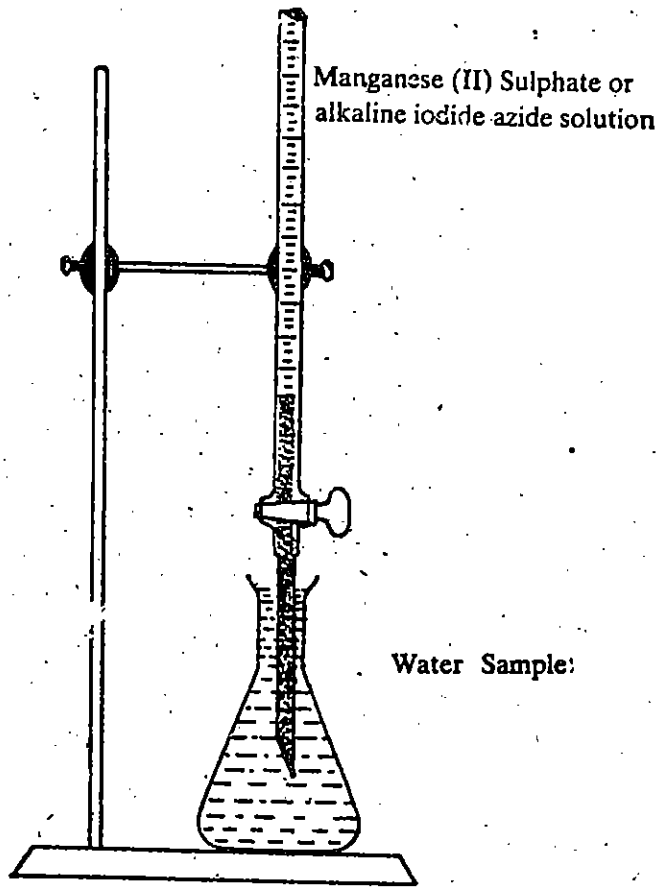


Fig. 6.3: Arrangement for the addition of manganese (II) sulphate and alkaline iodide-azide solutio

Sodium thiosulphate solution (*M*/80): Prepared by dissolving 3.15g sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in distilled water and making up to the mark in a 1dr volumetric flask with distilled water. If the solution is to be kept for more than a fe days, 0.1g sodium carbonate or three drops of chloroform may be added to avoid decomposition of sodium thiosulphate.

Standard potassium dichromate solution (*M*/480): It is prepared by accurately weighing about 0.125g of dry potassium dichromate in a weighing bottle by the usu method, transferring it into a $1dm^3$ volumetric flask, dissolving in a small quantity o water, making it up to the mark with distilled water, and mixing thoroughly.

Dilute Sulphuric acid: As mentioned in Experiment 7

Starch solution: A smooth paste of 2g of soluble starch is made and added a little a a time to $1dm^3$ of boiling water with constant stirring. Heating is continued until the solution becomes clear. The solution is cooled and preserved by adding 1.25 g salicy acid or a fe. drops of toluene.

6.5.3 Procedure

As you know, sodium thiosulphate is not a primary standard, therefore, you would first have to standardise it by titrating with a standard solution of potassium dichromate.

Solid sodium bicarbonate is added to make a cover of carbon dioxide in the reaction flask during the titration to prevent oxidation of hydroiodic acid by oxygen of air.

1) **Titration of standard potassium dichromate with given thiosulphate solution** Fill the burette with the given solution of sodium thiosulphate. Note the initial reading of the burette and record it in the observation Table I. Pipette out 20 cm^3 of the given standard solution of potassium dichromate into a conical flask add 10 cm^3 of 10% KI solution, 2g sodium bicarbonate and 15 cm^3 dilute sulphuric acid. Cover the flask and keep it in dark for 2-3 minutes. Titrate

against sodium thiosulphate with constant stirring. When the solution acquires a greenish yellow colour, add 2.0 cm^3 of starch solution. Continue the addition of the thiosulphate solution dropwise till a light green colour is formed. This indicates the end point of the titration. Note the burette reading and record it in the observation Table I under the 'Final Reading' column. The difference of the two readings gives the volume of sodium thiosulphate solution used. Repeat the titration till concordant values are obtained.

b) **Titration of water sample:**

i) Fill a 250 cm^3 stoppered bottle with the water sample supplied. Insert the stopper carefully by allowing it to displace the water in the bottle neck without trapping air bubbles which could raise oxygen level by aerating the sample.

ii) Remove the stopper, and by using a jet attached to the burette (see Fig.6.3), add 1cm^3 of manganese (II) solution. Similarly add 1 cm^3 of alkaline iodide - azide solution. Point of the jet should be below the surface of water so that the dense reagent solutions sink to bottom displacing water. Restopper the bottle and shake the mixture well.

iii) Allow the brown precipitate of manganese (III) hydroxide to settle completely for 15 minutes and add 2 cm^3 of concentrated sulphuric acid or 2 cm^3 of concentrated phosphoric (V) acid with the help of a 2 cm^3 dropper or measuring pipette after removing the stopper. Restopper and gently shake to dissolve the precipitate. This should produce the characteristic brownish red colour of iodine. Whole of the precipitate should dissolve. If some of the dark brown precipitate persists after a few minutes, a few drops more of sulphuric acid can be added.

iv) With a pipette, transfer 100 cm^3 of the above solution for titration in a 250 cm^3 conical flask and titrate the liberated I_2 with standardised sodium thiosulphate solution until the sample solution becomes pale yellow. Add 2 cm^3 of starch solution and continue the titration till the blue colour disappears. Repeat the titration to get another reading.

6.5.5 Observations

Molarity of potassium dichromate solution $M_1 = M/480$

Observation Table I
Potassium dichromate vs sodium thiosulphate

Sl. No.	Volume of potassium dichromate solution in cm^3	Burette reading		Volume of sodium thiosulphate in cm^3 (Final – Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Water sample vs sodium thiosulphate

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of sodium thiosulphate in cm^3 (Final – Initial)
		Initial	Final	
1	100			
2	100			

6.5.6 Calculations

a) **Determination of the strength of sodium thiosulphate solution.**

Molarity of potassium dichromate solution = $M_1 = M/480$
Volume of potassium dichromate solution = $V_1 = 20$ cm^3
Volume of sodium thiosulphate solution (from Table I) = V_2 = ... cm^3
Molarity of sodium thiosulphate solution = M_2 = ?
Using Eq. 6.9,

$$6M_1V_1 = M_2V_2$$

$$M_2 = \frac{6M_1V_1}{V_2}$$

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

b) **Determination of the dissolved oxygen (DO) in the water sample**
Molarity of sodium thiosulphate solution = $M_3 = M_2 =$ ..... mol dm^{-3}
Volume of sodium thiosulphate solution (from Table II) = $V_3 =$ ..... cm^3

Volume of water sample used for titration = $V_4 = 100$ cm^3
Molarity of dissolved oxygen = $M_4 = ?$.
Using Eq. 6.5.

$$4M_4V_4 = M_3V_3$$

$$M_4 = \frac{M_3V_3}{4V_4}$$

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

Dissolved oxygen (DO) in water sample in mg dm^{-3}

$$= M_4 \times \text{Molar mass of } O_2 \times 1000$$
$$= M_4 \times 32 \times 1000 \text{ ppm}$$
$$= \text{.....} \text{ ppm}$$

6.5.7 Result

Molarity of oxygen in the water sample = ... mol dm^{-3}
Amount of dissolved oxygen in the water sample in ppm = ...

In general, the minimum dissolved oxygen level needed to support a population of fish is 4 ppm, on this basis tell whether the water sample is suitable for the purpose of fisheries or not.

6.6 ANSWERS TO SAQs

Self-assessment Questions

1) In water sample hardness is due to the Ca^{2+} and Mg^{2+} ions. From Table 6.1, you can see that EDTA complexes with these ions are stable at pH 8-10. Further, metal ion indicator, eriochrome black T is worked in pH range 8.1-12.4. Therefore, water sample should be well buffered at pH 10.

2) Ca^{2+} ions do not form a sufficiently strong complex with eriochrome black T, so, in absence of Mg^{2+} ions in water sample we could not observe an accurate end point during titration with EDTA.

3) **Temporary hardness:** This hardness is removed on boiling, therefore, it is called as temporary hardness. This is due to bicarbonates of calcium and magnesium.
Permanent hardness: It is so called because it does not get removed on boiling. Permanent hardness is due to chlorides and sulphates of calcium and magnesium.

4) (a) T (b) T (c) T (d) F (DO causes corrosion).

5) Role of these chemicals can be summarised in the form of following chemical equations:

$$MnSO_4 + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4$$
$$4Mn(OH)_2 + O_2 + 2H_2O \longrightarrow 4Mn(OH)_3$$
$$Mn(OH)_3 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + O$$
$$2KI + H_2SO_4 + O \longrightarrow K_2SO_4 + H_2O + I_2$$
$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

NOTES

Uttar Pradesh
Rajarshi Tandon Open University

UGCHE-L 6
Chemistry Lab-II

Block

1

INORGANIC PREPARATIONS AND GRAVIMETRY

CHEMISTRY LAB-II

Chemistry is an experimental science. Chemists prepare new compounds and carry out experiments to investigate their composition and structure for putting them to proper use. This laboratory course has been designed to familiarise you with the principles involved and various experimental techniques and apparatus used in the preparations and purification of inorganic compounds and their analysis by classical chemical methods.

The course contains two blocks. Block 1 deals with inorganic preparations and gravimetric determinations. It starts with describing in Unit 1 the safety rules which have to be observed in a chemistry laboratory. It describes the kind of apparatus that is used and various laboratory operations relevant to this course. In Unit 2, we discuss how to prepare and purify inorganic compounds. In Unit 3, we describe some experiments for gravimetric determination of certain inorganic ions.

Block 2 deals with the qualitative analysis of the mixtures of inorganic salts. In Unit 4, we discuss the scheme of detection of anions in inorganic mixtures. Unit 5 deals with the principles involved in the analysis of cations, whereas in Unit 6 we discuss the actual scheme of analysis of cations. This scheme of analysis of the mixtures of inorganic salts not only enables you to test the presence of ions in a mixture, but it is also one of the most effective ways to learn the chemistry of elements and the principles of equilibria in aqueous solution.

Objectives

After studying this course and performing the experiments set for you to do, you should be able to:

- take proper safety measures while working in a chemistry laboratory,
- perform common laboratory operations such as heating, evaporation, precipitation, digestion, filtration, drying, ignition, cooling, weighing, etc.
- identify and properly handle the laboratory apparatus,
- prepare and purify simple inorganic compounds,
- perform gravimetric determinations of certain inorganic ions,
- perform qualitative analysis of mixtures of inorganic salts,
- discuss the principles involved in the preparation and analysis of inorganic compounds and
- perform calculations relating to the preparation and analysis of inorganic compounds.

Study Guide

This laboratory course is of 2 credits and involves six days of intense work. You would be required to perform the experiments described in two laboratory manuals of this course. Each of the experiments would be graded and you would have to appear for the viva-voce also. Seventy per cent marks are reserved for performing these set experiments. At the end of the course, you would be required to perform assigned experiments, which would be similarly graded. 30% marks are reserved for the assigned experiments.

We would advise you to study these manuals before you come to attend this course. This will enable you to get the maximum benefit from this course.

The maintenance of a complete and up to date record of your laboratory work is an important part of your scientific training. For recording experimental data, laboratory note books are available in the market. Purchase a 80-100 page chemistry note book for this course. Bring the laboratory manuals and your laboratory note book daily to the laboratory. For each experiment, you should write down the title of the experiment, principle, observations, calculations and the result. While performing an experiment, you can note down your observations immediately in the space given in the manuals. After the experiment is complete, you should record it in your note book. The laboratory note book should be submitted to your counsellor for corrections and grading. Marks have been allotted for doing the experiments as well as for recording them properly.

BLOCK 1 INORGANIC PREPARATIONS AND GRAVIMETRY

This block deals with the preparations of simple inorganic compounds and quantitative determinations of some inorganic ions. In Unit 1 we describe the safety rules, which you should observe while working in a chemistry laboratory. We also discuss the importance of keeping a record of experiments which one performs in a laboratory. We describe how to perform various laboratory operations, such as heating, evaporation, precipitation, digestion, filtration, ignition, cooling and weighing, which are relevant to this course.

In Unit 2, we discuss the preparation of three simple inorganic compounds-potash alum, potassium trioxalatoferrate(III) and tetraamminecopper(II) sulphate. We also describe how to purify these compounds and how to calculate their percent yield.

Unit 3 deals with gravimetric analysis. In this unit, we discuss the determination of aluminium, copper, iron and sulphate ions in water soluble compounds.

Objectives

After studying this block and performing the experiments set for you to do, you should be able to:

- identify and properly handle the laboratory apparatus,
- perform common laboratory operations, such as heating, evaporation, precipitation, digestion, filtration, drying, ignition, cooling, weighing, etc.
- prepare potash alum, tetraamminecopper(II) sulphate and potassium trioxalatoferrate(III),
- calculate percent yield, and
- perform the determinations of aluminium, copper, iron and sulphate ions by gravimetry.

UNIT 1 APPARATUS AND EXPERIMENTAL TECHNIQUES

STRUCTURE

1.1 INTRODUCTION

In this unit we will discuss some of the common experimental techniques which you will use for carrying out experiments in this Chemistry Laboratory course. We will also describe the apparatus required for various experiments, in addition to the common laboratory apparatus with which you are already familiar. Safety in laboratory and preparation of a laboratory note book are very important aspects of any laboratory course. We will, therefore, first of all describe the safety measures, which you should always take in a chemistry laboratory, and how to prepare a laboratory note book.

Objectives

After studying this unit, you should be able to:

- take proper safety measures while working in a chemistry laboratory,
- record experiments in a laboratory note book,
- identify and properly handle the laboratory apparatus, and
- perform common laboratory operations such as heating, evaporation, precipitation, digestion, filtration, drying, ignition, cooling, weighing, etc.

1.2 LABORATORY SAFETY

Chemistry laboratories are potentially dangerous places because they contain inflammable liquids, poisonous chemicals and fragile glassware. Where high pressure cylinders of gases are used, they also pose a potential danger. Safety in laboratory is important not only to you, but to other students and staff also in the laboratory. Therefore, proper precautions must always be taken and safe experimental procedures must be followed while working in a chemistry laboratory.

Some important general safety precautions are given below. Any special precautions or safety measures, if required, are given in the particular experiments. You should read all these carefully and follow them faithfully.

- Wear a lab coat or an apron when working in the lab.
- Be familiar with the layout of the laboratory especially where fire extinguishers, blankets or the first aid box is.
- Learn the location of the nearest exits from your laboratory to the outside of the building.
- Never work alone in the laboratory.
- Always wear safety glasses or goggles in the laboratory. Even if you are only washing glassware and are not doing any work yourself, other students working nearby may have an accident that involves you. Unlike many chemical reactions, damage to eyes is irreversible. If you wear spectacles, make sure that they contain shatter proof lenses.
- Check the glassware before using. It should not have any cracks or imperfections.
- Almost all organic liquids are inflammable and therefore should never be heated on a naked flame. You should use a water bath, an oil bath or an electric hot plate.
- Keep the test tube pointing away from yourself and others while heating it on a burner.
- Most of the chemicals you will work with are poisonous to some degree. Even common substances such as mercury, benzene and carbon tetrachloride are poisonous and potentially dangerous. Therefore, all chemicals must be handled with caution. As far as possible direct contact with skin must be avoided. Rubber or plastic gloves can be worn while handling especially toxic compounds. Never taste anything unless specifically directed to do so. Avoid inhaling vapours of any compound. A list of some hazardous chemicals and their harmful effects is given in Table 1.1.

Table 1.1 : List of hazardous chemicals and their effects

Hazardous Chemicals	Effect
Salts of Ag, As, Ba, Cu, Hg, Ni, Pb, Sb, Tl, V, $C_2O_4^{2-}$, F^-, MnO_4^-	Most of these are very dangerous but only if swallowed. $AgNO_3$ causes caustic burns.
H_2S	Almost as poisonous as HCN. Exposure dulls the sense of smell.
SO_2, NO_2, Cl_2, Br_2, I_2, HNO_3, H_2SO_4, HF	All are dangerous as well as unpleasant. When concentrated, all cause rapid destruction of the skin; HF is especially dangerous.
$HClO_3$, $HClO_4$ and their salts	Highly oxidising
Chlorinated alkanes, e.g., $CHCl_3$, CCl_4	Most of these are narcotic, causing mental confusion.
Benzene	Toxic vapours causing dizziness.
Benzoyl chloride	Irritant.
Ether, ethanol	Very highly inflammable
Nitrobenzene	Toxic vapours.
Phenol	Burns the skin.

- A fume hood must be used for handling dangerous substances and for carrying out reactions in which noxious gases are evolved.
- Ask your Counsellor for safe disposal of chemicals and glassware. Never pour solvents and other chemicals into the sink, put them into special containers for waste.
- Do not throw used filter papers or broken glassware into the sink, put them in dustbins.
- Wash your hands with soap when you leave the laboratory after doing an experiment.
- Ensure that gas and water taps are closed before leaving the laboratory.

However, even if you are a careful worker and follow the general rules of safety, the accidents can occur-that's why they are called accidents. For such occasions, you must be fully equipped and must know what to do in such a case. There should be a first-aid box in every laboratory containing some common things like Dettol, Burnol, Band-aid, bandages,

cotton, etc. Generally, the most common accidents that occur are cuts, burns, fires, poisoning and rarely, an explosion. Let us see one by one, what first aid should be given to a student, when such a mishap occurs.

i) **Cuts** : The most common accidents in the chemistry lab are cuts from broken glassware. If you have a cut, wash the wound well with cold water immediately. If bleeding is severe, apply pressure directly on to the wound to stop the bleeding. Then an antiseptic cream can be applied to the wound with a proper dressing.

ii) **Burns** : Burns generally caused by hot equipment can be treated as the cuts are treated, that is, wash the burnt part with cold water for sometime and then apply Burnol to it. Burns are very often caused by chemicals too. Table 1.2 gives you a list of remedies for a few chemical reagents.

iii) **Fire** : A small fire in a beaker, caused by the vapours of an inflammable liquid, can be extinguished by covering it with a watch glass.

If the clothes catch fire one should lie on the floor and fire can be smothered by wrapping a blanket around the body.

iv) **Poisoning** : If one happens to swallow a poisonous chemical, plenty of water should be given if the person is conscious. For a corrosive poison, calcium hydroxide solution (lime water) should be given as soon as possible. An antidote should be given only in the case of non-corrosive poisons.

v) **Explosion** : Sometimes a faulty teachnique during the experiment can lead to an explosion. You should work with highly oxidising or explosive chemicals only under strict supervision.

Table 1.2 : Remedies for a few chemical reagents

Chemical	Remedy
Acids like HNO_3, H_2SO_4, HCl	Wash with $NaHCO_3$ or 2M ammonium carbonate (leaves no residue on clothes), then apply vaseline or a soothing cream.
Alkalies, e.g., NaOH, KOH etc.	Wash with 1M acetic acid, then apply vaseline or a soothing cream.
Bromine	Wash with 2M Ammonia, keep the affected part dipped in $NaHSO_3$ till bromine is washed off, then apply vaseline.
Phenol	Wash with ethanol and then hospital treatment.
Sodium	Ethanol on a cotton wool pad.

1.3 LABORATORY NOTE BOOK

One of the most important characteristics of a scientist is the habit of keeping good record of the work that has been done. The record should reflect all the planning that has gone in as well as the observations at various stages of the experiment. A chemist must observe things like whether there was a colour change when the reactants were mixed or a reagent was added to the solution, whether a precipitate was formed or a gas evolved, was the reaction exothermic, and record them. These observations may appear insignificant but prove helpful in correct interpretation of an experimental result.

While preparing a laboratory note book, the following important features may be kept in mind.

- Record all observations and data in the note book at the time they are obtained. Never use scraps of paper for noting things like weights of reactants taken, melting or boiling points, etc. They might get lost or mixed up.
- The record should be so thorough and well organised that on reading it, it should be possible for any one to understand what has been done and repeat it. It may not be necessary to copy out the exact procedure, since this is given in your laboratory manual. However, results should be summarised, conclusions drawn for each experiment and explanation provided if the results vary from those expected. Certain marks have been allotted for maintaining a good laboratory note book.

- The laboratory note book is a complete log of all operations. Dates, time and other information must be entered regularly.
- A bound note book should be used for laboratory record. Special laboratory note books are available, one side of the pages being ruled and the other side blank.
- All entries must be made in ink. If you commit a mistake, it should be crossed and correct entry should be made.
- The first few pages in the note book should be left for making a list of contents.

1.4 LABORATORY APPARATUS AND OPERATIONS

Wet chemical analysis and preparatory chemistry require the use of apparatus and laboratory operations with which you should become familiar. It is presumed that you are already familiar with common laboratory apparatus and glassware such as test tubes boiling tubes, beakers, conical flasks, watch glasses, funnels, glass rods, glass tubes, china dishes, pipettes, burettes, burners, test-tube stand, funnel stand, burette stand etc. In this section at proper places we will familiarise you with some more glass ware and apparatus which will be used in various experiments in this course.

Heating, evaporation, precipitation, digestion, filtration, drying and ignition, cooling, weighing are some of the important laboratory operations which you will perform during this course. Let us study these operations and the apparatus required for them in some detail.

1.4.1 Heating

Heating is one of the common operations which you frequently perform in a chemistry laboratory. You resort to heating for a variety of reasons. Heating increases the solubility of most substances. It also increases the rate of chemical reactions. You have to heat substances to dry them. In gravimetric analysis, the precipitate is sometimes heated to a high temperature to convert it into a compound of constant composition.

In this laboratory courses, you will use the following heating devices:

i) Bunsen burner

ii) Water bath

iii) Electric oven

iv) Muffle furnace

The Bunsen burner is widely employed for heating in an inorganic chemistry laboratory. It is used to attain moderately high temperatures of up to 600°C. The maximum temperature is attained by adjusting the regulator so as to admit rather more air than is required to produce a non-luminous flame.

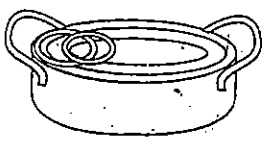


Fig. 1.1 : A copper water bath

Boiling Water baths are used for heating solutions up to 100°C, for slow evaporation of liquids to reduce their volumes and for digestion of precipitates. The simplest form of a water bath is a beaker in which water is boiled. The vessel to be heated is kept on the rim of the beaker. Copper water baths as shown in Fig. 1.1 are commercially available. These have a copper bowl fitted with a series of copper rings to adjust the size of opening. This allows heating of vessels of various sizes. The bath is partly filled with water and heated on a burner or electrically.

Electric ovens or drying ovens are very convenient heating devices. They have a temperature range from room temperature to about 300°C. The temperature can be thermostatically controlled to within ± 1-2°C. They are used mainly for drying solids or precipitates and glassware at comparatively low controlled temperatures.

Electrically heated muffle furnaces are used to ignite samples to high temperatures either to burn organic matter prior to inorganic analysis or to convert precipitates to a weighable form in gravimetric analysis. Temperatures of up to 1200°C can be attained with muffle furnaces.

1.4.2 Evaporation

During experiments, you may be asked to reduce the volume of a solution. Sometimes you may have to evaporate a solution to dryness. Both these operations can be conveniently carried out in a porcelain evaporating dish. Rapid evaporation can be achieved by heating the dish containing the solution directly on a wire gauze. If the solution is to be evaporated slowly, a water bath may be used in place of the wire gauze. If corrosive fumes may evolve during evaporation, the process must be carried out in a fume hood. When evaporating to dryness, in order to avoid bumping and spattering, you should remove the dish from the burner whilst there is still a little liquid left. The heat capacity of the hot dish is sufficient to complete the operation without further heating.

You may also accomplish the reduction in volume of a solution by direct heating in a small beaker over a wire gauze or by heating in a boiling tube held in a holder by a naked flame. But while evaporating in a boiling tube, care must be taken that the liquid does not bump violently.

1.4.3 Precipitation

Precipitation is one of the most important operations which you are very frequently required to perform in wet chemical analysis. **Precipitation** is a process in which ions present in solution are converted into an insoluble compound called **precipitate** by the addition of another compound called **precipitant** or precipitating reagent. Precipitation is usually carried out in test tubes (in qualitative analysis) or in beakers (in quantitative analysis).

The solution of precipitant is added slowly by means of a dropper, pipette or burette and with efficient stirring. The solution of the precipitant is added down the side of the precipitating vessel by avoiding splashing. Only a moderate excess of the precipitant should be added. A very large excess of precipitant may sometimes lead to dissolution or contamination of the precipitate. After the precipitate has settled, a few drops of the precipitant should always be added to ensure complete precipitation.

In qualitative analysis, the cations of Group II and IV are precipitated as their sulphides by passing hydrogen sulphide gas in their solution. A stream of gas from a Kipp's apparatus (Fig. 1.2) is bubbled through the solution contained in a test tube, beaker or conical flask. Since the gas is absorbed slowly, most of it escapes into air and is wasted. You should be aware that the gas is highly poisonous. Therefore, the gas should be used only in a fume hood and unnecessary exposure should be avoided.

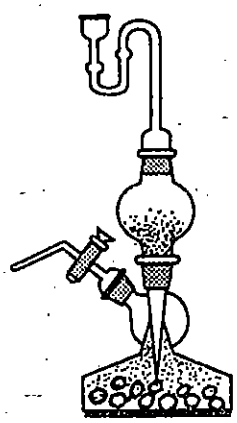


Fig. 1.2 : A Kipp's apparatus

1.4.4 Digestion

In gravimetric analysis, to ensure complete precipitation and to make all particles of filterable size the precipitate is digested before filtration. Digestion also helps in reducing the amount of absorbed impuries. In some cases digestion is carried out by settling the beaker aside and leaving the precipitate in contact with the mother liquor at room temperature for 12-24 hours. In others, where a higher temperature is permissible, digestion is usually effected by heating for 15-20 minutes near the boiling point of the solvent. The beaker is kept covered by a watch glass with its convex surface downward.

1.4.5 Filtration

Filtration is the process of separation of a solid (crystals or precipitable) from the liquid (mother liquor). Filtration is a very important and commonly used operation in chemistry laboratory. Filtration can be carried out either under atmospheric pressure (ordinary filtration) or under reduced pressure (suction filtration).

Filters for filtering precipitates are of various types. We will discuss here three types of them:

i) Filter papers

ii) Sintered glass crucible

iii) Porcelain Buchner funnel

Filter paper is frequently used to filter precipitates in qualitative analysis. In some gravimetric estimations, the precipitate is ignited at a high temperature to convert it to a well-defined compound of known composition. For example, Fe^{3+} is precipitated as hydrated iron oxide, $Fe_2O_3.xH_2O$, and ignited to Fe_2O_3 before weighing. When a precipitate is to be ignited, it should be collected in a ashless filter paper which leaves little residue on ignition. Filter paper is suitable when the precipitate is not easily reduced by the action of carbon of the paper on ignition.

Filter paper for quantitative analysis is made of various degrees of porosity. The filter paper used must be of such porosity as to retain the smallest particles of precipitate and yet permit rapid filtration. Filter papers of three grades are generally made, one for very fine precipitates such as $BaSO_4$, a second for average precipitates such as AgCl, which contain medium-sized particles, and a third for gelatinous precipitates such as $Fe_2O_3.xH_2O$.

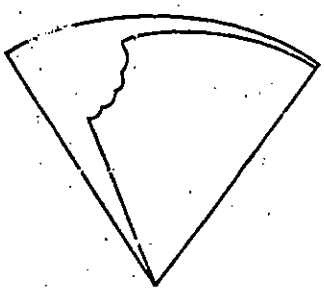


Fig. 1.3 : A properly folded filter paper

By proper folding and fitting of the filter paper in the funnel the rate of filtration can be increased. A properly folded filter paper is illusted in Fig. 1.3. The circle of filter paper is folded exactly in half. This is folded again in quarters in such a way that the vertices of the two quarters do not coincide, but are displaced about 3 mm at the corners. The outside corner of the paper is then torn off and the paper placed in a glass funnel in such a way that three layers of filter paper are on one side and a single layer on the other. To seal the paper into the funnel, the paper is moistened and the upper part pressed gently against the walls of the funnel with fingers. The upper edge of the filter paper should be about 1 cm from the upper rim of the glass funnel. The filter paper should never be more than about two-thirds full of the solution. After the filter paper is seated in the funnel, the liquid containing suspended precipitate is poured down a glass rod into the funnel as illustrated in Fig. 1.3. Care must be taken in transferring of the precipitate to avoid losses. The particles adhering to the beaker or rod are removed by scrubbing with walls with a moistened rubber policeman. Wash the remainder of the loosened precipitate from the beaker and from the policeman into the funnel.

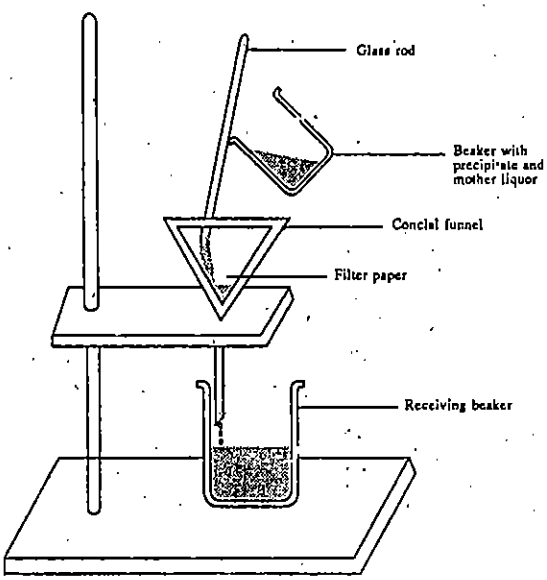


Fig. 1.4 : Procedure for filtering a precipitate

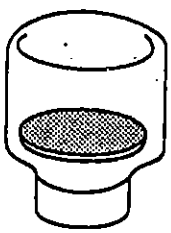


Fig. 1.5 : A sintered glass crucible

After the precipitate is transferred to the filter, it is washed with five or six small portions of wash liquid. Add the liquid around the top edge of the filter paper to wash the precipitate down into the funnel. Each portion should be allowed to drain before adding the next one.

Ordinary filtration is generally a slow operation. It can be speeded up by use of suction filtration. If the precipitate does not need to be ignited, it is most conveniently collected in a **sintered glass crucible** (Fig. 1.5) by suction filtration. This crucible has a porous disk that allows liquid to pass through, but retains solid particles. Suction can be applied by means of a water pump. Water pump sucks out air, reducing the pressure inside the filtration flask and thus speeding up the rate of filtration.

When a large quantity of precipitate or any other solid is to be filtered, a Buchner funnel, which is shown in Fig. 1.6 is employed. The **Buchner funnel** consists of a porcelain funnel in which a perforated plate is incorporated. A filter paper circle, cut correct to size covers the perforated plate. The Buchner funnel is fitted into the filter flask by means of a cork. The filter paper is wetted with water and suction put on before pouring in the solution to be filtered. A suction filtration unit consisting of a porcelain Buchner funnel, a filtration flask and a water pump is shown in Fig. 1.7.

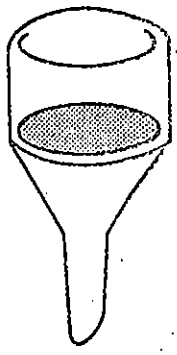


Fig. 1.6 : A Buchner funnel

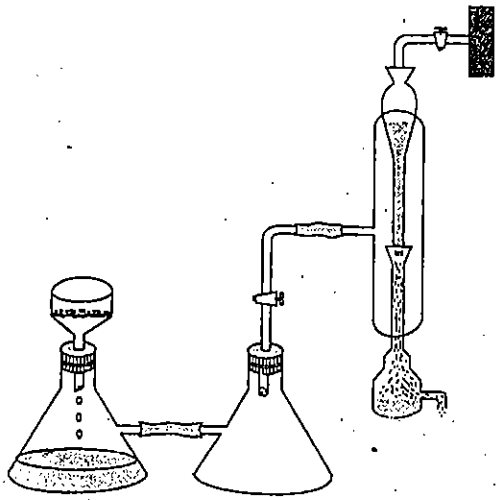


Fig. 1.7 : Suction filtration using a Buchner funnel

1.4.6 Drying and Ignition of Precipitates

In gravemetric analysis after a precipitate has been filtered and washed, it must be brought to a constant composition before weighing. This is achieved by drying or ignition of the precipitate. Whether a precipitate should be dried or ignited depends upon the nature of the precipitate and upon the type of filtering medium used. The precipitates such as $BaSO_4$, $PbSO_4$, $PbCrO_4$, AgCl, nickel dimethylglyoximate become dry and acquire a constant weight on heating up to 250°C. The precipitates of this type can be conveniently filtered in a sintered glass crucible and dried in an electric drying oven. Here we would like to point out that the precipitates of the above type can also be filtered in an ashless gravimetric filter paper and then ignited to a constant weight. But ignition requires a higher temperature of up to 1200°C. Therefore, it is more convenient to filter them in a sintered glass crucible and then dry in an electric drying oven. On the other hand, the gelatinous precipitates such as those of $Fe_2O_3.xH_2O$ and $Al(OH)_3$ clog the pores of sintered crucible and therefore, are filtered through an ashless filter paper. They also have a variable composition and should be ignited to convert them into a form of constant composition (such as Fe_2O_3 or Al_2O_3) suitable for weighing. Calcium is often precipitated as the oxalate, CaC_2O_4, which is not weighed as such but is decomposed by ignition to CaO and then weighed.

Place a silica crucible on a clay pipe triangle kept on a tripod stand (Fig. 1.8). Heat the crucible strongly for half an hour on a Bunsen burner flame. Remove the burner and allow the crucible to cool in air for 2-3 minutes. Then place the crucible in a desiccator with the help of a pair of tongs (Fig. 1.9). Allow the crucible to attain the room temperature and then weigh it. Repeat the process of heating, cooling and weighing till the weight of the crucible becomes constant.

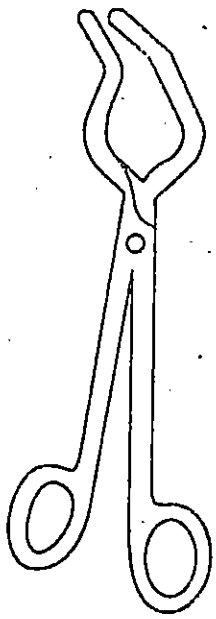


Fig. 1.9 : A pair of tongs

Detach carefully the well drained filter paper containing the precipitate from the funnel. Fold the filter paper into a packet so as to completely enclose the precipitate. Place the packet into the weighed silica crucible supported on a clay pipe triangle and tripod stand. Tilt the crucible slightly and partially cover with the lid.

Place a small flame under the crucible so that the filter paper and the precipitate become dry. Then increase the flame slightly so as to slowly carbonise the paper. Do not allow the paper to burn, as this may cause a mechanical loss of the precipitate. If the paper catches fire, put off the fire by covering the crucible with the lid with the help of a pair of tongs.

When the paper has completely carbonised, increase the size of burner flame until the bottom of the crucible is heated to redness. Continue heating strongly until the carbon residue is burnt away. Cool the crucible in a desiccator and then weigh. Repeat the process of heating, cooling and weighing till the weight of the crucible with the precipitate becomes constant.

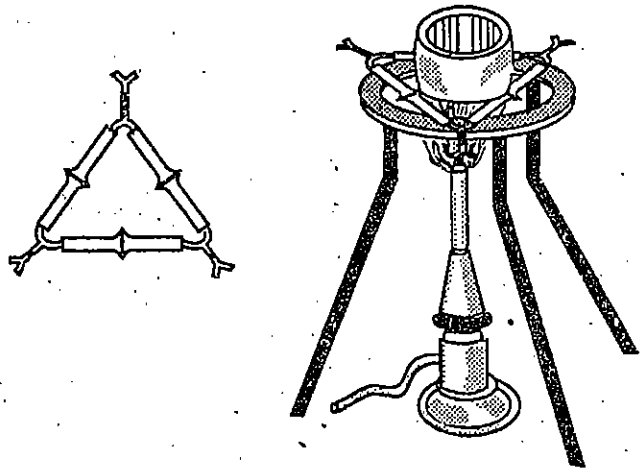


Fig. 1.8 : Heating a silica crucible

1.4.7 Cooling

After the crucible and the precipitate have been dried in an electric-drying oven or heated strongly on a burner flame, they should be cooled to room temperature before weighing. Cooling is done in a glass desiccator shown in Fig. 1.10. A desiccator is an airtight container that contains a drying agent or desiccant such as anhydrous calcium chloride. The desiccant absorbs moisture and keeps the air dry in the desiccator. The desiccant has to be changed from time to time as it becomes spent after absorbing moisture. The interface between the lid and the body of the desiccator is greased to make an airtight seal. The correct way to open a desiccator is to slide the lid sideways until it can be removed. When placing the lid on the table, the greased surface should always be kept upwards.

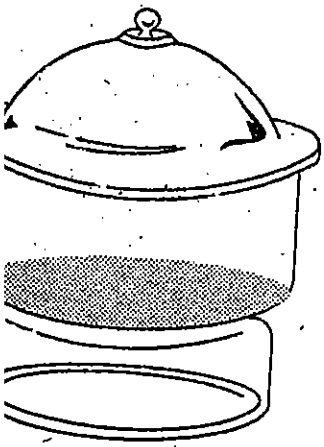


Fig. 1.10 : A desiccator

1.4.8 Weighing

In gravimetric analysis, you will be required to determine the mass of the precipitate accurately by weighing. It is, therefore, essential to learn the correct use of an analytical balance because accurate weighing is important for the accuracy of the result of gravimetric analysis.

You might have learnt the use of an analytical balance in the Chemistry Lab-I course. If you did not study that course, you would get an opportunity of using an analytical balance in this laboratory course.

Zero point is the point on the scale at which the pointer of the unloaded balance comes to rest.

A commonly used analytical balance is shown in Fig. 1.11. The various parts of the balance are labelled in the figure. Before using the balance, you have to first determine the **zero point** of the balance. For this purpose, the side doors of the balance are closed and the arrest knob(1) is slowly and carefully turned counter-clockwise. **Avoid jerks as they may disturb the setting of the balance.**

Ideally the zero point should coincide with the middle or the zero of the scale.

When the arrest knob is turned fully to the left, the pointer (2) starts swinging around the centre of the scale (3). The first two swings are ignored and starting with the third swing, the extreme positions of the swing are noted. The swings to the right are positive and those to the left are negative. The readings to the left and right are averaged separately and the mean of these averages is found, which is the zero point. The following example will make it clear.

	Reading on the left	Reading on the right
1.	– 5.0	+ 5.0
2.	– 4.0	+ 4.0
3.	– 3.0	+ 3.0
4.	– 2.0	
	– 14.0	+ 12

$$\text{Average} = \frac{-14.0}{4} = -3.5 \qquad \frac{12.0}{3} = 4$$

$$\text{Mean Value} = \frac{-3.5 + 4}{2} = 0.25$$

The zero point is +0.25, i.e., 0.25 units to the right.

Such small discrepancies between the zero point and the middle of the scale may be ignored as they are insignificant. However, if the deviation is large, e.g., greater than 1.5 units, the balance must be adjusted by means of the screws (4), for which you may request your counsellor.

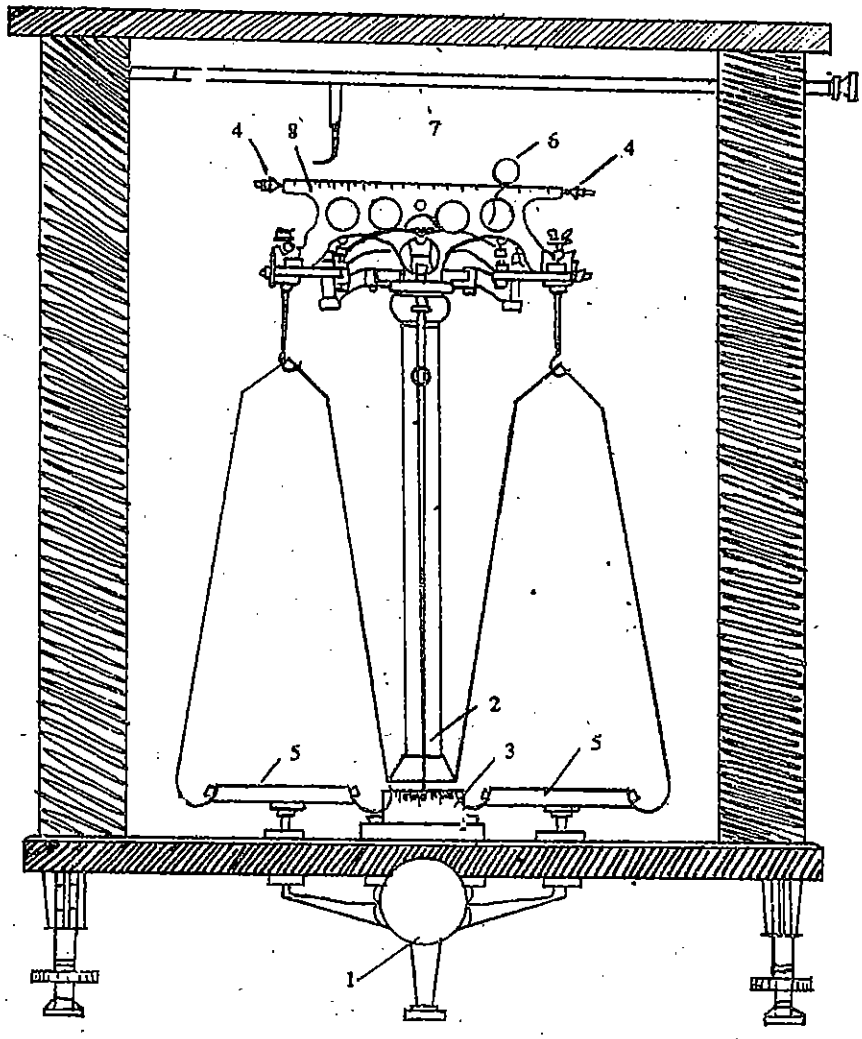


Fig. 1.11 : Analytical balance

After adjusting the zero point of the balance (if necessary), we come to actual weighing. For this purpose, we use a glass or a plastic weighing bottle, Fig. 1.12. First of all, the weighing bottle is weighed on a rough balance to find its approximate mass to the nearest gram. Then, the left side door of the analytical balance is opened and the weighing bottle is kept on the left side pan (5) and the door is closed. Similarly, through right side door,

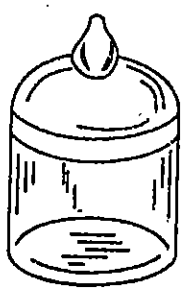


Fig. 1.12 : Weighing bottle

weights equal to the approximate mass of the weighing bottle are transferred to the right side pan from a weight box (Fig. 1.13).

You must close both the doors of the balance before raising the pans with the arrest knob.

FIG 1.13

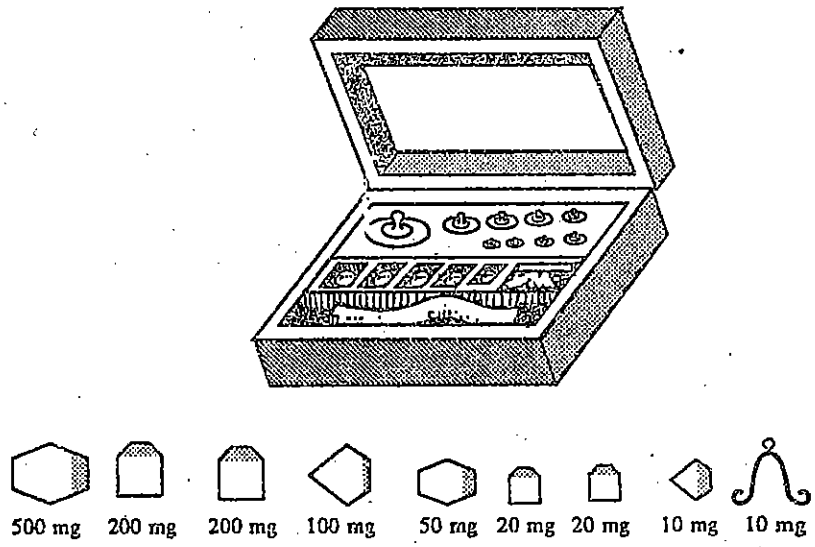


Fig. 1.3 : Weight box and weights

Always use forceps to transfer the weights. **Refrain from using your hands.**

The arrest knob is once again turned to the left and the movement of the pointer is seen. If it moves more to the left, then the weights transferred are in excess of the mass of the bottle. In that case some weights have to be removed. On the other hand, if the pointer moves to the right, then the added weights are not sufficient and we need to add more weights. Arrest the movement of the beam by turning the arrest knob fully towards the right and open the right side door to add or remove some weight(s), as the case may be. Recheck the movement of the pointer by turning the arrest knob. Continue this process till the addition of 1 gram weight makes the right hand pan heavier while its removal makes it lighter, e.g., if the weight is say 15.5 g, then 15 g weight would be lighter and 16 g weight would be heavier. After this, the fractional weights marked in mg, have to be added in the order of decreasing weight till the two sides are balanced. Do not use fractional weights of less than 10 mg, you should use a rider in such cases. A rider, Fig. 1.12 is a thin metallic wire suitably bent to be seated on the beam of the balance. It is normally ut on the right hand side of the beam (6) with the help of the rider carrier (7). By varying the position of the rider on the beam (8), the rest point is found, i.e., the two pans are balanced.

A rider is used for mass adjustments below 10 mg/.01 g.

The beam scale has got markings from 0-10 on either side. It is calibrated in such a way that each main division is numerically equal to mass in milligram, when the rider is put on it. Each main division is further divided into 5 subdivisions and each subdivision is equivalent to 0.2 mg. Thus the accuracy of such an analytical balance can be only up to 0.2 mg. The mass of an object can be calculated using the following formula :

Mass of the object = (Weights added in grams)
+ (Fractional weights added × 0.001) g
+ (Main division of the rider position × 0.001) g
+ (Subdivision of the rider position × 0.0002) g

Let us illustrate the use of this formula. Suppose that while weighing an object, the weights added to the right side pan are 15 g, 200 mg and 2 × 20 mg. Let the rider position be 2 on the main divisions and 3 on the subdivisions.

Then the mass of the object

$$= 15.00\ g + (240 \times 0.001)g + 2 \times 0.001)g + (3 \times 0.0002)g$$
$$= 15.2426\ g.$$

You have, so far, seen how to weigh an object accurately. If we want to weight a substance in the weighing bottle, we make use of the method of weighing by difference. For this, the weighing bottle is first approximately weighed. The substance to be weighed is put into the

bottle (a little more than required) and weighted accurately (w_1 g). The substance is then transferred into a container (e.g., beaker, volumetric flask) and the bottle is again weighed accurately (w_2 g). The difference of the two weights, i.e., (w_1 - w_2) gives the exact amount of the substance transferred.

Weight of substance transferred, w

= Weight of the bottle with substance
– Weight of the bottle after transferring the substance

or w_1 - w_2 g.

1.5 COMMON LABORATORY REAGENTS

You will be using a number of reagents and chemicals during your experiments. There are lab assistants to help you to get these reagents. Most of these chemicals are kept in the reagent selves and are properly labelled. The bench shelves have mostly the liquid reagents which include hydrochloric, sulphuric and nitric acids. Besides these, other solutions like silver nitrate, ammonium hydroxide, sodium hydroxide, barium chloride, etc., may also be kept there. You have to be very careful while using all these, especially, the acids. Mishandling any chemical may result in injury. You should thoroughly read the Section 1.2 in the unit before starting your experiments, which tells you about some safety measures in the laboratory.

The solid reagents are usually kept on a common table. You should use a spatula and take only the required amount of the compound from the bottle or the pack. Don't waste any chemical. The liquid reagents should be taken with the help of droppers.

The special chemicals and solutions required for any particular experiment will be provided by your counsellor at the time of performing the experiment.

1.6 SUMMARY

In this unit we have discussed the safety measures, which you should take while working in a chemistry laboratory. We also described the importance of keeping a record of experiments which you perform in the laboratory. We discussed the various laboratory operations which you would perform in this course. We also familiarised you with the common apparatus, which you will require for performing various experiments in this course.

UNIT 2 INORGANIC PREPARATIONS

STRUCTURE

2.1 INTRODUCTION

In Unit 1, we described various laboratory operations and the apparatus used in an inorganic chemistry laboratory. In this unit, we will discuss the preparation and the purification of three inorganic compounds - one double salt and two complexes. You will have to prepare and purify these compounds during the residential school of this course. You will perform qualitative tests on these compounds for identification of various ions present in them. In Unit 3, we will describe some experiments for performing gravimetric determinations of some ions present in these compounds.

Objectives

After studying this unit, you should be able to:

- prepare and purify potash alum, tetraamminecopper(II) sulphate and potassium trioxalatoferrate (III) trihydrate,
- perform various laboratory operations involved in these preparations,
- calculate percentage yield of these compounds,
- explain the principles involved in the preparation of these compounds, and
- perform qualitative tests for various ions present in these compounds.

2.2 EXPERIMENT 1 : PREPARATION OF POTASH ALUM

In this experiment you will learn how to prepare potash alum, which is a double salt.

2.2.1 Principle

When a solution containing potassium sulphate and aluminium sulphate in equimolar concentrations is evaporated to crystallisation point, a double salt commonly known as potash alum is formed:

$$K_2SO_4(aq) + Al_2(SO_4)_3.18H_2O\ (aq) + 6H_2O \xrightarrow{H^+(aq)} K_2SO_4.Al_2(SO_4)_3.24H_2O\ (aq)$$

The names and gram formula weights of important compounds involved in this experiment are listed below:

Name	Formula	Gram Formula Weight g/mole
Potassium sulphate	K_2SO_4	174.25
Aluminium sulphate	$Al_2(SO_4)_3.18H_2O$	666.42
Potash alum	$K_2SO_4.Al_2(SO_4)_3.24H_2O$	948.75

2.2.2 Requirements

Chemicals	Apparatus	
Potassium sulphate	Beakers 150 cm^3	2 No.
Aluminium sulphate	Bunsen burner	1 No.
Sulphuric acid	Evaporating dish	1 No.
Distilled water	Funnel glass	1 No.
	Funnel stand	1 No.
	Glass rod	1 No.
	Measuring cylinder	1 No.
	Porous plate	1 No.
	Tripod stand	1 No.
	Watch glass	1 No.
	Wire gauze	1 No.
	Filter paper	Few circles

2.2.3 Procedure

Weigh 10.0 g aluminium sulphate and powder it. Transfer to a 150 cm^3 beaker. Dissolve in 25 cm^3 distilled water containing 2 cm^3 concentrated sulphuric acid. Warm to dissolve and add more sulphuric acid if necessary to get a clear solution.

Weigh 3.0 g potassium sulphate and powder it. Transfer to another 150 cm^3 beaker. Add 25 cm^3 distilled water. Stir to dissolve. Warm if necessary.

Filter the two solutions through a previously moistened paper into an evaporating dish. Heat the solution on a wire gauze and concentrate the solution to the crystallisation point, till the rod dipped in the solution deposits a crust on it.

Cover with a watch glass and allow the solution to crystallise. When the crystallisation is complete, decant the mother liquor and wash the crystals with 5 cm^3 ice cold distilled water. Dry the crystals by pressing them gently between pads of filter papers. Allow to dry on a porous plate. Weigh the crystals and record the yield. Calculate the percentage yield.

2.2.4 Observations

(i) Weight of potassium sulphate taken = g

(ii) Weight of aluminium sulphate taken = g

(iii) Weight of potash alum formed = g
(experimental yield)

2.2.5 Calculation of Percent Yield

Your objective should be to prepare as high a yield of potash alum as possible. To measure the efficiency of the procedure, you should calculate the percent yield, where

$$\text{Percent yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

The theoretical yield is the calculated maximum amount of product which might be obtained under ideal conditions from the starting materials. In an experiment, the theoretical yield is seldom, if ever, reached. In this experiment, the theoretical yield will be the maximum amount of potash alum which might be obtained from the specified amounts of starting materials.

In calculating the theoretical yield, you should first calculate the moles of each reactant and then find the limiting reagent. The limiting reagent determines the theoretical yield of the product.

The reactant that is completely consumed in a chemical reaction is called limiting reagent.

$$\text{No. of moles of } Al_2(SO_4)_3.18H_2O \text{ taken} = \frac{\text{g of } Al_2(SO_4).18H_2O \text{ taken}}{\text{gram molecular weight}}$$

$$= \frac{10.0}{666.42} = 0.015 \text{ moles}$$

No. of moles of K_2SO_4 taken $$= \frac{3.0}{174.25} = 0.017 \text{ moles}$$

Since, aluminium sulphate and potassium sulphate react in equimolar ratio, the former is the limiting reagent because it is present in less amount. Thus the theoretical yield of potash alum is 0.015 moles. The theoretical yield in gram can be calculated by multiplying the yield in moles by the molecular weight.

Theoretical yield = $0.015 \times 948.26 = 14.2$ g

$$\text{Percent yield} = \frac{\text{experimental yield}}{14.2} \times 100\%$$

2.2.6 Result

The percent yield of potash alum = %

2.2.7 Qualitative Tests

Dissolve 0.5 g of the salt in 5 cm^3 of distilled water in a test tube and perform the following tests:

Al^{3+} Ions

To 0.5 cm^3 of aqueous solution,

i) add NaOH solution dropwise, a white precipitate will be formed which dissolves in excess of NaOH.

$Al^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(H_2O)_3(s)$

$Al(OH)_3(H_2O)_3(s) + OH^-(aq) \longrightarrow [Al(OH)_4(H_2O)_2]^-(aq) + H_2O(l)$

ii) add aqueous NH_3 solution, a white gelatenous precipitate will be formed.

$Al^{3+}(aq) + 3NH_3(aq) + 6H_2O(l) \longrightarrow Al(OH)_3(H_2O)_3(s) + 3NH_4^+(aq)$

K^+ Ions

To 1.0 cm^3 of aqueous solution, add acetic acid and sodium hexanitritocobaltate(III) solution, a yellow precipitate will be formed.

$$2K^+(aq) + Na^+(aq) + [Co(NO_2)_6]^{3-}(aq) \longrightarrow K_2Na[Co(NO_2)_6](s)$$

SO_4^{2-} Ions

To 1.0 cm^3 of aqueous solution, add dil. HCl and $BaCl_2$ solution, a white precipitate will be formed.

$SO_4^{2-}(aq) + Ba^{2+}(aq) \longrightarrow BaSO_4$ (s)

The above tests indicate the presence of K^+, Al^{3+} and SO_4^{2-} ions in the salt.

2.3 EXPERIMENT 2 : PREPARATION OF TETRAAMMINECOPPER(II) SULPHATE MONOHYDRATE

In this experiment you will synthesise a complex compound, tetraamminecopper(II) sulphate monohydrate.

2.3.1 Principle

When aqueous ammonia is added to a solution containing copper(II) sulphate, a pale blue precipitate of basic copper(II) sulphate is first formed. This dissolves in excess of aqueous ammonia solution giving a deep blue solution containing the complex ion,

tetraamminecopper(II). Addition of ethanol to this solution results in precipitation of a deep blue coloured complex, tetraammine copper(II) sulphate monohydrate:

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

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

$$[Cu(NH_3)_4]^{2+}(aq) + SO_4^{2-}(aq) \xrightarrow{\text{ethanol}} [Cu(NH_3)_4]SO_4.H_2O(s)$$

The names and gram molecular weights of important compounds involved in this experiment are listed below:

Name	Formula	Gram Formula Weight
Copper(II) sulphate	$CuSO_4.5H_2O$	249.5
Ammonia	NH_3	17
Tetraamminecopper(II) sulphate monohydrate	$[Cu(NH_3)_4]SO_4.H_2O$	245.74

2.3.2 Requirements

Chemicals	Apparatus	
Copper(II) sulphate	Beakers 250 cm^3	1 No.
Ammonia(aq), Sp. gr. 0.88 (15 M)	Bunsen burner	1 No.
Ethanol	Buchner funnel	1 No.
Distilled water	Filtration apparatus	1 No.
	Glass rod	1 No.
	Measuring cylinder	1 No.
	Tripod stand	1 No.
	Watch glass	1 No.
	Water bath	1 No.
	Filter paper	Few circles

2.3.3 Procedure

Weight out 2.0 g copper(II) sulphate and powder it. Add powdered crystals to a 250 cm^3 beaker. Prepare ammonia solution by adding 10 cm^3 ammonia(aq) to 5 cm^3 distilled water. Slowly add ammonia solution to the powder with stirring until all the copper(II) sulphate dissolves resulting in a deep blue solution. Add 1-2 cm^3 of ammonia solution in excess. Add ethanol dropwise and with stirring till a deep blue precipitate is formed. Heat the beaker on a water bath at 60°C, stir and wait till the blue precipitate just dissolves. Cover the beaker with a watch glass and set aside to crystallise. Beautiful dark blue needle like crystals separate after 1 hour. Filter off the crystals using a Buchner funnel and wash with 2-3 cm^3 ethanol at the pump. Allow the air to pass for 5 minutes.

Transfer the product to a watch glass and dry in a desiccator. Store the crystals in a weighed weighing bottle.

Weigh the dry crystals. Calculate the percent yield.

2.3.4 Observations

Weight of copper(II) sulphate taken = g

Weight of tetraamminecopper(II) sulphate monohydrate (experimental yield) = g

2.3.5 Calculations

No. of moles of copper(II) sulphate = $\frac{\text{g of } CuSO_4.5H_2O \text{ taken}}{\text{gram molecular weight}}$

$$= \frac{2.0}{249.5} \text{ moles}$$

No. of moles of complex formed = No. of moles of copper(II) sulphate taken

$$= \frac{2.0}{249.5} \text{ moles}$$

Theoretical yield in gram = No. of moles x gram molecular weight

$$= \frac{2.0}{249.5} \times 245.74 = 1.97 \text{ g}$$

$$\text{Percent yield} = \frac{\text{Experimental yield}}{\text{Theoretical yield}} \times 100\%$$

2.3.6 Result

The percent yield of the tetraamminecopper(II) sulphate monohydrate = %

2.3.7 Structure of the Complex

Tetraamminecopper(II) sulphate is an example of a complex, in which copper(II) ion is bound to four unidentate ammonia molecules. The coordination number of copper(II) is 4. The complex has a square planar structure (Fig. 2.1) and possesses one unpaired electron.

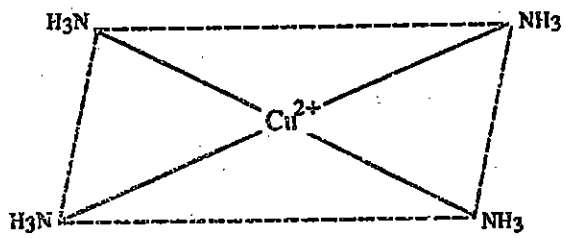


Fig. 2.1 : Structure of $[Cu(NH_3)_4]^{2+}$ ion

This can be explained on the basis of dsp^2 hybridisation of Cu^{2+} ion, which you might have studied in Unit 14 of the CHE-02 course.

2.3.8 Qualitative Tests

Dissolve 0.5 g of the complex in 5 ml of distilled water and perform the following tests:

Cu^{2+} ions

i) Take 0.5 cm^3 of the aqueous solution in a test tube. Acidify with acetic acid and add $K_4[Fe(CN)_6]$ solution. Formation of a reddish brown precipitate confirms the presence of Cu^{2+} ions.

$Cu^{2+}(aq) + [Fe(CN)_6]^{4-} \longrightarrow Cu_2[Fe(CN)_6](s)$

ii) Take 0.5 cm^3 of the aqueous solution in a test tube. Acidify with acetic acid and add KI solution. Appearance of an intense brown colour due to the formation of triiodide ions (I_3^-) confirms the presence of Cu^{2+} ions.

$2Cu^{2+}(aq) + 5I^-(aq) \longrightarrow 2CuI(s) + I_3^-(aq)$

NH_3

Take 1 cm^3 of aqueous solution in a test tube, add a few drops of NaOH solution and heat. Liberation of ammonia gas, which can be identified by its characteristic odour, indicates the presence of ammonia in the complex.

$NH_3\ (g) + H_2O\ (l) \longrightarrow NH_4^+(aq) + OH^-(aq)$

$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(g) + H_2O$

SO_4^{2-} ions

Take 1 cm^3 of aqueous solution in a test tube. Acidify with dil. HCl and add $BaCl_2$ solution. Formation of a white precipitate confirms the presence of SO_4^{2-} ions.

$SO_4^{2-}(aq) + Ba^{2+}(aq) \longrightarrow BaSO_4(s)$

The above tests for Cu^{2+}, NH_3 and SO_4^{2-} indicate that the complex is a labile complex which undergoes rapid exchange of ligands in solution.

2.4 EXPERIMENT 3 : PREPARATION OF POTASSIUM TRIOXALATOFERRATE(III) TRIHYDRATE

In this experiment, you will synthesise the complex compound potassium trioxalatoferrate(III) trihydrate.

2.4.1 Principle

The synthesis of potassium trioxalatoferrate(III) is achieved in two steps. The first step consists in preparation of the yellow iron(II) oxalate from ammonium iron(II) sulphate by reaction with oxalic acid in the presence of dilut sulphuric acid.

The second step involves the oxidation of iron(II) oxalate with H_2O_2 in the presence of excess oxalate ions when emerald green crystals of potassium trioxalatoferrate(III) are obtained.

Step 1

$$Fe(NH_4)_2(SO_4)_2(aq)+H_2C_2O_4(aq) \xrightarrow[\text{Heat}]{H_3O^+} FeC_2O_4.2H_2O(s) + (NH_4)_2SO_4(aq) + H_2SO_4(aq)$$

Step 2

$$2FeC_2O_4.2H_2O(s)+H_2C_2O_4(aq) + H_2O_2(aq) + 3K_2C_2O_4(aq) \xrightarrow{\text{Heat}} 2K_3[Fe(C_2O_4)_3].3H_2O(s)$$

The names and gram formula weights of important compounds involved in this experiment are listed below:

Name	Formula	Gram Formula Weight g/mole
Ammonium iron(II) sulphate	$Fe(NH_4)_2(SO_4)_2.6H_2O$	392.13
Oxalic acid	$H_2C_2O_4.2H_2O$	126.07
Potassium oxalate	$K_2C_2O_4.H_2O$	184.25
Hydrogen peroxide	H_2O_2	34.02
Potassium trioxalatoferrate(III)	$K_3[Fe(C_2O_4)_3].3H_2O$	491.25

2.4.2 Requirements

Chemicals	Apparatus	
Ammonium iron(II) sulphate	Beaker 250 cm^3	1 No.
Oxalic acid	Beaker 100 cm^3	1 No.
Potassium oxalate	Buchner funnel	1 No.
Dilute sulphuric acid (3 M)	Bunsen burner	1 No.
Hydrogen peroxide (3%)	Desiccator	1 No.

Chemicals	Apparatus	
Acetone	Filtration apparatus	1 No.
Ethanol	Glass rod	1 No.
Distilled water	Measuring cylinder	1 No.
	Tripod stand	1 No.
	Watch glass	1 No.
	Water bath	1 No.
	Wire gauze	1 No.
	Filter paper	Few circles

2.4.3 Procedure

Step 1 : Preparation of $FeC_2O_4.2H_2O$

Weigh 5.0 g ammonium iron(II) sulphate and transfer to a 250 cm^3 beaker. Add 15-20 cm^3 distilled water and 1 cm^3 dil. H_2SO_4. Stir to dissolve.

Add 10% oxalic acid (25 cm^3) solution to the above iron(II) solution and heat to boiling with continuous stirring. **[Caution: Do not leave it unattended as this solution is susceptible to spillover and there can be bumping once the solid starts separating].** Add more oxalic acid, if necessary to get the maximum yield of the yellow iron(II) oxalate, $FeC_2O_4.2H_2O$.

Allow the yellow product to settle. Carefully decant the hot supernatant liquid and repeatedly wash the precipitate with hot water. Retain the solid in the beaker for the next step.

Step 2 : Synthesis of $K_3[Fe(C_2O_4)_3].3H_2O$

Add a warm solution of potassium oxalate (5.0 g in 15 cm^3 distilled water) to the iron(II) oxalate precipitate in the beaker. Suspend a thermometer in the solution. Take 3% H_2O_2 (20 cm^3) in a measuring cylinder. Stir the solution and add hydrogen peroxide very slowly a few drops at a time with the help of a dropper so as to maintain the temperature around 40°C. In all 20 cm^3 of 3% H_2O_2 is added. The addition may take up to 30 minutes.

Heat to boiling. Add 10% $H_2C_2O_4$ solution, first 4-5 cm^3 in one lot and later dropwise until the precipitate just dissolves. In all about 10 cm^3 solution will be required. Keep the solution boiling till a green colour is obtained. Heat for another 5 minutes. Filter the solution in a 100 cm^3 beaker and allow to cool to room temperature in a dark cupboard since the product is photosensitive. Add 10 cm^3 ethanol to the beaker and redissolve any crystals formed by gentle warming on a water bath and put the solution in a dark cupboard to crystallise. Cover with a watch glass. Slower evaporation encourages the development of larger and purer crystals.

Photosensitive compounds are those compounds which decompose in the presence of light.

Filter the crystals on a Buchner funnel by suction. Wash with ethanol-water (1:1) mixture and finally with acetone. Dry in a desiccator over calcium chloride.

Weigh the crystals and record the yield.

2.4.4 Observations

i) Weight of ammonium iron(II) sulphate taken = g

ii) Weight of oxalic acid taken = g

iii) Weight of potassium oxalate taken = g

iv) Weight of complex formed (Experimental yield) = g

2.4.5 Calculation of Percent Yield

$$\text{No. of moles of } Fe(NH_4)_2(SO_4)_2.6H_2O = \frac{\text{g of } Fe(NH_4)_2(SO_4)_2.6H_2O}{\text{gram molecular weight}}$$

$$= \frac{5.0}{392.13} = 0.013 \text{ mole}$$

No. of moles of $K_3[Fe(C_2O_4)_3].3H_2O$ formed = 0.013 mole

Theoretical yield in gram = No. of moles x gram molecular weight

$$= 0.013 \times 491.25 = 6.40 \text{ g}$$

$$\text{Percent yield} = \frac{\text{Experimental yield}}{\text{Theoretical yield}} \times 100\%$$

$$= \frac{\text{Experimental yield}}{6.40} \times 100\%$$

2.4.6 Result

Percent yield of potassium trioxalatoferrate(III) trihydrate = %

2.4.7 Alternate Procedure for the Synthesis of Potassium Trioxalatoferrate(III) Trihydrate

There are two more procedures, which are straight forward, less time consuming and involve more cost efficient method of synthesis. These require the use of iron(III) nitrate or chloride instead of ammonium iron(II) sulphate.

Procedure A : Use iron(III) nitrate

Requirements

Chemicals	Apparatus	
Potassium oxalate, $K_2C_2O_4.H_2O$	Beaker 150 cm^3	2 No.
Iron(III) nitrate, $Fe(NO_3)_3.9H_2O$	Buchner funnel	1 No.
Distilled water	Desiccator	1 No.
Ethanol	Filtration apparatus	1 No.
Acetone	Glass rod	1 No.
Ice	Watch glass	1 No.
	Water bath	1 No.

$$Fe(NO_3)_3.9H_2O + 3K_2C_2O_4.H_2O \xrightarrow{H^+/H_2O} K_3[Fe(C_2O_4)_3.3H_2O + 3KNO_3$$

Prepare a solution of iron(III) nitrate (4.0 g in 20 cm^3 distilled water) in a 150 cm^3 beaker. Add this solution slowly to a stirred hot solution of potassium oxalate (containing 6.0 g of the salt in 40 cm^3 of distilled water) taken in another 150 cm^3 beaker. A clear green coloured solution is obtained. Heat for 2-3 minutes more.

Cool in an ice bath. Filter the crystals using a Buchner funnel. Wash with ice cold water, followed by ethanol and acetone.

The emerald green product may be redissolved in warm water (15-20 cm^3) and reprecipitated by cooling in ice bath at O°C. Collect the crystals by filtration. Wash with ethanol-water (1:1) mixture and finally with acetone.

Dry in a desiccator in a dark cupboard. Weigh the crystals and calculate the percent yield.

Procedure B : Use iron(III) chloride

Requirements

Chemicals	Apparatus	
Iron(III) chloride (anhydrous)	Beakers 150 cm^3	1 No.
Potassium oxalate, $K_2C_2O_4.H_2O$	Buchner funnel	1 No.
Distilled water	Desiccator	1 No.
Ethanol	Filtration apparatus	1 No.
Acetone	Glass rod	1 No.
Ice	Watch glass	1 No.
	Water bath	1 No.

$$FeCl_3(aq) + 3K_2C_2O_4.H_2O(aq) \longrightarrow K_3[Fe(C_2O_4)_3].3H_2O(aq) + 3KCl\ (aq)$$

Take 6.0 g of potassium oxalate in a 150 cm^3 beaker. Add 20-25 cm^3 of distilled water. Heat using a wire gauze to get a clear solution. Add 1.6 g iron(III) chloride in small lots to hot solution of $K_2C_2O_4$. Heat again till a green coloured solution is obtained.

Cool the solution in ice bath at 0°C. Keep at this temperature until crystallisation is complete. Filter the crystals using a Buchner funnel. Collect the product after washing with ethanol and acetone. Recrystallise the complex as in procedure A. Dry the complex in a desiccator in a dark cupboard. Weigh the complex and calculate the percent yield.

2.4.8 Structure

Potassium trioxalatoferrate(III) is an example of a complex compound, in which iron(III) is chelated to three bidentate oxalate groups forming six bonds. Coordination number of iron is six. It is octahedrally surrounded by six oxygen atoms, two each from each oxalate group as shown in Fig. 2.2.

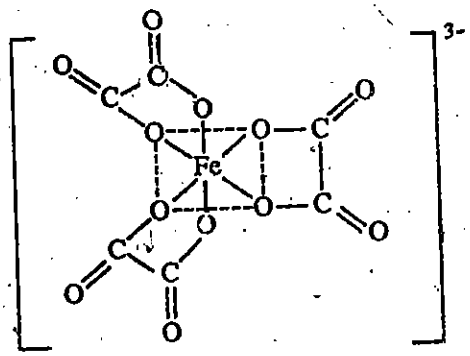


Fig. 2.2 : Structure of $[Fe(C_2O_4)_3]^{3-}$ ion.

2.4.9 Qualitative Tests

Dissolve 0.5 g of the complex salt in 5 cm^3 of distilled water in a test tube and perform th following tests:

K^+ ions

Take 0.5 cm^3 of the aqueous solution in a test tube. Add acetic acid and $Na_3[Co(NO_2)_6]$ solution. Appearance of a yellow precipitate confirms the presence of K^+ ions.

$$2K^+(aq) + Na^+(aq) + [Co(NO_2)_6]^{3-} \longrightarrow K_2Na[Co(NO_2)_6](s)$$

Fe^{3+} ions

i) Take 0.5 cm^3 of the aqueous solution in a test tube. Acidify with dil. H_2SO_4 and add KSCN solution. Appearance of a deep red colour confirms the presence of Fe^{3+} ions.

$Fe^{3+}(aq) + 3SCN^-(aq) \longrightarrow Fe(SCN)_3(aq)$

ii) Take 0.5 cm^3 of the aqueous solution in a test tube. Acidify with dil. H_2SO_4 and add $K_4[Fe(CN)_6]$ solution. An intense blue colour or precipitate confirms the presence of Fe^{3+} ions.

$4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3(s)$

$C_2O_4^{2-}$ ions

Take 1.0 cm^3 of the aqueous solution in a test tube. Acidify with dil. H_2SO_4. Warm and add dil. $KMnO_4$ solution dropwise. Decolourisation along with evolution of CO_2 confirms the presence of $C_2O_4^{2-}$ ions.

$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

The above tests for Fe^{3+} and $C_2O_4^{2-}$ ions indicate that the complex is a labile complex which undergoes rapid exchange of ligands in solution.

2.5 SUMMARY

In this unit we discussed the preparation and the purification of the following three inorganic compounds:

1) Potash alum
2) Tetraamminecopper(II) sulphate
3) Potassium trioxalatoferrate(III)

We also described the calculation of percent yield and the qualitative tests which one should perform to identify the ions present in them.

UNIT 3 GRAVIMETRIC ANALYSIS

STRUCTURE

3.1 INTRODUCTION

As you are aware that the aim of chemical analysis is to determine the composition of naturally occurring or artificially prepared substances. This is usually done in two steps. As a first step, qualitative analysis is performed to identify the different components of a substance. In the second step, the quantitative analysis is performed by which the relative amounts of these components are determined. In this laboratory course, you are required to perform the quantitative analysis of components of known substances only. In this unit we discuss some experiments for gravimetric determination of certain ions to illustrate quantitative analysis. In Block 2, we will describe the scheme of qualitative analysis of mixtures of inorganic salts.

Methods of performing quantitative analysis are broadly classified into two types:

i) Chemical methods which are based on quantitative performance of suitable chemical reactions. Titrimetry or volumetry and gravimetry are the examples of chemical methods of analysis.

ii) Instrumental methods which require the use of instruments for measuring some physical properties such as electrical or optical properties of substances for determining their composition. Conductometry, potentiometry and colorimetry are some of the examples of this class.

In the Chemistry Laboratory–I (CHE–03(L)) course, you might have performed some experiments on titrimetry, conductometry, potentiometry and colorimetry. In this course, you shall perform some experiments on gravimetry.

In gravimetric analysis, the component to be estimated is converted into an insoluble precipitate which is filtered, dried/ignited and weighed accurately. Knowing the stoichiometry of the chemical reaction involved in precipitation the mass of the precipitate is used to determine the amount of the component in the substance.

Objectives

After studying this unit, you should be able to:

- determine aluminium, copper, iron and sulphate in their soluble salts,
- perform various operations, i.e., precipitation, filtration, washing, drying, ignition, cooling and weighing involved in gravimetric determinations, and
- perform calculations involved in gravimetric determinations.

3.2 EXPERIMENT 4 : DETERMINATION OF ALUMINIUM AS ALUMINIUM OXIDE

In this experiment you will perform the gravimetric determination of aluminium as aluminium oxide.

3.2.1 Principle

The aluminium ions are precipitated as the hydrated aluminium hydroxide by means of aqueous ammonia solution in the presence of ammonium chloride. The precipitate is filtered and washed with ammonium chloride or ammonium nitrate solution. The precipitate is then ignited to the anhydrous oxide and weighed as Al_2O_3.

$Al^{3+}(aq) + 3NH_3(aq) + 6H_2O(l) \longrightarrow Al(OH)_3(H_2O)_3(s) + 3NH_4^+(aq)$

$2Al(OH)_3(H_2O)_3(s) \longrightarrow Al_2O_3(s) + 6H_2O(g)$

Aluminium hydroxide is amphoteric in character:

$Al(OH)_3(H_2O)_3(s) + 3H_3O^+ \longrightarrow Al^{3+}(aq) + 9H_2O\ (l)$

$Al(OH)_3(H_2O)_3(s) + OH^-(aq) \longrightarrow [Al(OH)_4(H_2O)_2]^-(aq) + H_2O(l)$

Precipitation of aluminium hydroxide begins at approximately pH 4 and is complete when the pH lies between 6.5 and 7.5. Therefore, the pH of the solution is adjusted by the addition of solid ammoniaum chloride and using methyl red as indicator.

If we know the weight of sample taken for analysis and the weight of aluminium oxide formed, we can determine the percentage of aluminium in the sample.

3.2.2 Requirements

Chemicals	Apparatus	
Potash alum	Beaker 400 cm^3	1 No.
Aqueous ammonia	Beaker 250 cm^3	1 No.
Methyl red indicator	Bunsen burner	1 No.
Ammonium chloride	Clay pipe triangle	1 No.
Distilled water	Desiccator	1 No.
	Funnel glass	1 No.
	Glass rod	1 No.
	Pair of tongs	1 No.
	Rubber policeman	1 No.
	Silica crucible	1 No.
	Tripod stand	1 No.
	Wash bottle	1 No.
	Watch glass	1 No.
	Whatman filter paper No.41	1 circle
	Wire gauze	1 No.

3.2.3 Procedure

1) Weigh out accurately about 1.5 to 2.0 g of potash alum from a weighing tube into a 400 cm^3 beaker. Dissolve it in about 150 cm^3 of distilled water. Alternatively, take 25 cm^3 of the solution prepared by your Councellor and dilute it to 150 cm^3 with distilled water. Place a glass rod in the beaker and cover it with a watch glass. Add 5.0 g pure ammonium chloride, a few drops of methyl red indicator and heat just to boiling using a wire gauze. Add ammonia solution (1:1) dropwise and with constant stirring until the colour of the solution just changes to a distinct yellow. Do not add ammonia

solution in too much excess as it can dissolve aluminium hydroxide because it is amphoteric in character. Heat for about two minutes.

2) Tear a circle of Whatman filter paper No. 42 into small pieces and put in a 250 cm^3 beaker. Add enough distilled water to dip the filter paper. Cover with a watch glass and heat to disintigrate the paper. Add 2 cm^3 concentrated nitric acid, if need be, and heat till the paper is converted into pulp. Neutralise the pulp by the addition of ammonia solution.

3) Add one spoonful of the filter paper pulp to the precipitate and filter using Whatman filter paper No. 41. Aluminium hydroxide is gelatinous and filters with difficulty. The precipitate is adsorbed on the paper pulp and filters more readily. Wash the precipitate thoroughly with hot 2% ammonium nitrate or chloride solution, which is made neutral with aqueous ammonia solution using methyl red indicator. The precipitate cannot be washed with hot water alone because it is readily peptised and will pass through the filter paper. Addition of electrolyte prevents peptisation. Continue washing the precipitate till the washings are free from the sulphate ions. Use a policeman to remove the last traces of the precipitate from the beaker and glass rod. Allow the liquid to drain out of the filter paper.

The process of dispersion of a gel or a flocculated precipitate to form a sol is called peptisation.

4) Transfer the moist filter paper containing the precipitate into a constant weight silica crucible. Heat gently on a low flame to drive out the moisture. Char the paper carefully taking care that it does not catch fire. Allow the paper to smoke slowly. An increase in the volume of smoke indicates that the paper is going to catch fire. Remove the burner immediately for sometime. When the paper has charred completely, heat the crucible strongly. Raise the temperature to 1200°C using a blow pipe burner or by heating the crucible in a muffle furnace maintained at 1200°C.

Heat for about 30 minutes to get non–hygroscopic Al_2O_3. Allow to cool the crucible with precipitate in air for 1–2 minute. Then keep the hot crucible in desiccator with the help of a pair of tongs. Let the crucible and the precipitate cool to room temperature. Weigh accurately and record the weight. Repeat heating, cooling and weighing till a constant weight is obtained.

3.2.4 Observations

Weight of alum

i) Weight of empty weighing bottle = g

ii) Weight of weighing bottle + alum = g

iii) Weight of weighing bottle after transferring the alum into beaker = g

Weight of crucible

iv) 1st weight of crucible = g

v) 2nd weight of crucible = g

Weight of crucible + Al_2O_3

vi) 1st weight of crucible + Al_2O_3 = g

vii) 2nd weight of crucible + Al_2O_3 = g

3.2.5 Calculations

Calculate the percentage of Al^{3+} ions in potash alum as follows:

Weight of potash alum taken for experiment = ii) – iii) g
= w g

Weight of Al_2O_3 formed = vii) – v) g = x g

You know that one mole of potash alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$) contains two moles of Al^{3+} ions which are converted into one mole of alumina on precipitation and ignition.

Thus,

$K_2SO_4.Al_2(SO_4)_3.24H_2O$	$\equiv 2Al^{3+}$	$\equiv Al_2O_3$
948.76 g	$\equiv$ 53.96 g	$\equiv$ 101.96 g
w g	$\equiv$ y g?	$\equiv$ x g

Hence, weight of Al^{3+} ions in x g of Al_2O_3

$$y = \frac{53.96}{101.96} \times x \text{ g}$$

Now this y g of Al^{3+} ions are present in w g of the potash alum taken for analysis. Hence, percentage of Al^{3+} ions in potash alum

$$\%Al^{3+} = \frac{y}{w} \times 100$$

$$= \frac{53.96\ x}{101.96\ w} \times 100\%$$

$$\%Al^{3+} = \frac{53.96}{101.96} \times \frac{\text{Weight of } Al_2O_3 \text{ formed}}{\text{Weight of alum taken}} \times 100\%$$

Compare this value with the theoretical percentage of Al^{3+} ions in potash alum. Theoretically, 948.76 g of potash alum contains 53.96 g of Al^{3+} ions. Hence, percentage (theoretical) of Al^{3+} ions in potash alum.

$$\%\ Al^{3+}\ (\text{theoretical}) = \frac{53.96}{948.76} \times 100\% = 5.69\%$$

If you have performed the experiment carefully, the experimental and the theoretical values should agree within 0.5% with each other. Following a similar procedure, you can calculate the percentage of Al^{3+} ions in any other aluminium compound.

3.2.6 Result

You can report your result in any one of the following forms as instructed by your counsellor.

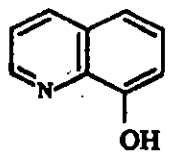
Weight of Al_2O_3 formed = g

or

Percentage of Al^{3+} ions in potash alum = %

3.3 EXPERIMENT 5 : DETERMINATION OF ALUMINIUM AS ALUMINIUM 8–HYDROXYQUINOLINATE

In Experiment 4 you performed the determination of aluminium ions as aluminium oxide in potash alum. In this experiment, you will perform the determination of aluminium ions as aluminium 8–hydroxyquinolinate or oxinate.



8-Hydroxyquinoline

8-Hydroxy quinoline

3.3.1 Principle

Aluminium ions are precipitated as aluminium(III) oxinate from ammonium acetate–acetic acid buffered solution at pH 5.0 by the addition of 8–hydroxyquinoline (oxine) solution in acetic acid. The precipitate is filtered through a sintered glass crucible, washed with water, dried at 130–140°C in an electric oven and weighed as aluminium(III) oxinate.

$$Al^{3+}(aq) + 3C_9H_7ON\ (aq) \longrightarrow Al(C_9H_6ON)_3(s) + 3H^+(aq)$$

3.3.2 Requirements

Chemicals	Apparatus	
Potash alum	Beaker 400 cm^3	1 No.
Concentrated	Beaker 250 cm^3	1 No.
hydrochloric acid	Bunsen burner	1 No.
Acetic acid	Desiccator	1 No.
Ammonium acetate	Filtration apparatus	1 No.
8–Hydroxyquinoline	Glass rod	1 No.
Distilled water	Pair of tongs	1 No.
	Rubber policeman	1 No.
	Sintered glass crucible (porosity G4)	1 No.
	Tripod stand	1 No.
	Wash bottle	1 No.
	Watch glass	2 No.
	Water bath	1 No.
	Wire gauze	1 No.

3.3.3 Procedure

Weigh out accurately about 0.5 g of potash alum from a weighing bottle into a 400 cm^3 beaker. Dissolve in 20–25 cm^3 of distilled water. Alternatively, take 25 cm^3 of the solution prepared by your counsellor. Add 1 cm^3 of conc. HCl and dilute the solution to 150 cm^3. Add 5–6 cm^3 of 8–hydroxyquinoline (oxine) reagent (a 10% solution in 20% acetic acid) and heat to 70–80°C. Slowly add 25 cm^3 of 2M ammonium acetate solution dropwise and with constant stirring to ensure complete precipitation. If the supernatant liquid is yellow to orange in colour, it means enough 8–hydroxyquinoline has been added. Heat the contents on a boiling water bath for half an hour so that the precipitate becomes granular and of easily filterable form. Allow to cool.

Filter the precipitate through a constant weight sintered glass crucible of porosity G4. Wash the precipitate first with hot water and then with cold water. Continue washing till the filtrate is almost colourless. Dry the precipitate at 130–140°C in an electric drying oven. Cool in a desiccator and weigh as $Al(C_9H_6NO)_3$. Repeat the process of heating, cooling and weighing till the weight becomes constant.

3.3.4 Observations

Weight of potash alum

i) Weight of empty weighing bottle = g

ii) Weight of weighing bottle + potash alum = g

iii) Weight of weighing bottle after transferring potash alum = g

Weight of sintered crucible

iv) 1st weight of sintered crucible = g

v) 2nd weight of sintered crucible = g

Weight of sintered glass crucible + precipitate

vi) 1st weight of crucible + precipitate = g

vii) 2nd weight of crucible + precipitate = g

3.3.5 Calculations

Calculate the percentage of aluminium ions in potash alum as follows:

Weight of potash alum taken for experiment = ii) – iii) g

= w g

Weight of $Al(C_9H_6NO)_3$ formed = vii) – v) g = x g

You know that one mole of potash alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$) contains two moles of aluminium ions which are converted into two moles of aluminium(III) 8–hydroxyquinolinate. Thus,

$K_2SO_4.Al_2(SO_4)_3.24H_2O$	$\equiv 2Al^{3+}$	$\equiv 2Al(C_9H_6NO)_3$
948.76 g	$\equiv 2 \times 26.98$ g	$\equiv 2 \times 459.43$ g
w g	$\equiv$ y g?	$\equiv$ x g

Hence, weight of Al^{3+} ions in x g of $Al(C_9H_6NO)_3$

$$y = \frac{26.98}{459.43} \times x \text{ g}$$

Now this y g of Al^{3+} ions are present in w g of the potash alum taken for analysis. Hence, percentage of Al^{3+} ions in potash alum

$$\% Al^{3+} = \frac{y}{w} \times 100$$

$$= \frac{26.98 \times x}{459.43 \times w} \times 100\%$$

$$\% Al^{3+} = \frac{26.98 \times \text{weight of } Al(C_9H_6NO)_3 \text{ formed}}{459.43 \times \text{weight of potash alum taken}} \times 100\%$$

Compare this value with the theoretical percentage of Al^{3+} ions (5.69%, calculated in Experiment 4) in potash alum.

If you have performed the experiment carefully, the experimental and the calculated values should agree within 0.5% with each other. Following a similar procedure, you can calculate the percentage of Al^{3+} ions in any other substance.

3.3.6 Result

You can report your result in any one of the following forms as instructed by your counsellor.

Weight of $Al(C_9H_6NO)_3$ formed = g

or

Percentage of aluminium ions in potash alum = %

3.4 EXPERIMENT 6 : DETERMINATION OF COPPER AS COPPER(I) THIOCYANATE

In this experiment you will perform the gravimetric determination of copper ions in a copper compound such as tetraamminecopper(II) sulphate or copper(II) sulphate.

3.4.1 Principle

Copper ions are precipitated as copper(I) thiocyanate from a mildly acidic solution by the addition of a ammonium thiocyanate solution. As you are aware that the copper(II) ions exist in +2 oxidation state in solution, these are first reduced to +1 oxidation state with sulphurus acid and then precipitated as copper(I) thiocyanate. The precipitate is filtered in a sintered glass crucible, washed with 0.1% ammonium thiocyanate solution, dried at 120°C and weighed as copper(I) thiocyanate.

$2Cu^{2+}(aq) + HSO_3^-(aq) + H_2O(l) \longrightarrow 2Cu^+(aq) + HSO_4^-(aq) + 2H^+(aq)$

$Cu^+(aq) + SCN^-(aq) \longrightarrow CuSCN(s)$

If we know the weight of sample taken for analysis and the weight of CuSCN formed, we can determine the percentage of copper(II) ions in the sample.

3.4.2 Requirements

Chemicals	Apparatus	
Tetraamminecopper (II) sulphate	Beaker 400 cm^3	1 No.
Hydrochloric acid	Beaker 250 cm^3	1 No.
Sodium or ammonium	Bunsen burner	1 No.
hydrogensulphite or	Desiccator	1 No.
sulphurous acid	Filtration apparatus	1 No.
Ammonium thiocyanate	Glass rod	1 No.
Ethanol	Pair of tongs	1 No.
Distilled water	Rubber policeman	1 No.
	Sintered glass crucible (G4)	1 No.
	Tripod stand	1 No.
	Wash bottle	1 No.
	Watch glass	2 No.
	Water bath	1 No.
	Wire gauze	1 No.

3.4.3 Procedure

Weigh accurately about 0.4 g of the copper complex from a weighing bottle into a 400 cm^3 beaker. Dissolve in 150 cm^3 distilled water. Alternatively, you can take 25 cm^3 of a copper(II) solution prepared by your counsellor into a 400 cm^3 beaker and add 100–125 cm^3 of distilled water to it. Acidify with 2 to 3 cm^3 dilute hydrochloric acid until the solution is distinctly acidic to litmus. Add 2 to 3 g sodium or ammonium hydrogensulphite or 20 to 30 cm^3 of saturated sulphurous acid solution. Place a stirring glass rod and cover the beaker with a watch glass. Heat the contents to near boiling. Make sure that the vapour over the liquid distinctly smells of sulphur dioxide (check with acidified $K_2Cr_2O_7$ paper).

Add slowly and with constant stirring 10% ammonium thiocyanate solution so that a white precipitate of copper(I) thiocyanate is thrown down. Add a slight excess of ammonium thiocyanate to effect complete precipitation. The mother liquor should be colourless and smell of sulphur dioxide. Digest on a boiling water bath for nearly half an hour. Allow to stand for about two hours or preferably overnight so that the precipitate becomes compact and settles at the bottom of the beaker.

Filter the precipitate through a constant weight sintered glass crucible, porisity G4. Wash the precipitate several times with 0.1% ammonium thiocyanate solution containing sulphurous acid to prevent any oxidation of copper(I) thiocyanate. Finally wash several times with 20% ethanol until the filtrate is free from SCN^- (Test the filtrate with $FeCl_3$ solution). Dry the precipitate to a constant weight at 110–120°C. Keep in a desiccator for half an hour and weigh as CuSCN. Repeat heating, cooling and weighing till the weight becomes constant.

3.4.4 Observations

Weight of complex

i) Weight of empty weighing bottle = g

ii) Weight of weighing bottle + complex = g

iii) Weight of weighing bottle after transferring the complex to beaker = g

Weight of sintered crucible

iv) 1st weight of sintered crucible = g

v) 2nd weight of sintered crucible = g

Weight of sintered crucible + CuSCN

vi) 1st weight of crucible + CuSCN = g

vii) 2nd weight of crucible + CuSCN = g

3.4.5 Calculations

Calculate the percentage of Cu^{2+} ions in $[Cu(NH_3)_4]SO_4.H_2O$ as follows:

Weight of complex taken for analysis = ii) – iii) = w g

Weight of CuSCN formed = vii) – v) = x g

You know that one mole of $[Cu(NH_3)_4]SO_4.H_2O$ contains one mole of Cu^{2+} ions which are converted into one mole of CuSCN on reaction with NH_4SCN.

$[Cu(NH_3)_4]SO_4.H_2O$	$\equiv Cu^{2+}$	$\equiv$ CuSCN
245.74 g	$\equiv$ 63.54 g	$\equiv$ 121.62 g
w g	$\equiv$ y g?	$\equiv$ x g

Hence, weight of Cu^{2+} ions in x g of CuSCN

$$y = \frac{63.54}{121.62} \times x \text{ g}$$

Now this y g of Cu^{2+} ions are present in w g of the complex taken for analysis. Therefore, the percentage of Cu^{2+} ions in the complex will be

$$\%Cu^{2+} = \frac{y}{w} \times 100$$

or $$\% Cu^{2+} = \frac{63.54 \times x}{121.62 \times w} \times 100\%$$

$$\%Cu^{2+} = \frac{63.54}{121.62} \times \frac{\text{Weight of CuSCN formed}}{\text{Weight of complex taken}} \times 100\%$$

Compare this value with the theoretical percentage of Cu^{2+} ions in the complex. Theoretically 245.74 g of complex contains 63.54 g of the Cu^{2+} ions. Hence theoretical percentage of Cu^{2+} ions in the complex:

$$\% Cu^{2+}(\text{theoretical}) = \frac{63.54}{245.74} \times 100\% = 25.86\%$$

If you have performed the experiment carefully, the experimental and the theoretical values should agree within 0.5% with each other. Following a similar procedure, you can calculate the percentage of Cu^{2+} ions in any other compound.

3.4.6 Result

You can report your result in any one of the following forms as instructed by your Counsellor :

Weight of CuSCN formed = g

or

Percentage of Cu^{2+} ions in the complex tetraamminecopper(II) sulphate = %

3.5 EXPERIMENT 7 : DETERMINATION OF IRON AS IRON(III) OXIDE

In this experiment you will perform the determination of iron(III) in the complex potassium trioxalatoferrate(III) by precipitation of iron(III) as iron(III) hydroxide and then by ignition of precipitate to iron(III) oxide.

3.5.1 Principle

Iron is precipitated as iron(III) hydroxide by the addition of aqueous ammonia solution to iron(III) solution. As iron(II) hydroxide is only partially precipitated by aqueous ammonia, iron(II) is oxidised to iron(III) by concentrated nitric acid in the presence of dilute hydrochloric acid prior to precipitation. The precipitate of iron(III) hydroxide is filtered, washed, ignited to iron(III) oxide and weighed.

$$3Fe^{2+}(aq) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$$

$$Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$$

3.5.2 Requirements

Chemicals	Apparatus	
Potassium trioxalatoferrate(III)	Beaker 400 cm^3	1 No.
Nitric acid	Beaker 250 cm^3	1 No.
Hydrochloric acid	Bunsen burner	1 No.
Aqueous ammonia	Clay pipe triangle	1 No.
Ammonium nitrate	Desiccator	1 No.
Distilled water	Funnel glass	1 No.
	Funnel stand	1 No.
	Glass rod	1 No.
	Pair of tongs	1 No.
	Rubber policeman	1 No.
	Silica crucible	1 No.
	Tripod stand	1 No.
	Wash bottle	1 No.
	Watch glass	2 No.
	Water bath	1 No.
	Weighing bottle	1 No.
	Whatman filter paper No. 41	1 No.
	Wire gauze	1 No.

3.5.3 Procedure

Ammonia dissolves traces of silica from the glass bottle. The silica remains suspended in a bottle of ammonia. If unfiltered ammonia is used for precipitation, silica will add on to the weight of the precipitate.

Weigh out accurately about 1.2 g of the complex potassium trioxalatoferrate(III) from a weighing bottle into a 400 cm^3 beaker. Add 20–25 cm^3 distilled water. Alternatively, take 25 cm^3 of the iron solution prepared by your Counsellor. Add 1 cm^3 concentrated hydrochloric acid and 3 cm^3 concentrated nitric acid. Place a glass rod in the beaker and cover with a watch glass. Heat the contents gently on burner using a wire gauze in a fume hood till the brown fumes of nitrogen dioxide cease to evolve and the solution acquires a deep yellow colour. Cool, wash the sides of the beaker and dilute the solution to 200 cm^3 with distilled water. Heat to boiling. Remove the flame and slowly add pure filtered 1:1 ammonia solution (50% ammonia, 50% water) in slight excess till the vapour over the liquid in beaker smells of ammonia. (Check with red litmus paper or with a rod dipped in HCl). This ensures complete precipitation of iron.

Add a spoonful of filter paper pulp to the precipitate and digest on a boiling water both for about 20 minutes. Check for complete precipitation by addition of ammonia solution from the side of the beaker. The supernatant liquid should be colourless.

Allow the precipitate to settle. Filter by decantation through Whatman filter paper No. 41. Do not allow the precipitate to leave the beaker at this stage otherwise it will clog the pores of the filter paper. Do not fill more than two thirds of filter paper with the liquid.

Wash the precipitate in the beaker with hot 2% ammonium nitrate solution three to four times. Allow each portion of wash liquid to run through before adding the next portion.

Test the filtrate for the absence of chloride ions (Test with dilute nitric acid and silver nitrate solution, no white precipitate or turbidity should be obtained).

Transfer the precipitate to the filter paper completely with the help of hot water from a wash bottle. Remove the precipitate adhering to the glass rod and the sides of the beaker with the help of a rubber policeman.

When the filter paper has drained completely, fold over the edges and transfer to the weighed silica crucible. Heat carefully on a very low flame so that the filter paper chars slowly without catching fire. In case the paper catches fire, remove the burner and cover the crucible with the lid. After the paper has charred completely, burn off the carbon at as low a temperature as possible with free access of air in order to avoid reduction of iron(III) oxide. Finally ignite the precipitate at red heat for 15 minutes. Do not allow the flame into the crucible, it will blow away the precipitate.

Ammonium chloride solution cannot be used in place of a solution of ammonium nitrate because volatile $FeCl_3$ will be formed during ignition and this will result in loss of weight of the precipitate.

Allow to cool the precipitate in air for 1–2 minutes and then cool in a desiccator. Weigh when the crucible has cooled to room temperature. Repeat heating, cooling and weighing till the weight becomes constant.

3.5.4 Observations

Weight of Complex

i) Weight of empty weighing bottle = g

ii) Weight of weighing bottle + complex = g

iii) Weight of weighing bottle after transferring the complex = g

Weight of Crucible

iv) 1st weight of empty silica crucible = g

v) 2nd weight of empty silica crucible = g

Weight of Iron(III) oxide

vi) 1st weight of crucible + iron(III) oxide = g

vii) 2nd weight of crucible + iron(III) = g

3.5.5 Calculations

Calculate the percentage of Fe^{3+} ions in potassium trioxalatoferrate(III) as follows:

Weight of the complex taken for analysis = ii) – iii) g = w g

Weight of Fe_2O_3 formed = vii) – v) g = x g

You know that one mole of potassium trioxalatoferrate(III), $K_3[Fe(C_2O_4)_3].3H_2O$, contains one mole of Fe^{3+} ions which are converted into one-half mole of Fe_2O_3 on precipitation and ignition. Thus,

$K_3[Fe(C_2O_4)_3].3H_2O \equiv Fe^{3+} \equiv \frac{1}{2}Fe_2O_3$

491.25 g ≡ 55.85 g ≡ ½ [illegible] g

w g ≡ y g? ≡ x g

Hence, weight of Fe^{3+} in x g of Fe_2O_3

$$y = \frac{55.85}{79.85} \times x \text{ g}$$

Now this y g of Fe^{3+} ions are present in w g of the complex taken for analysis. Hence, percentage of Fe^{3+} ions in the complex,

$$\%Fe^{3+} = \frac{y}{w} \times 100\%$$

$$= \frac{55.85}{79.85} \times \frac{x}{w} \times 100\%$$

$$\text{or } \% Fe^{3+} = \frac{55.85 \times \text{weight of } Fe_2O_3 \text{ formed} \times 100}{79.85 \times \text{weight of potassium trioxalatoferrate(III) taken}} \%$$

Compare this value with the theoretical percentage of Fe^{3+} ions in potassium trioxalatoferrate(III). Theoretically, 491.25 g of the complex contains 55.85 g of Fe^{3+} ions.

Hence, percentage (theoretical) of Fe^{3+} ions in the complex,

$$\% Fe = \frac{55.85}{491.25} \times 100\% = 11.37\%$$

If you have performed the experiment carefully, the experimental and the theoretical values should agree within 0.5% with each other. Following a similar procedure, you can calculate the percentage of Fe^{3+} ions in any iron compound.

3.5.5 Result

You can report your result in any one of the following forms as instructed by your Counsellor.

Weight of Fe_2O_3 formed = g

Percentage of Fe^{3+} ions in potassium trioxalatoferrate(III) = %

3.6 EXPERIMENT 8 : DETERMINATION OF SULPHATE IONS AS BARIUM SULPHATE

In this experiment you will perform the gravimetric estimation of sulphate ions in a substance, which is soluble in water, such as the tetraamminecopper(II) sulphate or potash alum.

3.6.1 Principle

The sulphate ions are precipitated as barium sulphate by slowly adding a dilute solution of barium chloride to a hot solution of sulphate ions, which is slightly acidified with hydrochloric acid. The precipitate of barium sulphate is filtered off, washed with water, carefully ignited at red heat and weighed as barium sulphate.

$$SO_4^{2-}(aq) + Ba^{2+}(aq) \longrightarrow BaSO_4(s)$$

If we know the weight of sample taken for analysis and the weight of the barium sulphate formed, we can determine the percentage of sulphate ions in the sample.

3.6.2 Requirements

Chemicals	Apparatus	
Tetraamminecopper(II) sulphate	Beaker 400 cm^3	1 No.
Hydrochloric acid	Beaker 250 cm^3	1 No.
Barium chloride solution	Bunsen burner	1 No.
Distilled water	Clay pipe triangle	1 No.
	Desiccator	1 No.
	Funnel glass	1 No.
	Funnel stand	1 No.
	Glass rod	1 No.
	Pair of tongs	1 No.
	Rubber policeman	1 No.
	Silica crucible	1 No.
	Tripod stand	1 No.

Chemicals	Apparatus	
	Wash bottle	1 No.
	Watch glass	1 No.
	Water bath	1 No.
	Weighing bottle	1 No.
	Whatman filter paper No. 42	1 No.
	Wire gauze	1 No.

3.6.3 Procedure

Weigh accurately (to nearest 0.2 mg) about 0.4 g of the complex tetraammminecopper(II) sulphate or about 0.5 g of the double salt potash alum from a weighing bottle into a 400 cm^3 beaker. Dissolve the sample in 150 cm^3 of distilled water. Alternatively, you may take 25 cm^3 of a solution prepared by your counsellor into a 400 cm^3 beaker and add 100–125 cm^3 of distilled water to it. Add about 2 cm^3 of concentrated hydrochloric acid, place a stirring rod and cover the beaker with watch glass. Heat the contents to near boiling (80–90°C).

In another beaker heat the barium chloride solution (2%) to near boiling (80–90°C).

Pour the hot barium chloride solution quickly and with vigorous stirring to the sulphate solution. Stir the mixture thoroughly for 2–3 minutes. Allow the barium sulphate precipitate to settle and test for complete precipitation by adding barium chloride solution from the side of the beaker.

Digest the precipitated barium sulphate on a boiling water bath for 1 to 2 hours. The supernatant liquid will become clear and the precipitate will settle down to the bottom of the beaker. During this process, the tiny crystals of barium sulphate initially formed undergo recrystallisation to give larger and more readily filterable crystals.

Decant the hot supernatant liquid by decantation through Whatman filter paper no 42. Make sure that the filter paper is not filled more than two third full with the liquid. Alternatively, the precipitate of barium sulphate can be filtered through a sintered glass crucible of porosity G4 using suction filtration.

Wash the precipitate in the beaker with hot distilled water. Transfer the supernatant liquid by decantation through the filter paper. Continue to wash the precipitate with hot water till the filtrate shows negative test for chloride ions.

Transfer the precipitate carefully to the filter paper and wash it down to the cone of the filter paper with water from wash bottle. Use the rubber policeman to transfer the last bits of precipitate sticking to the glass rod and the side of the beaker. Make sure that no precipitate is adhering to the beaker or the glass rod.

Allow the filter paper to drain completely or dry the filter paper with the precipitate on a hot air cone. Remove when slightly moist. Fold it carefully and place it into a constant weight silica crucible. Gently char the filter paper on a low flame. When no more smoke is visible gradually raise the temperature of the flame till the paper is converted into ash and the crucible glows with a dull redness. Continue to rotate the crucible with a pair of tongs in order to burn off any carbon or tar sticking to the crucible. Finally heat the crucible strongly for 15 to 20 minutes.

Allow the crucible to cool in air for 2 minutes. Place it in a desiccator and allow to cool to room temperature. Record the weight. Heat the crucible till a constant weight is obtained.

If proper care is not taken during ignition $BaSO_4$ may be partially reduced to BaS by carbon from the filter paper:

$$BaSO_4 + 2C \longrightarrow BaS + 2CO_2$$

Barium sulphide is subsequently oxidised back to $BaSO_4$ by O_2 present in air. Alternatively, the precipitate can be treated with 3–4 drops of dilute sulphuric acid and then strongly heated to convert barium sulphide, if any, to barium sulphate.

$BaS + 2O_2 \longrightarrow BaSO_4$

$BaS + H_2SO_4 \longrightarrow BaSO_4 + H_2S$

3.6.4 Observations

Weight of complex

i) Weight of empty weighing bottle = g

ii) Weight of weighing bottle + complex = g

iii) Weight of weighing bottle after transferring the complex to beaker = g

Weight of silica crucible

iv) 1st weight of silica crucible = g

v) 2nd weight of silica crucible = g

Weight of silica crucible + barium sulphate

vi) 1st weight of silica crucible + barium sulphate = g

vii) 2nd weight of silica crucible + barium sulphate = g

3.6.5 Calculations

Calculate the percentage of SO_4^{2-} ions in $[Cu(NH_3)_4]SO_4.H_2O$ as follows:

Weight of complex taken for analysis = ii) – iii) = w g

Weight of $BaSO_4$ formed = vii) – v) = x g

You know that one mole of $[Cu(NH_3)_4]SO_4.H_2O$ contains one mole of SO_4^{2-} ions which are converted into one mole of $BaSO_4$ on reaction with $BaCl_2$.

$[Cu(NH_3)_4]SO_4.H_2O$	$\equiv SO_4^{2-}$	$\equiv BaSO_4$
245.74 g	≡ 96.06 g	≡ 233.37 g
w g	≡ y g?	≡ x g

Hence, weight of sulphate ions in x g of barium sulphate

$$y = \frac{96.06 \times x}{237.37} \text{ g}$$

Now this y g of sulphate ions are present in w g of the complex taken for analysis.

Therefore, percentage of sulphate ions in the complex will be

$$\%SO_4^{2-} = \frac{y}{w} \times 100$$

$$= \frac{96.06 \times x}{237.37 \times w} \times 100\%$$

$$\boxed{\%\ SO_4^{2-} = \frac{96.06 \times \text{weight of } BaSO_4 \text{ formed}}{237.37 \times \text{weight of complex taken}} \times 100\%}$$

Compare this value with the theoretical percentage of sulphate ions in the complex. Theoretically, 245.74 of $[Cu(NH_3)_4]SO_4.H_2O$ contains 96.06 g of SO_4^{2-} ions.

Hence, theoretical percentage of SO_4^{2-} ions in the complex

$$\boxed{\%\ SO_4^{2-}\ (\text{theoretical}) = \frac{96.06}{245.74} \times 100\% = 39.09\%}$$

If you have performed the experiment carefully, the experimental and the theoretical values should agree within 0.5% with each other. Following a similar procedure, you can calculate the percentage of SO_4^{2-} ions in any other compound.

3.6.6 Result

You can report your result in any one of the following forms as instructed by your counsellor.

Weight of $BaSO_4$ formed = g

or

Percentage of sulphate ions in the complex tetraamminecopper(II) sulphate = %

3.7 SUMMARY

In this unit we described the gravimetric determination of aluminium, copper, iron and sulphate ions present in a water soluble compound. We discussed how to perform various operations involved in gravimetric determinations and also how to calculate the percentage of these ions in their compounds.

3.8 FURTHER READING

1. *Vogel's Qualitative Inorganic Analysis*, G. Svehla, Orient Longman, Sixth edition, 1987.
2. *A Text Book of Quantitative Inorganic Analysis*, A.I. Vogel, J. Bassett, R.C. Denney, G.H. Jeffery, J. Mendham, Longman, Fourth edition, 1978.

NOTES

BLOCK - 2

QUANTITATIVE INORGANIC ANALYSIS

BLOCK 2 QUALITATIVE INORGANIC ANALYSIS

Qualitative analysis of an inorganic mixture involves the detection of the anions and the cations present in the mixture. In this course you will study the classical methods of qualitative analysis. These can be broadly divided into two categories–dry tests and wet tests. Dry tests are performed on solid samples and usually at high temperatures while wet tests are performed on solutions. Although flame tests for some of the cations will be discussed in brief, main emphasis in this laboratory course will be on the wet chemical tests.

Qualitative analysis may be carried out on various scales. In macro analysis the quality of the sample used is 0.1 to 0.5 g and the volume taken for analysis is about 20 cm^3. In semimicro analysis these quantities are reduced by a factor of 10- 20, i.e., about 0.05 g sample and 1 cm^3 solution are used. The amount of substance used in micro analysis is about 1/100 of the quantity used in micro analysis, i.e., a few milligrams of solid or some tenths of a cubic centimeter of solution. Highly sensitive reactions are employed, which permit detection of individual ions even if they are present in small amounts.

The semimicro scale is the most appropriate for qualitative inorganic analysis because of some special advantages. Some of the advantages are reduced consumption of chemicals, greater speed of analysis, increased sharpness of separation, reduced consumption of harmful hydrogen sulphide, etc. But because of two reasons, you will perform qualitative analysis on macro scale during this course. First, semimicro analysis requires the use of some special apparatus and reagents which may not be available in all the study centres. Second, if you have not been exposed to qualitative inorganic analysis at macro scale earlier, you may find it difficult to perform analysis at semimicro scale. Once you become familiar with macro analysis, you can switch over to semimicro analysis without much difficulty.

The study of qualitative inorganic analysis is invaluable for every student of chemistry because this is where the student comes across and handles various materials which are studied in theory course. Also, it provides the students an excellent opportunity of learning by doing the chemistry of elements and the principles of equilibria in aqueous solution.

This block consists of three units. Unit 4 deals with the detection of the anions present in an inorganic mixture. In Unit 5 we discuss the principles involved in the analysis of cations, whereas in Unit 6 we describe the scheme of analysis of the cations.

Objectives

After studying this block and performing the experiments set for you to do, you should be able to:

- describe the principles involved in the qualitative analysis of a mixture of inorganic salts,
- detect the presence of the anions and the cations in a mixture of inorganic salts,
- perform tests for detection of the anions and the cations present in a mixture of inorganic salts,
- write chemical equations for the tests for the anions and the cations present in a mixture of inorganic salts,
- perform flame tests for certain cations present in a mixture of inorganic salts,
- perform tests, make observations and draw correct inference about the presence or the absence of the anions and the cations in an inorganic mixture, and
- perform separation of the cations into analytical groups by selective precipitation.

UNIT 4 DETECTION OF THE ANIONS

Structure

4.1 INTRODUCTION

You know that the qualitative analysis involves the detection of the anions and the cations present in an inorganic mixture. Sometimes the knowledge of anions present in a mixture provides important clues about the cations which may be present in a mixture and the scheme of analysis to be followed. Therefore, it is desirable to first detect the presence of anions and after that the cations. In this unit, we will discuss the scheme of detection of anions which will be followed by the scheme of analysis of cations in Units 5 and 6.

Objectives

After studying this unit, you should be able to:

- identify anions present in a mixture,
- describe tests for various anions,

- explain the chemistry of various tests for anions,
- prepare water extract and sodium carbonate extract,
- perform tests for identification of anions present in a mixture,
- remove interfering anions from the mixture, and
- perform tests for identifying special combinations of anions.

4.2 CLASSIFICATION OF THE ANIONS

For the systematic identification of the anions present in any mixture, the anions are divided into following three classes:

4.2.1 Anions of Class I

The anions of Class I evolve gases or vapours on treatment with dil. HCl or dil. H_2SO_4. These anions are carbonate, sulphite, sulphide, thiosulphate, nitrite and acetate, which are the anions of weak acids.

4.2.2 Anions of Class II

The anions of Class II evolve gases or vapours on treatment with conc. HCl or Conc. H_2SO_4. These anions are fluoride, chloride, bromide, iodide, nitrate and oxalate.

4.2.3 Anions of Class III

The anions of this class do not evolve any gas on treatment with acids. These are identified by formation of precipitate on treatment with certain reagents. Sulphate, borate and phosphate ions are the anions of Class III.

Here we would like to emphasise that unlike scheme of classification of cations, the scheme of classification of anions is not a rigid one since some of the anions belong to more than one of the classes, e.g., acetate. Also, it is not always necessary to test for the presence of anions of Class I before testing for the presence of anions of Class II or Class III in any mixture.

4.3 PRELIMINARY TESTS FOR THE ANIONS

In this unit the tests for all these anions will be systematically discussed. We shall first discuss the preliminary tests for detecting the presence of anions of Class I and Class II, which will be followed by their confirmatory tests. As there are no preliminary tests for the anions of Class III only their confirmatory tests will be discussed.

4.3.1 Preliminary Tests for the Anions of Class I

Take about 0.2 g of dry mixture in a test tube. Add 2 cm^3 of dilute hydrochloric or sulphuric acid. If a gas is evolved, note its colour and odour and draw inference with the help of Table 4.1. Heat the test tube if necessary. If no gas is evolved, anions of this class are absent in the mixture.

Table 4.1 : Preliminary Tests for the Anions of Class I

Sl. No.	Observation	Inference	Explanation/ Reaction
1.	Colourless gas evolved with brisk effervescence. On passing the gas in lime water, it turns milky.	CO_3^{2-} may be present	$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$ $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

Sl. No.	Observation	Inference	Explanation / Reactopm
2.	Colourless, suffocating gas with smell of burning sulphur; the gas turns acidified $K_2Cr_2O_7$ paper green.	SO_3^{2-} may be present	$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g)$ $Cr_2O_7^{2-}(aq) + 2H^+(aq) + 3SO_2(g) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$ (green)
3.	Colourless, suffocating gas with smell of burning sulphur and there is a deposit of sulphur in the test tube. The gas turns acidified $K_2Cr_2O_7$ paper green.	$S_2O_3^{2-}$ may be present	$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g) + S(s)$
4.	Colourless gas with smell of rotten eggs, turns moistened lead acetate paper black.	S^{2-} may be present	$S^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g)$ $Pb^{2+}(aq) + H_2S(g) \rightarrow PbS(s) + 2H^+(aq)$ (black)
5.	Light brown gas which turns KI-starch paper blue.	NO_2^- may be present	$2NO_2^-(aq) + 2H^+(aq) \rightarrow H_2O(l) + NO(g) + NO_2(g)$
6.	Colourless vapours with smell of vinegar on warming the test tube.	CH_3COO^- may be present	$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(g)$

When salts of the anions of Class I are treated with strong, non-oxidising acids, corresponding acids are generated in the solution.

$$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2CO_3(aq)$$

$$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2SO_3(aq)$$

$$NO_2^-(aq) + H^+(aq) \rightarrow HNO_2(aq)$$

$$S^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(aq)$$

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$

Out of these H_2CO_3, H_2SO_3 and HNO_2 are thermally unstable and decompose into gaseous products, whereas H_2S and CH_3COOH are evolved as vapours on warming:

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l)$$

$$H_2SO_3(aq) \rightarrow SO_2(g) + H_2O(l)$$

$$2HNO_2(aq) \rightarrow NO(g) + NO_2(g) + H_2O(l)$$

4.3.2 Preliminary Tests for the Anions of Class II

Take 0.2-0.3 g of the mixture in a dry test tube and add 2–3 cm^3 of conc. sulphuric acid dropwise. Observe the reaction at room temperature and then warm the test tube gently. If no gas or vapours are evolved, the anions of this class are absent. Draw inference with the help of Table 4.2.

Table 4.2 : Preliminary Tests for the Anions of Class II

Sl. No.	Observation	Inference	Explanation/Reaction
1.	Colourless, pungent smelling gas is evolved, which gives white dense fumes of NH_4Cl when a glass rod dipped in aqueous ammonia is placed in the evolved gas.	Cl^- may be present	$Cl^-(aq) + H^+(aq) \rightarrow HCl(g)$ $HCl(g) + NH_3(g) \rightarrow NH_4Cl(g)$

Sl. No.	Observation	Inference	Explanation/Reaction
2.	Reddish brown gas is evolved and the solution in the test tube acquires a yellow-red colour.	Br^- may be present	$Br^-(aq) + 6H^+(aq) + 3SO_4^{2-}(aq) \rightarrow 2HSO_4^-(aq) + SO_2(g) + Br_2(g) + 2H_2O(l)$
3.	Violet vapours of I_2 are evolved, which turn the moist starch paper blue.	I^- may be present	$2I^-(aq) + 6H^+(aq) + 3SO_4^{2-}(aq) \rightarrow 2HSO_4^-(aq) + SO_2(g) + I_2(g) + 2H_2O(l)$
4.	Oily drops inside the test tube and the pungent smelling gas leaves a white deposit on a moistened glass rod.	F^- may be present	$2F^-(aq) + 2H^+(aq) \rightarrow 2HF(g)$
5.	Pungent smelling, brown fumes of NO_2 are evolved. The evolution of NO_2 increases on heating the reaction mixture with copper turnings.	NO_3^- may be present	$NO_3^-(aq) + H^+(aq) \rightarrow HNO_3(aq)$ $4HNO_3(aq) \rightarrow 4NO_2(g) + O_2(g) + 2H_2O(l)$ $Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$
6.	Colourless, odourless gas is evolved which turns lime water milky and burns with a blue flame	$C_2O_4^{2-}$ may be present	$C_2O_4^{2-}(aq) + 2H^+(aq) \rightarrow CO(g) + CO_2(g) + H_2O(l)$ $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$ $CO(g) + O_2(g) \rightarrow CO_2(g)$

4.4 PREPARATION OF SOLUTION FOR IDENTIFICATION OF THE ANIONS

The preliminary tests described in the preceding section do not always offer very conclusive evidence for the presence of anions in a mixture. Therefore, further tests have to be performed for confirmation of those anions which are indicated by the preliminary tests and for the detection and confirmation of the anions of Class III which have no preliminary tests. These tests are called confirmatory tests and are performed on the solution of anions which is prepared as described below.

4.4.1 Preparation of Water Extract

All common acetates, nitrites, nitrates and thiosulphates are soluble in water. Confirmatory tests for these anions can be performed with the water extract of the mixture. Water extract can be prepared by boiling 1-2 g of the mixture with 10–15 cm^3 of distilled water in a boiling tube for a minute or two. Residue, if any, is filtered. The filtrate is called **water extract (W.E.)**.

4.4.2 Preparation of Sodium Carbonate Extract

If the mixture is found to be partially or wholly insoluble in water, it is boiled with saturated sodium carbonate solution. This treatment converts the anions present in mixture into soluble sodium salts as a result of double decomposition, e.g.,

$$BaSO_4(s) + Na_2CO_3(aq) \xrightarrow{H_2O} BaCO_3(s) + Na_2SO_4(aq)$$

$$PbCl_2(s) + Na_2CO_3(aq) \xrightarrow{H_2O} PbCO_3(s) + 2NaCl(aq)$$

For preparing sodium carbonate extract, take 0.5-1.0 g of powdered mixture, 1.0-2.0 g of sodium carbonate and 5–10 cm^3 of distilled water in a boiling tube or a 50 ml beaker. Heat with stirring for 5-10 minutes. Cool the contents and filter. The filtrate is called sodium carbonate extract (S.E.). This extract is used for confirming the presence of most anions except for carbonate since sodium carbonate has been added during its preparation.

4.5 CONFIRMATORY TESTS FOR THE ANIONS

After preparation of the water extract or the sodium carbonate extract, the following tests are performed to confirm the presence of various anions in the mixture.

4.5.1 Tests for the Sulphide Ions

1. Take 1 cm^3 of sodium carbonate extract in a test tube and add 1 – 2 cm^3 of sodium nitroprusside solution. A purple or violet colour confirms sulphide ions:

$$S^{2-}(aq) + [Fe(CN)_5NO]^{2-}(aq) \rightarrow \underset{\text{purple or violet colour}}{[Fe(CN)_5NOS]^{4-}(aq)}$$

2. Take 1 – 2 cm^3 of S.E. in a test tube, acidify it with acetic acid and boil to remove CO_2. Then add 1–2 cm^3 of lead acetate solution. Formation of black precipitate confirms sulphide ions:

$$S^{2-}(aq) + Pb^{2+}(aq) \rightarrow PbS(s)$$

4.5.2 Tests for the Sulphite Ions

Take 2–3 cm^3 of S.E. and add 2–3 cm^3 of $BaCl_2$ solution to it. A white precipitate may appear due to the presence of SO_3^{2-}, SO_4^{2-} or excess of CO_3^{2-} ions present in the solution. Filter the precipitate and divide into three parts.

1. To the first part, add dil. HCl. Evolution of SO_2 gas which turns acidified dichromate paper green confirms the presence of SO_3^{2-} ions:

$$BaSO_3(s) + 2H^+(aq) \rightarrow Ba^{2+}(aq) + SO_2(g) + H_2O(l)$$

2. To the second part, add a few drops of $KMnO_4$ solution and acidify with dil. H_2SO_4. If the pink colour of $KMnO_4$ is discharged, the presence of SO_3^{2-} ions is confirmed:

$$BaSO_3(s) + H_2O(l) \rightarrow BaSO_4(s) + 2H^+(aq) + 2e] \times 5$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)] \times 2$$

$$5BaSO_3(s) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 2BaSO_4(s) + 2Mn^{2+}(aq) + 3H_2O(l)$$

3. To the third part, add I_2 solution. If colour of iodine is discharged, SO_3^{2-} is confirmed:

$$BaSO_3(s) + I_2(aq) + H_2O(l) \rightarrow BaSO_4(s) + 2HI(aq)$$

4.5.3 Tests for the Thiosulphate Ions

1. Take 1–2 cm^3 of S.E. in a test tube and acidify with dil. H_2SO_4. Evolution of SO_2 accompanied by a yellow precipitate of sulphur confirms the presence of thiosulphate ions:

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + S(s) + H_2O(l)$$

2. Take 1 – 2 cm^3 of S.E. in a test tube and acidify with acetic acid. Add 1 cm^3 of $AgNO_3$ solution. Formation of white precipitate which turns yellow, orange–brown and finally black in quick succession confirms the presence of thiosulphate ions:

$$S_2O_3^{2-}(aq) + 2Ag^+(aq) \rightarrow Ag_2S_2O_3(s)$$

$$Ag_2S_2O_3(s) + H_2O(l) \rightarrow \underset{\text{Black}}{Ag_2S(s)} + 2H^+(aq) + SO_4^{2-}(aq)$$

4.5.4 Tests for the Nitrite Ions

1. Take 5 drops of W.E. in a test tube. Dilute with 5 drops of distilled water. Add 5 M acetic acid until the solution is just acidic. Cool the test tube in a cold water bath. Add 2-3 drops of freshly prepared 0.2 M $FeSO_4$ solution to the cooled solution. Appearance of a brown colour throughout the solution confirms the presence of nitrite ions:

$$NO_2^-(aq) + CH_3COOH(aq) \rightarrow HNO_2(aq) + CH_3COO^-(aq)$$

$$3HNO_2(aq) \rightarrow HNO_3(aq) + H_2O(l) + 2NO(g)$$

$$[Fe(H_2O)_6]^{2+}(aq) + NO(g) \rightarrow [Fe(H_2O)_5NO]^{2+}(aq) + H_2O(l)$$

2. To 1 cm^3 of W.E. add 5 drops of KI solution, 1 cm^3 of starch solution and 1 cm^3 of dil. H_2SO_4 . Appearance of a deep blue colour confirms the presence of nitrite ions:

$$2NO_2^-(aq) + 4H^+(aq) + 2I^-(aq) \rightarrow 2NO(g) + I_2(aq) + 2H_2O(l)$$

$$I_2(aq) + \text{Starch} \rightarrow \text{Blue coloured complex}$$

3. Take 5 drops of W.E in a test tube, acidify with 6 M acetic acid. Add a pinch of thiourea and stir well. Add 2 drops of $FeCl_3$ solution. A blood red colour confirms nitrite ions:

$$NO_2^-(aq) + H_2NCSNH_2(s) \rightarrow N_2(g) + CNS^-(aq) + H_2O(l)$$

$$Fe^{3+}(aq) + 3CNS^-(aq) \rightarrow Fe(SCN)_3(aq)$$
(Blood red colour)

You should note that the nitrite ion is a moderately strong oxidising agent in acidic medium. It oxidises S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$ and I^- ions to S, SO_4^{2-}, SO_4^{2-} + S , and I_2 respectively. Therefore, these anions cannot be present if NO_2^- ions are present in the mixture.

$$S^{2-}(aq) + NO_2^-(aq) + 2H^+(aq) \rightarrow S(s) + NO(g) + H_2O(l)$$

$$SO_3^{2-}(aq) + 2NO_2^-(aq) + 2H^+(aq) \rightarrow SO_4^{2-}(aq) + 2NO(g) + H_2O(l)$$

$$S_2O_3^{2-}(aq) + 2NO_2^-(aq) + 2H^+(aq) \rightarrow SO_4^{2-}(aq) + S(s) + 2NO(g) + H_2O(l)$$

$$2I^-(aq) + 2NO_2^-(aq) + 4H^+(aq) \rightarrow I_2(s) + 2NO(g) + 2H_2O(l)$$

4.5.5 Tests for the Acetate Ions

1. Take 1 g of the mixture, 1 cm^3 of conc. H_2SO_4 and 2–3 cm^3 of rectified spirit in a test tube. Warm the contents gently for several minutes. Ethyl acetate is formed, which can be recognised by its pleasant, fruity odour. This confirms the presence of acetate ions in the mixture:

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$

$$CH_3COOH(aq) + C_2H_5OH(aq) \xrightarrow{H_2SO_4} CH_3COOC_2H_5(g) + H_2O(l)$$

It is preferable tc use iso-amyl alcohol, if easily available in the laboratory, because the banana like odour of the resulting iso-amyl acetate is more readily distinguished.

2. Take 0.5 cm^3 of W.E. in a test tube. Add $Ba(NO_3)_2$ solution to precipitate SO_4^{2-} and PO_4^{3-} ions if present. Filter the precipitate and discard it. Now add 0.5 cm^3

of 0.1 M $La(NO_3)_3$ solution and add 0.01 M I_2 solution dropwise till the colour of I_2 persists. Wait for a minute and add 1 drop of 1 M aqueous ammonia. If a blue or blue-brown ring is developed around the ammonia drop within a few minutes, presence of acetate ions is confirmed. The ring probably develops due to the adsorption of iodine by basic lanthanum acetate.

4.5.6 Tests for the Nitrate Ions

Take 2 cm^3 W.E. in a test tube. Add 4 cm^3 concentrated sulphuric acid, mix the two liquids thorcughly and cool the mixture under a stream of cold water from the tap. Pour 3 cm^3 of saturated solution of $FeSO_4$ slowly down the side of the test tube so that it forms a separate layer on top of the solution in the test tube. A brown ring will be formed at the zone of contact of the two liquids:

$$NO_3^-(aq) + 4H^+(aq) + 3Fe^{2+}(aq) \rightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$$

$$[Fe(H_2O)_6]^{2+}(aq) + NO(g) \rightarrow [Fe(H_2O)_5NO]^{2+}(aq) + H_2O(l)$$

This test for nitrate ion is based on its ability to oxidise Fe^{2+} to Fe^{3+} in acidic solution with the production of NO gas. Since NO is more soluble in water at low temperature, in well cooled solution it reacts with excess Fe^{2+} present in solution to form brown nitrosyliron(II) complex ion, $[Fe(H_2O)_5NO]^{2+}$. Nitrite, bromide and iodide ions interfere in this test.

4.5.7 Tests for the Oxalate Ions

Take 2–3 cm^3 of S.E. in a test tube. Acidify with acetic acid. Add aqueous ammonia till a smell of ammonia persists (you may test with litmus paper). Heat for 2 minutes to remove excess of ammonia. Add $CaCl_2$ solution. Formation of a white precipitate indicates the presence of oxalate ions.

$$C_2O_4^{2-}(aq) + Ca^{2+}(aq) \rightarrow CaC_2O_4(s)$$

Filter the precipitate and dissolve it in dil. H_2SO_4. Warm the solution and add 1 cm^3 of $KMnO_4$ solution. If pink colour is discharged with the evolution of CO_2 gas, the presence of oxalate ions is confirmed.

$$CaC_2O_4(s) + 2H^+(aq) \rightarrow H_2C_2O_4(aq) + Ca^{2+}(aq)$$

$$5H_2C_2O_4(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

4.5.8 Tests for the Chloride Ions

1. Acidify 2–3 cm^3 of S.E. with dil. HNO_3. Boil off CO_2. Then add $AgNO_3$ solution. Formation of a curdy white precipitate, which is soluble in aqueous ammonia, confirms the presence of chloride ions in the mixture.

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

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

2. Heat 0.5 g of dry mixture with 0.5 g of $K_2Cr_2O_7$ and 2 cm^3 of conc. H_2SO_4 in a dry test tube, red vapours of chromyl chloride will be evolved. Pass the vapours in dil. NaOH solution, a yellow solution will be obtained. Acidify the solution with acetic acid and then add lead acetate solution. Formation of a yellow precipitate of lead chromate, which is soluble in NaOH, confirms the presence of chloride ions.

$$4NaCl(s) + K_2Cr_2O_7(s) + 3H_2SO_4(l) \rightarrow K_2SO_4(s) + 2Na_2SO_4(s) + \underset{\text{Chromyl chloride gas}}{CrO_2Cl_2(g)} + 3H_2O(l)$$

$$CrO_2Cl_2(g) + 4NaOH(aq) \rightarrow Na_2CrO_4(aq) + 2NaCl(aq) + 2H_2O(l)$$

$$Na_2CrO_4(aq) + Pb(CH_2COO)_2(aq) \rightarrow PbCrO_4(s) + 2CH_3COONa(aq)$$

Due to the formation of chromyl chloride gas, this test is called **chromyl chloride test.** The test fails if the mixture contains chlorides of Hg^{2+}, Sn^{2+}, Pb^{2+} or Ag^{+}.

4.5.9 Tests for the Bromide Ions

1. Acidify 2–3 cm^3 of S.E. with dil. HNO_3 and boil off CO_2. Add $AgNO_3$ solution. Formation of a light yellow precipitate which is partially soluble in aqueous ammonia solution, confirms the presence of bromide ions:

$$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$$
Light yellow ppt.

2. Take 2 cm^3 of S.E., acidify it with dil. HCl and boil off CO_2. Add 2 cm^3 of carbon disulphide, dichloromethane or carbon tetrachloride. Then add chlorine water dropwise and shake. Bromide ions are oxidised to bromine, which imparts an orange colour to the organic layer. This confirms the presence of bromide ions in the mixture.

$$2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$$

$$Br_2(l) + CS_2(l) \rightarrow \text{Orange colour}$$

4.5.10 Tests for the Iodide Ions

1. Acidify 2–3 cm^3 of S.E. with dil. HNO_3 and boil off CO_2. Add $AgNO_3$ solution. Formation of a pale yellow precipitate insoluble in aqueous ammonia confirms the presence of iodide ions in the mixture.

$$I^-(aq) + Ag^+(aq) \rightarrow AgI(s)$$
Pale yellow ppt.

2. Take 2 cm^3 of S.E. in a test tube. Acidify it with dil. HCl and boil off CO_2. Add 2 cm^3 of carbon disulphide, dichloromethane or carbon tetrachloride. Then add chlorine water dropwise and shake. Iodide ions are oxidised to iodine, which imparts a violet colour to the organic layer.

$$2I^-(aq) + Cl_2(aq) \rightarrow I_2(s) + 2Cl^-(aq)$$

$$CS_2(l) + I_2(s) \rightarrow \text{Violet colour}$$

The violet colour disappears on addition of excess of chlorine water. This confirms the presence of iodide ions in the mixture:

$$I_2(s) + Cl_2(aq) \rightarrow 2ICl(aq)$$
Iodine monochloride (colourless)

4.5.11 Tests for the Fluoride Ions

1. Take 0.5 g of powdered mixture, an equal amount of sand and 2 cm^3 of conc. H_2SO_4 in a dry test tube. Heat the test tube, vapours of SiF_4 will be given off. Hold a moistened glass rod in the vapours. Formation of a waxy white deposit on the glass rod, confirms the presence of fluoride ions in the mixture.

$$4NaF(s) + SiO_2(s) + 4H_2SO_4(l) \rightarrow SiF_4(g) + 4NaHSO_4(s) + 2H_2O(l)$$

$$3SiF_4(g) + 4H_2O(l) \rightarrow \underset{\text{Silicic acid}}{H_4SiO_4(s)} + \underset{\text{Hydrofluosilicic acid}}{2H_2SiF_6(aq)}$$
(waxy white deposit)

2. Take 2 cm^3 of S.E. in a test tube. Acidify with acetic acid and boil off CO_2. Add $CaCl_2$ solution. A white precipitate of CaF_2 may be formed.

$$2F^-(aq) + Ca^{2+}(aq) \rightarrow CaF_2(s)$$

Filter the precipitate and dissolve it in dil. H_2SO_4. Warm and add a few drops of $KMnO_4$. Pink colour of $KMnO_4$ is not discharged (difference from oxalate). This confirms the presence of flouride ions in the mixture.

So far we have discussed the confirmatory tests for the anions of Class I and II which are indicated by preliminary tests with sulphuric acid. Now, we shall discuss the confirmatory tests for the anions of Class III, i.e., sulphate, phosphate and borate ions, which are not indicated by preliminary tests.

4.5.12 Test for the Sulphate Ions

Take 2–3 cm^3 of S.E. in a test tube. Acidify it with dil. HCl and boil off CO_2. Add $BaCl_2$ solution. Appearance of a white precipitate, which is insoluble in conc. HCl and conc. HNO_3, confirms the presence of sulphate ions.

$$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$$

4.5.13 Tests for the Phosphate Ions

Take 1–2 cm^3 of S.E. in a test tube, acidify it with 6 M HNO_3 and then add 2–3 cm^3 of ammonium molybdate solution. Warm the solution gently to 40° C. A canary yellow precipitate is slowly formed, which is soluble in ammonium acetate, aqueous ammonia and caustic alkali. This confirms the presence of phosphate ions.

$$HPO_4^{2-}(aq) + 3NH_4^+(aq) + 12MoO_4^{2-}(aq) + 23H^+(aq) \rightarrow (NH_4)_3[P(Mo_3O_{10})_4](s) + 12H_2O(l)$$

Ammonium phosphomolybdate

Arsenate ion interferes in this test, as it also produces a similar yellow precipitate of ammonium arsenomolybdate.

$$AsO_4^{3-}(aq) + 3NH_4^+(aq) + 12MoO_4^{2-}(aq) + 24H^+(aq) \rightarrow (NH_4)_3[As(Mo_3O_{10})_4](s) + 12H_2O(l)$$

Both ammonium phosphomolybdate and ammonium arsenomolybdate dissolve on boiling with ammonium acetate solution, but only the latter yields a white precipitate on cooling. The presence of phosphate ions in the mixture is further confirmed by testing in the filtrate of Group II after precipitation of As_2S_3 or As_2S_5 as follows:

Take 2–3 cm^3 of the filtrate in a china dish and boil off H_2S from it. Add 1 cm^3 of 6 M HNO_3 and 1 cm^3 of ammonium molybdate solution. Warm and wait for 5 minutes. If a yellow precipitate is formed, it confirms the presence of phosphate ions in the mixture.

4.5.14 Test for the Borate Ions

The test for borate ions is based on the reaction of borate ions with methanol in presence of concentrated sulphuric acid, which acts as a dehydrating agent. On heating volatile methyl borate is formed, which burns with a green edged flame. This confirms the presence of borate ions:

$$BO_3^{3-}(aq) + 3H^+(aq) + 3CH_3OH(l) \xrightarrow{\text{conc.}H_2SO_4} B(OCH_3)_3(g) + 3H_2O(l)$$

$$2B(OCH_3)_3(g) + 9O_2(g) \rightarrow B_2O_3(s) + 6CO_2(g) + 9H_2O(l)$$

Isolate the vapours from the mixture before burning otherwise Ba^{2+} and Cu^{2+} salts interfere because these salts also impart a green colour to the alcohol flame.

Take 0.5 g of the mixture, 1 cm^3 of concentrated sulphuric acid and 1 cm^3 of methanol or ethanol in a china dish. Invert a funnel in the dish. Place the dish on a wire gauze and heat gently. Allow the vapours to pass out off the stem of the funnel. Burn the vapours. A green coloured flame confirms borate ions in the mixture.

4.6 SPECIAL TESTS FOR THE MIXTURES OF THE ANIONS

Confirmatory tests for some anions discussed in the preceding section fail in presence of certain other anions in the mixture. For example, the silver nitrate test for the bromide ions fails if iodide ions are also present in the mixture, because both form a yellow precipitate with silver nitrate. In this section, we shall discuss the confirmatory tests for anions which can be performed in presence of other anions also.

4.6.1 Test for Carbonate Ions in Presence of Sulphite and/or Thiosulphate Ions

Sulphites and thiosulphates on treatment with dil. H_2SO_4 produce SO_2, which like CO_2 turns lime water turbid or milky. Hence, it cannot be inferred whether the turbidity is due to carbonate, sulphite or thiosulphate.

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$

$$Ca(OH)_2(aq) + SO_2(g) \rightarrow CaSO_3(s) + H_2O(l)$$

In order to test for carbonate ions in presence of sulphite or thiosulphate ions, take 0.5 g of mixture and 0.5 g of $K_2Cr_2O_7$ in a test tube. Add 2–3 cm^3 of dil. H_2SO_4. Heat the test tube and pass the evolved gas through lime water. If lime water turns milky, it confirms the presence of carbonate ions in the mixture. SO_2 liberated by reaction of sulphite and/or thiosulphate with dil. H_2SO_4 is trapped by $K_2Cr_2O_7$ in the test tube, which turns green.

$$Cr_2O_7^{2-}(aq) + 2H^+(aq) + 3SO_2(g) \rightarrow 2Cr^{3+}(aq) + H_2O(l) + 3SO_4^{2-}(aq)$$

4.6.2 Tests for Nitrate Ions in Presence of Nitrite Ions

In presence of nitrite, nitrate cannot be tested either by heating with conc. H_2SO_4 or by the ring test because both liberate NO_2. Therefore, nitrite must be destroyed completely before testing for the nitrate. Nitrite ions can be destroyed by any one of the following methods:

1. Add sulphamic acid, H_2NSO_3H, to the water extract containing NO_2^- and NO_3^- ions. Acidify the solution with dilute H_2SO_4. Nitrite will be decomposed and nitrogen gas will be evolved.

$$H_2NSO_3H(aq) + NO_2^-(aq) \rightarrow HNO_2(aq) + H_2NSO_3^-(aq)$$

$$H_2NSO_3^-(aq) + HNO_2(aq) \rightarrow N_2(g) + H^+(aq) + SO_4^{2-}(aq) + H_2O(l)$$

2. Take 2–3 cm^3 of water extract, add 1 g solid NH_4Cl and boil till effervescence ceases.

$$NO_2^-(aq) + NH_4Cl(aq) \rightarrow N_2(g) + 2H_2O(l) + Cl^-(aq)$$

3. Take 2–3 cm^3 of water extract, add urea and acidify with dil. H_2SO_4. Boil the solution till evolution of gases ceases.

$$NH_2CONH_2(aq) + 2NO_2^-(aq) + 2H^+(aq) \rightarrow 2N_2(g) + CO_2(g) + 3H_2O(l)$$

Now divide the nitrite free solution thus obtained in two parts.

a) Perform ring test with one part to confirm the presence of nitrate ions.

b) Acidify the other part with dil. H_2SO_4. Add a little KI and 1 cm^3 starch solution. Absence of any blue colour indicates the complete removal of nitrite ions. Now add a piece of granulated zinc to the solution. Appearance of a blue colour confirms the presence of nitrate ions:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + 2H(g)$$

$$NO_3^-(aq) + 2H(g) \rightarrow NO_2^-(aq) + H_2O(l)$$

$$2I^-(aq) + 2NO_2^-(aq) + 4H^+(aq) \rightarrow 2NO(g) + I_2(s) + 2H_2O(l)$$

$$I_2(s) + \text{Starch} \rightarrow \text{Blue coloured complex}$$

4.6.3 Tests for Nitrate Ions in Presence of Bromide and/or Iodide Ions

1. Bromide and iodide interfere in the ring test of nitrate because of the colour of liberated bromine and iodine. In order to identify nitrate in presence of iodide and/or bromide, the interfering halide should be expelled before performing the ring test. This can be done by boiling 2–3 cm^3 of water extract or sodium carbonate extract with excess of chlorine water in a china dish, till no more vapours of Br_2 or I_2 evolve:

$$2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(g)$$

$$2I^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + I_2(g)$$

Now perform the ring test on the halide free solution to identify the nitrate ion in the mixture.

2. Alternatively, take 2–3 cm^3 of water extract in a test tube. Acidify with dil. H_2SO_4. Now add 1 cm^3 of KI solution, 1 cm^3 of starch solution and a few granules of zinc. Appearance of a blue colour confirms the presence of nitrate ions in the mixture.

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + 2H(g)$$

$$NO_3^-(aq) + 2H(g) \rightarrow NO_2^-(aq) + H_2O(l)$$

$$2I^-(aq) + 2NO_2^-(aq) + 4H^{+(aq)} \rightarrow 2NO(g) + I_2(g) + 2H_2O(l)$$

$$I_2 + \text{Starch} \rightarrow \text{Blue coloured complex}$$

4.6.4 Tests for Chloride, Bromide and Iodide Ions in Presence of Each Other

As you know that chloride, bromide and iodide ions react with $AgNO_3$ solution to form a precipitate, special tests are required to identify if more than one of them are present in the mixture. These anions can be detected in presence of one another by any one of the following methods:

1. Acidify 2–3 cm^3 of S.E. with excess of dil. H_2SO_4 in a china dish. Add 0.5 g of potassium persulphate and heat gently. Add distilled water if necessary to prevent dryness. Evolution of violet vapours of I_2 will confirm the presence of I^- ions.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(g)$$

Boil till evolution of I_2 ceases. If the solution after elimination of I_2 is brown, it indicates the presence of Br^- ions. Continue boiling, brown vapours of Br_2 will be evolved:

$$2Br^-(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + Br_2(g)$$

Add more $K_2S_2O_8$ if required. Continue boiling till the residual solution becomes colourless. Cool the solution, add dil. HNO_3 and $AgNO_3$ solution. A curdy white precipitate soluble in ammonia confirms the presence of Cl^- ions in the mixture:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

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

2. Acidify 2 – 3 cm^3 of S.E. with dil. H_2SO_4 in a china dish. Boil off CO_2. Add solid sodium nitrite and boil. Evolution of violet vapours of I_2 confirms the presence of iodide ions:

$$2NO_2^-(aq) + 2I^-(aq) + 4H^+(aq) \rightarrow 2NO(g) + I_2(g) + 2H_2O(l)$$

Add distilled water if necessary to prevent dryness. Continue boiling till all iodine is expelled. Cool the solution and divide into 2 parts.

To 1st part add 1 cm^3 CS_2 (or CH_2Cl_2 or CCl_4), 2 cm^3 chlorine water and shake. Appearance of an orange colour in organic layer confirms the presence of bromide ions:

$$2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$$

$$CS_2(l) + Br_2(l) \rightarrow \text{Orange colour}$$

If Br^- is present, boil the 2nd part with 1 cm^3 of conc. HNO_3 to expel Br_2 gas. This treatment can be avoided if Br^- ion is absent. Then add $AgNO_3$ solution. Formation of a curdy white precipitate confirms the presence of Cl^- ions:

$$2Br^-(aq) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow 2NO_2(g) + Br_2(g) + 2H_2O(l)$$

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

4.6.5 Tests for Bromide and Iodide Ions in Presence of Each Other

Take 2–3 cm^3 of S.E. in a test tube and acidify with dil. HCl. Add 2 cm^3 of CS_2 (or CH_2Cl_2 or CCl_4) and chlorine water dropwise with shaking. Appearance of violet colour in organic layer confirms iodide ions in the mixture.

$$2I^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + I_2(s)$$

$$I_2(s) + CS_2(l) \rightarrow \text{Violet colour}$$

Continue adding chlorine water and shaking till violet colour disappears due to the formation of colourless iodic acid:

$$I_2(s) + 5Cl_2(aq) + 6H_2O(l) \rightarrow 12H^+(aq) + 10Cl^-(aq) + 2IO_3^-(aq)$$

Continue adding chlorine water and shaking. If the organic layer becomes orange, bromide is confirmed:

$$2Br^-(aq) + Cl_2(aq) \rightarrow Br_2(l) + 2Cl^-(aq)$$

$$CS_2(l) + Br_2(l) \rightarrow \text{Orange colour}$$

4.6.6 Tests for Sulphide, Sulphite, Thiosulphate and Sulphate Ions in Presence of Each Another

Take 2–3 cm^3 of S.E. containing the above anions in a test tube. Add solid $CdCO_3$. If a yellow precipitate is formed, sulphide ion is confirmed.

$$S^{2-}(aq) + CdCO_3(s) \rightarrow CdS(s) + CO_3^{2-}(aq)$$

Filter the precipitate and add $Sr(NO_3)_2$ solution. A white precipitate may be

obtained due to the formation of $SrCO_3$, $SrSO_3$ and $SrSO_4$.

$$CO_3^{2-}(aq) + Sr^{2+}(aq) \rightarrow SrCO_3(s)$$

$$SO_3^{2-}(aq) + Sr^{2+}(aq) \rightarrow SrCO_3(s)$$

$$SO_4^{2-}(aq) + Sr^{2+}(aq) \rightarrow SrSO_4(s)$$

SrS_2O_3 being soluble will remain in the solution. Filter the precipitate and proceed as follows:

<table>
<tr><td>Filtrate may contain SrS_2O_3. Add a few drops of $AgNO_3$ solution. A white precipitate turning yellow, orange, brown and finally black confirms thiosulphate.
$S_2O_3^{2-}(aq) + 2Ag^+(aq) \rightarrow Ag_2S_2O_3(s)$
$Ag_2S_2O_3(s) + H_2O(l) \rightarrow Ag_2S(s) + 2H^+(aq) + SO_4^{2-}(aq)$
Black</td><td colspan="2">Residue may contain $SrCO_3$, $SrSO_3$ and $SrSO_4$. Add dil. HCl and filter</td></tr>
<tr><td></td><td>Filtrate may contain $SrSO_3$. Add conc. HNO_3 and heat. Formation of a white ppt. confirms sulphite ions.
$SrSO_3(aq) + O \rightarrow SrSO_4(s)$</td><td>White residue of $SrSO_4$ confirms the presence of sulphate ions</td></tr>
</table>

4.6.7 Test for Sulphate Ions in the Presence of Fluoride Ions

Since BaF_2 also is insoluble in dil. HCl, the presence of F^- ions interferes with the $BaCl_2$ test for the SO_4^{2-} ions. But in dilute acetic acid, PbF_2 is soluble whereas $PbSO_4$ is insoluble. Therefore, the following test is employed for the identification of SO_4^{2-} ions in the presence of F^- ions.

Take 2–3 cm^3 of S.E. in a test tube. Acidify with dilute acetic acid and boil off CO_2 Now add lead acetate solution. Formation of a white precipitate confirms the presence of SO_4^{2-} ions in the mixture.

$$SO_4^{2-}(aq) + Pb^{2+}(aq) \rightarrow PbSO_4(s)$$

4.7 REMOVAL OF INTERFERING ANIONS

Most of the fluorides, borates, oxalates and phosphates are soluble in dilute strong acids but are insoluble in neutral and basic solutions. Therefore, when aqueous ammonia solution is added to the filtrate of Group II, not only the hydroxides of Al^{3+}, Cr^{3+} and Fe^{3+} precipitate, but the fluorides, borates, oxalate or phosphates of cations of Group III to VI also precipitate from the solution. In this way, these anions interfere in the analysis of cations of Group III to VI. Therefore, fluoride, borate, oxalate and phosphate are known as interfering anions. These anions must be eliminated before proceeding for precipitation of the cations of Group III.

4.7.1 Removal of Oxalate Ions

Oxalate ions can be removed by repeatedly evaporating the solid mixture or the filtrate of Group II with concentrated nitric acid to near dryness. This process is repeated several times until the residue gives a negative test for the oxalate ions. Nitric acid oxidises the oxalate ions to CO_2 and water.

$$C_2O_4^{2-}(aq) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow 2CO_2(g) + 2NO_2(g) + 2H_2O(l)$$

Take the filtrate of Group II in a china dish. Boil off H_2S (test with lead acetate paper). Add 2–3 cm^3 of conc. HNO_3 and evaporate to near dryness. Do not heat the residue to complete dryness as iron(III) oxide, chromium(III) oxide and aluminium (III) oxide are rendered insoluble. Repeat the process 2-3 times until the residue gives a negative test for oxalate ions. Dissolve the residue in dil. HCl and use the solution for the analysis of cations of Group III-VI.

4.7.2 Removal of Fluoride Ions

Fluoride ions can be removed by repeatedly evaporating the dry mixture or the filtrate of Group II with conc. HCl in a china dish. Fluoride ions are volatilised off as hydrofluoric acid:

$$F^-(aq) + H^+(aq) \rightarrow HF(g)$$

Take the filtrate of Group II in a china dish. Boil off H_2S (test with lead acetate paper). Add 2–3 cm^3 of conc. HCl and evaporate to almost dryness. Repeat the process 2-3 times till fluoride ions are completely eliminated. Extract the residue in dil. HCl and use the solution for the analysis of the cations of Group III-VI.

4.7.3 Removal of Borate Ions

Boil off H_2S from the filtrate of Group II taken in a china dish (test with lead acetate paper). Evaporate to almost dryness. Cool and add 2 cm^3 of conc. HCl and 2 cm^3 of methyl or ethyl alcohol. Alternatively take 0.5 g of the dry mixture in a china dish and add 2 cm^3 of conc. HCl and 2 cm^3 of methyl or ethyl alcohol. Heat on a water bath until nearly dry. Repeat this process a second time. Borate ions are volatilised off as methyl or ethyl borate:

$$BO_3^{3-}(aq) + 3CH_3OH(aq) + 3H^+(aq) \rightarrow B(OCH_3)_3(g) + 3H_2O(l)$$

Finally extract the residue in 2–3 cm^3 of dil. HCl and use for the analysis of cations of Group III-VI.

4.7.4 Removal of Phosphate Ions

Removal of phosphate ions is based on the fact that zirconyl phosphate, $ZrO(HPO_4)_2$, is precipitated from a solution containing hydrochloric acid not exceeding 1 M concentration.

$$HPO_4^{2-}(aq) + ZrO^{2+}(aq) \rightarrow ZrO(HPO_4)_2(s)$$

The precipitate is of variable composition depending on the concentrations of ZrO^{2+}, PO_4^{3-} and H^+ ions. Species like $Zr(HPO_4)_2$, $ZrPO_4$ and $ZrO(H_2PO_4)_2$ may be formed.

Transfer the filtrate of Group II in a china dish and boil off H_2S (test with lead acetate paper). Add a few drops of conc. HNO_3 and adjust the HCl concentration so that it does not exceed 1M. Add 1.0-2.0 g solid NH_4Cl. Then add zirconyl nitrate solution dropwise and stir with a glass rod. Heat on a boiling water bath for 2 minutes. Cool and filter. Add a few more drops of zirconyl nitrate solution to make sure that all the phosphate ions have been precipitated. Use the filtrate for the analysis of cations of Group III-VI.

4.8 SUMMARY

In this unit you learnt the tests for detection and identification of individual anions, which may be present in an inorganic mixture. You also learnt special tests for the mixture of the anions. Certain anions, e.g., the oxalate, fluoride, borate and the phosphate, if present in a mixture, interfere in the scheme of identification of the cations present in the mixture. These anions are called the interfering anions. Therefore, the interfering anions should be identified and then removed before attempting to identify the cations present in the mixture. You also learnt the tests for the identification of the interfering anions and the treatment which should be given to the mixture for the removal of the interfering anions.

UNIT 5 DETECTION OF THE CATIONS - I

Structure

5.1 INTRODUCTION

In Unit 4 you studied the detection of the anions present in a mixture. Therein you have learnt that the anions are classified into groups. For carrying out the detection of anions, group tests are first performed to find out the presence or absence of a group of anions. Individual anions of a group are then identified by performing specific tests for anions.

In this unit and in the following unit you will learn the scheme of analysis of the cations present in any mixture. You may be required to detect the presence of three or four cations in a mixture.

The scheme of analysis of cations also, which you will study in this course, involves separation of cations into several groups and then identification of individual cations. This scheme of analysis is based upon the concepts of solubility, solubility product, common ion effect and complex formation. In this unit you will study these concepts and their application in qualitative analysis. In the following unit you will study the actual scheme of analysis and the tests and reactions involved in the scheme.

Objectives

- After studying this unit, you should be able to:
- define solubility, solubility product and explain the relation between them,
- calculate solubility product from solubility data and vice-versa,
- explain the application of solubility product data in classification and analysis of cations,
- explain the common ion effect,
- describe the effect of complex formation on the solubility of a salt,

- describe the conditions for selective precipitation of a salt from solution, and
- explain how to adjust the concentration of an ion in solution.

5.2 CLASSIFICATION OF CATIONS INTO ANALYTICAL GROUPS

In this course you may be required to detect the presence of three or four cations in a mixture out of the following 26 cations:

Ag^+, Hg_2^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, K^+, and NH_4^+.

If we had separate specific tests for each of these ions and each such test was applicable to an individual ion even in presence of others, then we could apply them one by one and thus detect different ions present in any mixture, although it would be a cumbersome process. But, we do not have such tests which will be applicable only to individual cations and will not be interfered by other cations.

Therefore, a systematic scheme of identification of cations in any mixture has been developed. In this scheme cations are first separated into seven small groups and then cations of each group are identified individually by applying specific tests.

The separation of cations into groups is based on similar chemical properties. For example, formation of a precipitate on reaction with some common reagent. Thus, when dilute hydrochloric acid (0.2 M) is added to a solution of various cations, only Ag^+, Hg_2^{2+} and Pb^{2+} form a white precipitate (which can be filtered) whereas all the other cations remain in solution. Ag^+, Hg_2^{2+} and Pb^{2+} constitute analytical Group I of the scheme and dilute hydrochloric acid is the group reagent of Group I.
Classification of cations along with group reagents and the formulae of precipitates formed is given in Table 5.1.

Table 5.1 :Classification of Cations into Analytical Groups

Analytical group	Cations	Group reagent	Precipitate
I	Ag^+, Hg_2^{2+}, Pb^{2+}	0.2 M HCl	AgCl, Hg_2Cl_2, $PbCl_2$
II	Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+}, Bi^{3+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}	H_2S in presence of 0.3 M HCl	PbS, HgS, CdS, CuS, Bi_2S_3, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS and SnS_2
III	Al^{3+}, Cr^{3+}, Fe^{3+}	0.1 M NH_4OH in presence of 1.5 M NH_4Cl	$Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$
IV	Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}	H_2S in presence of NH_4Cl and NH_4OH	ZnS, MnS, CoS, NiS
V	Ca^{2+}, Sr^{2+}, Ba^{2+}	$(NH_4)_2CO_3$ in presence of NH_4Cl and NH_4OH	$CaCO_3$, $SrCO_3$, $BaCO_3$
VI	Mg^{2+}	$(NH_4)_2HPO_4$ in presence of NH_4Cl and NH4OH	$Mg(NH_4)PO_4$
Zero	K^+, NH_4^+	No common group reagent	

You should realise that an analytical group number in the above table does not refer to a group number in the periodic table.

Classification of cations into analytical groups as shown in Table 5.1 is based on whether or not a cation forms an insoluble salt on reacting with a group reagent under specified conditions. Thus, all cations which form an insoluble salt on reacting with a group reagent fall in one analytical group. Whether a salt will be soluble or insoluble in a solution, depends on the solubility and the solubility product of the salt which you will study in the next section. But before that you may like to try the following SAQ.

SAQ 1

Both Cu^{2+} and Co^{2+} form a precipitate on reaction with H_2S, then why do they belong to two different analytical groups? Explain in one or two sentences.

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5.3 SOLUBILITY AND SOLUBILITY PRODUCT

When a solid is added to a given amount of solvent, the solid has a tendency to pass into solution. If we go on adding the solid to the solution at a given temperature, a state is reached when some of the solid remains undissolved. The solution is then said to be **saturated. The amount of solute that can be dissolved in a specified amount of solvent at a specified temperature to give a saturated solution is called its solubility.** Solubility is generally expressed in the units of moles per cubic decimeter (mol dm^{-3}) or in grams per cubic decimeter (g dm^{-3}). Solubility when expressed in moles per cubic decimeter is called **molar solubility** and when expressed in grams per cubic decimeter is called **gram solubility.**

Nearly all compounds dissolve in water to some extent, their solubility varying over a very wide range. Compounds that dissolve in water to give a solution with a concentration of about 0.02 moles per cubic decimeter at room temperature are usually considered as soluble compounds. If the concentration of the solution of a compound is less than 0.02 mol dm^{-3} at room temperature, the compound is classified as sparingly soluble.

Silver chloride with a solubility of 1.37×10^{-5} mol dm^{-3} in water indeed is a sparingly soluble salt. As a result when silver chloride is placed in water, only a very small amount of it dissolves in water to give a saturated solution. As you know that all the sparingly soluble salts are strong electrolytes, the AgCl that dissolves will be completely dissociated into Ag^+ and Cl^- ions. Thus there will be an equilibrium between undissolved AgCl and its ions in solution:

$$AgCl(s) \overset{H_2O}{\rightleftharpoons} AgCl(aq) \overset{H_2O}{\rightleftharpoons} Ag^+(aq) + Cl^-(aq)$$

The equilibrium constant for the above reaction can be written as:

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl(s)]} \qquad \text{(Eq. 5.1)}$$

Water is not included in the above expression because it is neither consumed nor produced in the reaction. The terms $[Ag^+]$ and $[Cl^-]$ in the above expression represent the concentrations of Ag^+ and Cl^- ions in moles per cubic decimeter when the reaction is at equilibrium and the solution is saturated with AgCl. The term [AgCl(s)] represents the concentration of solid AgCl i.e., the number of moles of AgCl in one cubic decimeter of solid AgCl, which can be calculated from the density and molecular weight of AgCl. Thus,

$$[AgCl(s)] = \frac{\text{Volume} \times \text{density}}{\text{molecular weight}} = \frac{1000 \times 5.56}{143.34}$$

$$= 38.8 \text{ mol/dm}^3 = \text{constant}$$

Hence, from equation 5.1, you will get,

$$K_c \times [AgCl(s)] = [Ag^+][Cl^-]$$

Since, the product of K_c and [AgCl(s)] will be constant, we can introduce a new constant K_{sp} in place of $K_c \times [AgCl(s)]$. Hence,

$$K_c \times [AgCl(s)] = K_{sp} = [Ag^+][Cl^-] \qquad \text{(Eq. 5.2)}$$

Here, K_{sp} is known as **solubility product constant** or simply **solubility product**. In general, for any sparingly soluble salt like A_xB_y which may dissociate as following:

$$A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

The equilibrium constant $K_c = \dfrac{[A^{y+}]^x \cdot [B^{x-}]^y}{[A_xB_y(s)]}$

or $$K_c \times [A_xB_y(s)] = K_{sp} = [A^{y+}]^x[B^{x-}]^y \qquad \text{(Eq. 5.3)}$$

Expressed in words the **solubility product constant of a sparingly soluble salt is equal to the product of concentrations of ions in its saturated solution with each concentration raised to the power equal to the number of ions in one formula unit of the compound.** Solubility product constants of some common inorganic salts are listed in Table 5.2.

Table 5.2 : Solubility Product Constants at 25° C

Name of Solid	Formula	K_{sp}
Aluminium hydroxide	$Al(OH)_3$	1.9×10^{-33}
Aluminium phosphate	$AlPO_4$	1.3×10^{-20}
Antimony sulphide	Sb_2S_3	2.0×10^{-93}
Barium carbonate	$BaCO_3$	8.1×10^{-9}
Barium hydroxide	$Ba(OH)_2$	5.0×10^{-3}
Barium sulphate	$BaSO_4$	1.1×10^{-10}
Bismuth sulphide	Bi_2S_3	2.0×10^{-72}
Cadmium sulphide	CdS	4.0×10^{-29}
Calcium carbonate	$CaCO_3$	4.8×10^{-9}
Calcium hydroxide	$Ca(OH)_2$	7.9×10^{-6}
Cobalt sulphide (α)	$CoS(\alpha)$	6.0×10^{-21}
Copper(II) sulphide	CuS	8.7×10^{-36}
Iron(II) hydroxide	$Fe(OH)_2$	8.0×10^{-15}
Iron(III) hydroxide	$Fe(OH)_3$	6.3×10^{-38}
Iron(II) sulphide	FeS	5.0×10^{-18}
Iron(III) sulphide	Fe_2S_3	1.0×10^{-88}
Lead chloride	$PbCl_2$	1.6×10^{-5}

Lead sulphide	PbS	8.0×10^{-28}
Magnesium carbonate	$MgCO_3$	4.0×10^{-5}
Magnesium hydroxide	$Mg(OH)_2$	1.5×10^{-11}
Manganese(II) hydroxide	$Mn(OH)_2$	2.0×10^{-13}
Manganese(II) sulphide	MnS	5.0×10^{-15}
Mercury(I) chloride	Hg_2Cl_2	1.1×10^{-18}
Mercury(II) sulphide	HgS	3.0×10^{-53}
Nickel hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Nickel sulphide (α)	$NiS(\alpha)$	3.0×10^{-21}
Silver bromide	AgBr	5.0×10^{-13}
Silver chloride	AgCl	1.8×10^{-10}
Silver iodide	AgI	1.5×10^{-16}
Silver sulphide	Ag_2S	7.0×10^{-50}
Strontium carbonate	$SrCO_3$	9.4×10^{-10}
Strontium hydroxide	$Sr(OH)_2$	3.2×10^{-4}
Strontium sulphate	$SrSO_4$	2.8×10^{-7}
Tin(II) sulphide	SnS	8.0×10^{-29}
Zinc hydroxide	$Zn(OH)_2$	4.5×10^{-17}
Zinc sulphide	ZnS	1.1×10^{-21}

* When freshly precipitated from basic solution, the more soluble alpha (α) forms of CoS and NiS are formed.

Before we discuss the relation between solubility and solubility product, you may like to attempt SAQ 2 on solubility product constant.

SAQ 2

Write solubility product expressions for saturated solutions of Ag_2CO_3 and Bi_2S_3

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5.3.1 Relation Between Solubility and Solubility Product

You have studied the concepts of solubility and solubility product. We will now establish a relation between the two so that you could find out the one if you know the other.

Let S mol dm^{-3} be the solubility of the sparingly soluble salt A_xB_y, then the corresponding concentrations of cations and anions in its saturated solution will be xS mol dm^{-3} and yS mol dm^{-3}, respectively:

$$\underset{}{A_xB_y(s)} \overset{H_2O}{\rightleftharpoons} \underset{S}{A_xB_y(aq)} \overset{H_2O}{\rightleftharpoons} \underset{xS}{xA^{y+}(aq)} + \underset{yS}{yB^{x-}(aq)}$$

Substituting the values of $[A^{y+}]$ and $[B^{x-}]$ in Eq. 5.3, we get,

$$K_{sp} = [xS]^x [yS]^y$$

or $$K_{sp} = x^x \cdot y^y \cdot S^{x+y} \qquad (Eq.\ 5.4)$$

Can you apply Eq. 5.4 to find out the relation between the solubility and the solubility product constant for AgCl, CaF_2 and As_2S_3 ?

In case of AgCl, x = 1, y = 1, hence from Eq. 5.4

$$K_{sp}(AgCl) = S^{1+1} = S^2$$

Since the solubility of AgCl at 25° C is 1.37×10^{-5} mol dm^{-3},

$$K_{sp}(AgCl) = (1.37 \times 10^{-5})^2 = 1.88 \times 10^{-10}$$

In case of CaF_2, we have x = 1, y = 3, hence from Eq. 5.4,

$$K_{sp}(CaF_2) = 1^1 \cdot 2^2 \cdot S^{1+2} = 4S^3$$

In case of As_2S_3, we have x = 2, y = 3, hence from Eq. 5.4,

$$K_{sp}(As_2S_3) = 2^2 \cdot 3^3 \cdot S^{2+3} = 4 \times 27\, S^5 = 108\, S^5$$

Thus, if you know the solubility of a sparingly soluble salt, its solubility product constant can be easily calculated and vice-versa.

SAQ 3

Solubility product constant of CaF_2 is 4.0×10^{-11}, can you calculate the solubility of CaF_2 in water?

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5.3.2 Use of Solubility Products in Comparing Relative Solubilities of Salts

The value of dissociation constant, K_a, of an acid, HA, is directly proportional to the concentration of H_3O^+ ions furnished by the acid in solution:

$$HA + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

You can see that the value of K_a is directly proportional to the concentration of H_3O^+ in solution or in otherwords to the strength of the acid. Thus, by looking at the following K_a values, you can immediately conclude that formic acid is a stronger acid than acetic acid:

Formic acid (HCOOH), $K_a = 1.8 \times 10^{-4}$

Acetic acid (CH_3COOH), $K_a = 1.8 \times 10^{-5}$

Similarly the value of dissociation constant, K_b, of a base B, is directly proportional to the concentration of OH^- ions furnished by the base in solution:

$$B + H_2O \rightleftharpoons HB^+(aq) + OH^-(aq)$$

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

By comparing the dissociation constants of methylamine ($K_b = 4.8 \times 10^{-4}$) and ammonia ($K_b = 1.8 \times 10^{-5}$), you can immediately say that the former is a stronger base than the latter.

Now the question arises, can we in the same manner use the solubility product data to compare the relative solubilities of salts in solution?

Answer is yes, if the salts produce the same number of cations and anions in solution. For example, CuS and NiS produce the same number of cations and anions in solution and their solubility products are 8.7×10^{-36} and 3.0×10^{-21}, respectively. For these salts $K_{sp} = S^2$, therefore you can immediately conclude that the solubility of NiS is higher than that of CuS in water.

But, if the salts produce different number of cations and anions on dissolution in water, you cannot predict their relative solubilities so easily from their solubility product data. Although the solubility product of $CaCO_3$ (4.8×10^{-9}) is larger than that of Ag_2CO_3 (8.1×10^{-12}), it will be erroneous to conclude that $CaCO_3$ is more soluble than Ag_2CO_3 in water because they do not produce the same number of ions in solution. In fact $CaCO_3$ is less soluble (6.9×10^{-5} mol dm^{-3}) than Ag_2CO_3 (1.3×10^{-4} mol dm^{-3}) in water.

5.4 THE COMMON ION EFFECT

In preceding section, you studied the relation between solubility and solubility product of a sparingly soluble salt. In this section, you will study the common ion effect which in fact means the effect of common ions on the solubility of a sparingly soluble salt.

By a common ion we mean an ion that is common to two substances in the same solution/mixture. For example, the common ion in a solution of a mixture of AgCl and $AgNO_3$ is the Ag^+ ion. Similarly the common ion in a solution of a mixture of AgCl and NaCl is the Cl^- ion. We will try to find out what will happen to the solubility of AgCl, if it is dissolved in a solution containing $AgNO_3$ or NaCl i.e., containing a common ion.

A qualitative answer to this question can be easily found on the basis of Le Chatelier principle. According to this principle, when the concentration of either Ag^+ or Cl^- ions is increased, the solubility equilibrium should shift towards left forming more of solid AgCl in order to oppose the effect of the increase in concentration of either Ag^+ or Cl^- ions.

$$AgCl(s) \overset{H_2O}{\rightleftharpoons} Ag^+(aq) + Cl^-(aq)$$

This means, there will be a decrease in the solubility of AgCl in presence of a common ion such as Ag^+ or Cl^- as compared to that in pure water. Now let us derive an expression that will be useful in calculating the solubility of sparingly soluble salts in presence of common ions.

Solubility of Silver Chloride in Presence of Silver Nitrate

Let us assume that silver chloride is dissolved in a solution containing C mol dm^{-3} of $AgNO_3$. In solution, then, there will be Ag^+, Cl^- and NO_3^- ions present. The Cl^- and NO_3^- ions are provided by the dissolution of AgCl and $AgNO_3$ in water, respectively. However, there are two sources of Ag^+ ions in solution. One is from

dissolution of $AgNO_3$ and the other from dissolution of AgCl in water. A solution of $AgNO_3$ of concentration C mol dm^{-3} will furnish C mol dm^{-3} of Ag^+ ion (and C mol dm^{-3} of NO_3^- ions) in solution. If S mol dm^{-3} is the solubility of AgCl at equilibrium in presence of $AgNO_3$, then AgCl will furnish S mol dm^{-3} of Ag^+ ions (and S mol dm^{-3} of Cl^- ions) in solution. This phenomenon can be represented as given below:

$$AgCl(s) \overset{H_2O}{\rightleftharpoons} Ag^+(aq) + Cl^-(aq)$$

Initial concentration — C M, 0 M

Equilibrium concentration — (C+S) M, S M

(from $AgNO_3$), (from AgCl)

Substituting the values of $[Ag^+(aq)]$ and $[Cl^-(aq)]$ in solubility product expression of AgCl, we get

$$K_{sp}(AgCl) = [Ag^+][Cl^-]$$

$$= (C + S)(S)$$

or $$S = \frac{K_{sp}}{C + S}$$

In pure water, the solubility of AgCl is 1.37×10^{-5} mol dm^{-3}. In a solution of $AgNO_3$, we expect it to be even smaller. It is, therefore, quite reasonable to expect that the Ag^+ ion concentration from dissolution of AgCl, S, will be much smaller as compared to the Ag^+ ion concentration from dissolution of $AgNO_3$ i.e., C>>S. Hence,

$$S = \frac{K_{sp}}{C}$$

The K_{sp} of AgCl is 1.88×10^{-10} and if the concentration of $AgNO_3$ solution, C, is 1.0 mol dm^{-3}, then the solubility of AgCl, S, at equilibrium in this solution will be

$$S = \frac{K_{sp}}{C} = \frac{1.88 \times 10^{-10}}{1.0} = 1.88 \times 10^{-10} \text{ mol dm}^{-3}$$

If you compare the solubility of AgCl in 1.0 mol dm^{-3} solution of $AgNO_3$ with that of AgCl in pure water, you will find that the solubility of AgCl in former is roughly 100,000 times less than that in the latter.

$$\frac{\text{Solubility of AgCl in 1.0 mol dm}^{-3}\ AgNO_3 \text{ solution}}{\text{Solubility of AgCl in pure water}}$$

$$= \frac{1.88 \times 10^{-10} \text{ mol dm}^{-3}}{1.37 \times 10^{-5} \text{ mol dm}^{-3}}$$

$$= 1.37 \times 10^{-5}.$$

This decrease in the solubility of AgCl in a solution of $AgNO_3$ is due to the common ion effect. We can similarly show that the solubility of AgCl, S, in a solution containing C mol dm^{-3} of NaCl will be as follows:

$$S = \frac{K_{sp}}{C} = \frac{1.88 \times 10^{-10}}{C} \text{ mol dm}^{-3}.$$

Thus, we can say that the solubility of sparingly soluble salts such as AgCl is further decreased due to the common ion effect.

We derived an expression for the solubility of AgCl in a solution of $AgNO_3$ and NaCl of concentration C mol dm^{-3}. Can you now find out the solubility of CaF_2 in i) pure water and ii) 0.10 mol dm^{-3} NaF ?. The K_{sp} of CaF_2 is 4.0×10^{-11}.

i) Let us assume that the solubility of CaF_2 in pure water is S. According to Eq. 5.4,

$$K_{sp} = x^x \cdot y^y \cdot S^{x+y}$$

For CaF_2, $x = 1$ and $y = 2$

Hence, $K_{sp} = 1^1 . 2^2 . S^{1+2} = 4S^3$

or $4.0 \times 10^{-11} = 4S^3$

$$\therefore S^3 = \frac{4.0 \times 10^{-11}}{4}$$

$$\therefore S = (1.0 \times 10^{-11})^{1/3}$$

$$= 2.2 \times 10^{-4} \text{ mol dm}^{-3}.$$

i) Let S be the solubility of CaF_2 at equilibrium in a solution of NaF of concentration 0.10 mol dm^{-3}. According to the solubility equilibrium expression,

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

Initial concentration	0M	0.10 M (from NaF)
Equilibrium concentration	SM	(2S + 0.10) M
	(from CaF2)	(from NaF)

$$K_{sp} \text{ of } CaF_2 = [Ca^{2+}] [F^-]^2$$

$$\text{or } 4.0 \times 10^{-11} = (S) (2S + 0.10)^2$$

Since S is very small in comparison to 0.10, hence

$$4.0 \times 10^{-11} = S(0 + 0.10)^2$$

or $$S = \frac{4.0 \times 10^{-11}}{(0.10)^2} = 4.0 \times 10^{-9} \text{ mol dm}^{-3}.$$

You can again see that the solubility of CaF_2 in a solution of 0.10 M NaF is 5.5×10^4 times smaller than that in pure water.

Now that we have seen how the presence of common ion affects the equilibrium of sparingly soluble salt, we come to the following conclusions:

- In a saturated solution, the solubility product, K_{sp}, is equal to the product of the concentrations of the constituent ions raised to suitable powers, i.e., the ionic product, Q.
  $K_{sp} = Q$.
- When the ionic product is less than the solubility product, i.e., $Q < K_{sp}$, the solution is unsaturated and the concentration of the ions can be increased by dissolving more of the salt.

Ionic product of a compound is equal to the product of the concentrations of the constituent ions, each raised to the power that corresponds to the number of ions in one formula unit of the compound.

- When the concentration of either of the two ions of a sparingly soluble salt in solution is increased by the addition of a soluble salt containing a common ion, the ionic product increases i.e., $Q > K_{sp}$. The equilibrium responds in such a way that the value of K_{sp} is preserved. As a result, the solubility of sparingly soluble salt decreases and it precipitates out from the solution.

5.5 COMPLEX FORMATION

In the preceding section you studied the concept of common ion effect and its effect on the solubility of sparingly soluble salts. In this section you will study the concept of complex formation which finds extensive application in qualitative analysis.

You might have studied in the CHE-02 course that an ion or a compound, in which a central metal ion/atom is attached to a group of ions and/or molecules such that the normal valency of the metal is exceeded, is known as a complex ion or a complex compound. $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$, $[Cd(CN)_4]^{2-}$ and $[HgCl_4]^{2-}$ are some of the examples of complex ions. In complex ions/compounds, the ions/molecules attached to the central metal ion/atom are called as ligands. NH_3, CN^- and Cl^- are the examples of ligands. Each ligand is bonded to the central metal ion/atom by donation of atleast one pair of electrons.

When the Cu^{2+} ion combines with the ammonia molecules in aqueous solution, a deep blue complex ion, $[Cu(NH_3)_4]^{2+}$, is formed:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

To deal with the complex ion equilibria quantitatively, we use the equilibrium constant for the complexation reaction. The equilibrium constant for the complexation reaction is known as the **formation constant**, K_f. The formation constant for the above complexation reaction can be represented as follows:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}]\,[NH_3]^4}$$

Formation constants of some complex ions are listed in Table 5.5. The higher is the value of the formation constant, the greater is the stability of the complex ion in solution.

Table 5.5 : Formation Constants of Some Complex Ions

Complex ion	Equilibrium reaction	K_f
$[AgCl_2]^-$	$Ag^+ + 2Cl^- \rightleftharpoons [AgCl_2]^-$	1.1×10^5
$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.6×10^7
$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	5.6×10^{18}
$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	1.7×10^{13}
$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.1×10^{13}
$[Cu(CN)_3]^{2-}$	$Cu^+ + 3CN^- \rightleftharpoons [Cu(CN)_3]^{2-}$	2.0×10^{27}
$[CdCl_4]^{2-}$	$Cd^{2+} + 4Cl^- \rightleftharpoons [CdCl_4]^{2-}$	6.3×10^2
$[Cd(CN)_4]^{2-}$	$Cd^{2+} + 4CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	7.1×10^{18}
$[Co(NH_3)_6]^{2+}$	$Co^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3×10^5

Complex ion	Equilibrium reaction	K_f
$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
$[Zn(NH_3)_4]^{2+}$	$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$	2.9×10^9
$[Fe(CN)_6]^{4-}$	$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.0×10^{37}
$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1.0×10^{42}
$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
$[PbCl_4]^{2-}$	$Pb^{2+} + 4Cl^- \rightleftharpoons [PbCl_4]^{2-}$	40

Sometimes complex ion equilibria are written for the dissociation of a complex ion that is, the reverse of the formation reaction. In this case, the equilibrium constant is called the **dissociation constant**, K_d, or **instability constant**, K_i. Thus for the reaction

$$[Cu(NH_3)_4]^{2+}(aq) \rightleftharpoons Cu^{2+}(aq) + 4NH_3(aq)$$

$$K_d = K_i = \frac{[Cu^{2+}][NH_3]^4}{[[Cu(NH_3)_4]^{2+}]} = 1/K_f$$

Effect of Complex Formation on Solubility

In the preceding unit, you studied that a white precipitate of silver chloride dissolves when a moderately concentrate solution of ammonia is added to the precipitate:

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

The Ag^+ ions from AgCl combine with NH_3 to form the complex ion $[Ag(NH_3)_2]^+$. As the complex compound $[Ag(NH_3)_2]$ Cl is soluble in water, AgCl dissolves in water in presence of NH_3 molecules. The dissolution of AgCl in aqueous NH_3 can be better explained, if we consider that the above complexation reaction involves two equilibria simultaneously:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq),\ K_{sp} = 1.8 \times 10^{-10} \quad (I)$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq),\ K_f = 1.6 \times 10^7 \quad (II)$$

The value of the formation constant, K_f, of $[Ag(NH_3)_2]^+$ is quite large, it suggests that the equilibrium in complexation reaction is shifted far to the right. The equilibrium concentration of $Ag^+(aq)$ becomes so low that the ionic product $[Ag^+]\ [Cl^-]$ does not exceed the solubility product of AgCl and it dissolves. To appreciate the effect of complex formation on solubility, let us now calculate the solubility of AgCl in aqueous 1 M NH_3 solution.

As you know from the above, the overall reaction for the dissolution of AgCl in aqueous ammonia can be written as following; the equilibrium constant, K, for the overall reaction is the product of K_{sp} for AgCl and K_f for $[Ag(NH_3)_2]^+$.

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq),\ K = 2.9 \times 10^{-3}.$$

If the solubility of AgCl is x mol dm^{-3}, according to the above equation the concentration of $[Ag(NH_3)_2]^+$ and Cl^- ions are also expected to be x mol dm^{-3}.

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

Initial concentration	1.0 M	0 M	0 M
Equilibrium concentration	$(1-2x)$ M	x M	x M

$$K = \frac{[[Ag(NH_3)_2]^+][Cl^-]}{[NH_3]^2}$$

or $$2.9 \times 10^{-3} = \frac{x \cdot x}{(1-2x)^2}$$

on taking square root of both sides, we get,

$$5.4 \times 10^{-2} = \frac{x}{1-2x}$$

or $$5.4 \times 10^{-2}(1-2x) = x$$

or $$5.4 \times 10^{-2} - 0.108x = x$$

or $$5.4 \times 10^{-2} = 1.108x$$

Hence, $$x = \frac{5.4 \times 10^{-2}}{1.108} = 4.9 \times 10^{-2}\ \text{M}.$$

Thus the solubility of AgCl in aqueous 1 M NH_3 is 4.9×10^{-2} mol dm^{-3}, which is much greater than that in pure water.

Advantage of this higher solubility of AgCl in aqueous ammonia solution is taken in the separation of AgCl(s) from Hg_2Cl_2(s) in the analysis of the cations of analytical Group I. As^{3+}/As^{5+}, Sb^{3+}/Sb^{5+} and Sn^{2+}/Sn^{4+} form soluble complexes on reaction with disulphide ion, S_2^{2-}. This fact is utilised in the separation of the cations of analytical Group IIA from those of Group IIB. In the following sections and in Unit 6, you will learn more about the application of complex formation in qualitative analysis.

5.6 THE SEPARATION OF CATIONS INTO ANALYTICAL GROUPS

In the preceding two sections you learnt the concepts of the solubility product, common ion effect and complex formation. Let us now discuss the scheme of separation of cations into analytical groups, which is based mainly on these concepts.

5.6.1 Precipitation of Cations of Analytical Group I

Solubility products of AgCl, Hg_2Cl_2 and$PbCl_2$ are very small in comparison to those of the other metal chlorides. To a solution containing various cations, if enough hydrochloric acid is added to raise the Cl^- concentration to 0.2 M, the solubility products of only AgCl, Hg_2Cl_2 and $PbCl_2$ are exceeded. As a result most of the Ag^+, Hg_2^{2+} and Pb^{2+} ions precipitate from the solution as their chlorides whereas all other cations remain in solution.

Let us calculate the residual Ag^+ ion concentration in a solution when the Cl^- ion concentration is 0.20 M. This we can do with the help of solubility product expression.

We know that the K_{sp} of AgCl is 1.8×10^{-10}.

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

If we substitute the value of $[Cl^-]$ in this expression we get,

$$[Ag^+](0.2) = 1.8 \times 10^{-10}$$

Hence,
$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.2} = 9.0 \times 10^{-10}\ M$$

Thus the residual Ag^+ ion concentration in a solution of Cl^- ions of concentration 0.2 M is extremely small and we can say that Ag^+ ions are completely precipitated from the solution. If you calculate you will find that the residual Hg_2^{2+} ion concentration is even smaller than that of Ag^+ ion.

The residual Pb^{2+} ion concentration in a solution of Cl^- ions of concentration 0.2 M is 4×10^{-4} M as shown below:

$$K_{sp}(PbCl_2) = [Pb^{2+}][Cl^-]^2 = 1.6 \times 10^{-5}$$

Hence,
$$[Pb^{2+}] = \frac{1.6 \times 10^{-5}}{[Cl^-]^2} = \frac{1.6 \times 10^{-5}}{0.2 \times 0.2} = 4.0 \times 10^{-4}\ M$$

You can see that the residual lead ion concentration is inversely proportional to the square of chloride ion concentration. Theoretically the residual Pb^{2+} ion concentration should decrease on increasing the Cl^- ion concentration by adding concentrated HCl. But if we increase the Cl^- ion concentration too much, precipitate of $PbCl_2$ and AgCl starts redissolving due to the formation of soluble complex ions with the Cl^- ions:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq),\ K_{sp} = 1.6 \times 10^{-5}$$

$$Pb^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq),\ K_f = 40$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq);\ K_{sp} = 1.8 \times 10^{-10}$$

$$Ag^+(aq) + 2Cl^-(aq) \rightleftharpoons [AgCl_2]^-(aq),\ K_f = 1.1 \times 10^5$$

One consequence of chloro complex formation is that the Ag^+ and Pb^{2+} ions remain in solution and do not precipitate as their chlorides. Another consequence of addition of too much Cl^- ions is that stable chloro complexes of other cations also, e.g., Cd^{2+} and Bi^{3+} may be formed:

$$Cd^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CdCl_4]^{2-}(aq),\ K_f = 6.3 \times 10^2$$

$$Bi^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [BiCl_4]^-(aq),\ K_f = 4 \times 10^5$$

Due to the formation of stable chloro complexes, the concentration of $Cd^{2+}(aq)$ and $Bi^{3+}(aq)$ is reduced and these ions then may not precipitate on passing H_2S gas. The qualitative analysis scheme thus represents a delicate balance between many such competing processes. You should follow it carefully to avoid errors in analysis.

5.6.2 The Separation of Group II Cations from Group IV Cations

Cations of both Group II (Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sb^{3+}, Sb^{5+}, As^{3+}, As^{5+}, Sn^{2+}, Sn^{4+}) and Group IV (Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) precipitate as their sulphides on passing H_2S gas in their solution. The cations of Group II precipitate on passing H_2S gas in their solution in HCl medium. The cations of Group IV on the other hand precipitate when H_2S is passed in their solution in the presence of NH_4OH. The key to separate the cations of Group II from those of Group IV is the large difference between the solubility product constants of their sulphides listed in Table 5.5.

Table 5.5 : Solubility Product Constants and Molar Solubilities of Sulphides of Group II and Group IV at 25° C

Group II			Group IV		
Sulphide	K_{sp}	Molar solubility	Sulphide	K_{sp}	Molar solubility
Sb_2S_3	2.0×10^{-93}	1.1×20^{-19} M	ZnS	1.1×10^{-21}	3.3×10^{-11} M
Bi_2S_3	2.0×10^{-72}	1.8×10^{-15} M	NiS	3.0×10^{-21}	5.5×10^{-11} M
HgS	3.0×10^{-53}	5.5×10^{-27} M	CoS	6.0×10^{-21}	7.8×10^{-11} M
CuS	8.7×10^{-36}	3.0×10^{-18} M	MnS	5.0×10^{-15}	7.1×10^{-8} M
CdS	4.0×10^{-29}	6.3×10^{-15} M			
SnS	8.0×10^{-29}	8.9×10^{-15} M			
PbS	8.0×10^{-28}	2.8×10^{-14} M			

You can see from the data in Table 5.5 that PbS is the most soluble of the Group II sulphides and ZnS is the least soluble of the Group IV sulphides. If we could separate PbS from ZnS, then we would have no difficulty in separating the other cations of Group II from those of Group IV. This is because the differences in solubilities in case of other sulphides are even larger than that of PbS and ZnS.

You know that a sparingly soluble salt precipitates out from its solution on addition of common ion so that the solubility product of the salt is exceeded. If we could find out the sulphide ion concentration such that the solubility product of only PbS is exceeded, in that case only PbS will precipitate from the solution whereas ZnS will remain in solution and we will be able to separate PbS from ZnS.

Let us calculate the S^{2-} ion concentration to separate Pb^{2+} from Zn^{2+} if both cations have a concentration of 0.02 M.

We calculate the S^{2-} ion concentration at which ZnS just starts to precipitate from a 0.02 M solution of Zn^{2+} ions. We know that

$$K_{sp}(ZnS) = [Zn^{2+}][S^{2-}]$$

Substituting the value of K_{sp} and Zn^{2+} in the above expression we can get the concentration of S^{2-} ions at which ZnS just starts to precipitate.

$$1.1 \times 10^{-21} = 0.02 \times [S^{2-}]$$

Hence, $$[S^{2-}] = \frac{1.1 \times 10^{-21}}{0.02} = 5.5 \times 10^{-20} \text{ M}$$

Thus at a S^{2-} ion concentration of 5.5×10^{-20} M, ZnS just begins to precipitate. If we keep the sulphide ion concentration below 5.5×10^{-20} M, no ZnS precipitates.

Now we find out what happens to Pb^{2+} ions when the S^{2-} concentration is 5.5×10^{-20} M. The ionic product of PbS under these conditions

$$Q = [Pb^{2+}][S^{2-}]$$

$$= 0.02 \times 5.5 \times 10^{-20} = 1.1 \times 10^{-21}$$

Hence, $$Q > K_{sp}$$

As the ionic product of PbS is greater than the solubility product of PbS, which is 8.0×10^{-28}, PbS will precipitate from the solution.

Let us now calculate what fraction of the Pb^{2+} ions will remain in solution when the

S^{2-} ion concentration is maintained at 5.5×10^{-20} M. We know

$$K_{sp}(PbS) = [Pb^{2+}][S^{2-}]$$

Substituting the values of K_{sp} and S^{2-}, we get,

$$8.0 \times 10^{-28} = [Pb^{2+}] \times 5.5 \times 10^{-20}$$

Hence,
$$[Pb^{2+}] = \frac{8.0 \times 10^{-28}}{5.5 \times 10^{-20}} = 1.4 \times 10^{-8} \text{ M}$$

You can see that out of 0.02 M Pb^{2+} ions, only 1.4×10^{-8} M Pb^{2+} ions remain in solution, rest of the Pb^{2+} ions precipitate as PbS. We can also say that only

$\frac{1.4 \times 10^{-8} \text{ M}}{0.02 \text{ M}} \times 100\% = 0.00007\%$ Pb^{2+} ions remain in solution, i.e., the precipitation of PbS is nearly complete. Thus we can conclude that if the S^{2-} ion concentration is maintained at 5.5×10^{-20} M, we can separate the cations of the Group II from those of the Group IV by precipitation as their sulphides.

Adjusting the Concentration of Sulphide Ions in Solution

We have calculated that if the sulphide ion concentration is kept below 5.5×10^{-20} M, Pb^{2+} ions can be separated from Zn^{2+} ions in solution containing 0.02 M of each cation. Now two questions arise:

Q1. What is the concentration of S^{2-} ions in a saturated solution of H_2S ?

Q2. How to adjust the concentration of S^{2-} ions to a given value?

Let us first find out the answer to the question 1. A saturated solution of H_2S has a concentration of 0.1 M. Hydrogen sulphide is a weak dibasic acid as is indicated by the values of K_1 (1.0×10^{-7}) and K_2 (1.3×10^{-13}).

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-(aq),\ K_1 = 1.0 \times 10^{-7}$$

$$H_2S + H_2O \rightleftharpoons H_3O^+ + S^{2-}(aq),\ K_2 = 1.3 \times 10^{-13}$$

Let x mol dm^{-3} of H_2S ionise in the first step. Hence the concentration of unionised H_2S in solution will be $(0.1 - x)$ mol dm^{-3} as depicted below:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-(aq),\ K_1 = 1.0 \times 10^{-7}$$

Initial concentration	0.1 M	0M	0M
After first ionisation	$(0.1 - x)$ M	xM	xM

$$K_1 = \frac{[H_3O^+][HS^-]}{[H_2S]}$$

or
$$1.0 \times 10^{-7} = \frac{x \cdot x}{0.1 - x}$$

As H_2S is a very weak acid, the amount of H_2S that ionises in the first step, x M, will be very small and can be disregarded in the denominator of the above expression.

Hence,
$$1.0 \times 10^{-7} = \frac{x^2}{0.1 - 0}$$

or
$$x^2 = 1.0 \times 10^{-8}$$

or
$$x = 1.0 \times 10^{-4} \text{ M}$$

Hence, $[H_3O^+] = 1.0 \times 10^{-4}\ M = [HS^-]$

In the second step, HS^- produced in the first step ionises to give H_3O^+ and S^{2-}. Let y mol dm^{-3} be the concentration of HS^- which ionises in this step to give y mol dm^{-3} of H_3O^+ and S^{2-} each:

$$HS^-(aq) + H_2O \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$$

Initial concentration	1.0×10^{-4} M	1.0×10^{-4} M	0M
After second ionisation	$(1.0 \times 10^{-4} - y)$ M	$(1.0 \times 10^{-4} - y)$ M	yM

$$K_2 = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

or $$1.3 \times 10^{-13} = \frac{(1.0 \times 10^{-4} + y) \times y}{1.0 \times 10^{-4} - y}$$

Value of K_2 (1.3×10^{-13}) is small which suggests that the value of y will be very small. Hence we can assume that $1.0 \times 10^{-4} + y = 1.0 \times 10^{-4}$ and $1.0 \times 10^{-4} - y = 1.0 \times 10^{-4}$. Therefore, the above expression changes to

$$1.3 \times 10^{-13} = \frac{1.0 \times 10^{-4}\, y}{1.0 \times 10^{-4}}$$

or $y = 1.3 \times 10^{-13}$ M = S^{2-} ion concentration

Thus our assumption that y is very small is correct. But it does give us the equilibrium concentration of S^{2-} ions in solution. The concentration of different species present in a saturated solution of H_2S will be as following:

$$[H_2S] = (0.1 - x)\ M = 0.1 - 1.0 \times 10^{-4}\ M \simeq 0.1\ M$$

$$[S^{2-}] = y = 1.3 \times 10^{-13}\ M$$

$$[HS^-] = 1.0 \times 10^{-4} - y = 1.0 \times 10^{-4} - 1.3 \times 10^{-13} \simeq 1.0 \times 10^{-4}\ M$$

$$[H_3O^+] = 1.0 \times 10^{-4} + y = 1.0 \times 10^{-4} + 1.3 \times 10^{-13} \simeq 1.0 \times 10^{-4}\ M$$

In the preceding section we learnt that PbS (and obviously the other sulphides of Group II) is completely precipitated and ZnS just begins to precipitate at S^{2-} ion concentration of 5.5×10^{-20} M. Thus in a saturated solution of H_2S, though the S^{2-} ion concentration is small, but it is large enough to precipitate the sulphides of cations of both Group II and Group IV. Hence to effect separation of the cations of the Group II from those of the Group IV, we need to adjust the concentration of the S^{2-} ions.

Now we shall try to find out the answer to second question i.e., how to adjust the concentration of S^{2-} ions in a saturated solution of H_2S.

As discussed above, a saturated solution of H_2S in water has a concentration of 0.1 M, in which the concentration of S^{2-} ions is 1.3×10^{-13} M. In aqueous solution, H_2S dissociates in a stepwise manner as shown below:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq),\ K_1 = 1.0 \times 10^{-7}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq),\ K_2 = 1.3 \times 10^{-13}$$

By adding the above two equations, we get the equation for the overall dissociation of H_2S into S^{2-} ions:

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq)$$

The equilibrium constant expression for the overall reaction is equal to the product of the equilibrium constant expressions for the individual steps:

$$K = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = \frac{[H_3O^+][HS^-]}{[H_2S]} \times \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

or $$K = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = K_1 \times K_2$$

or $$K = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = 1.0 \times 10^{-7} \times 1.3 \times 10^{-13} = 1.3 \times 10^{-20}$$

Hence, $$[S^{2-}] = \frac{1.3 \times 10^{-20}[H_2S]}{[H_3O^+]^2}$$

A saturated solution of H_2S has an initial concentration of 0.1 M. As H_2S is a very weak acid, we can safely assume that the concentration of H_2S at equilibrium is approximately equal to its initial concentration.

Hence, $$[S^{2-}] = \frac{1.3 \times 10^{-20} \times 0.1}{[H_3O^+]^2}$$

or $$[S^{2-}] = \frac{1.3 \times 10^{-21}}{[H_3O^+]^2}$$

Thus in a saturated aqueous solution of H_2S, the concentration of S^{2-} ions is inversely proportional to the square of hydrogen ion concentration. By adjusting the hydrogen ion concentration of a solution of H_2S, the concentration of S^{2-} ions can be suitably adjusted. The variation of the S^{2-} ion concentration in a saturated solution of H_2S with the pH of the solution is given in Table 5.6.

Table 5.6 : Variation of the S^{2-} ion concentration in a saturated solution of H_2S with the pH of the solution

pH	$[S^{2-}]$ mol dm^{-3}
1	1.3×10^{-19}
3	1.3×10^{-15}
5	1.3×10^{-11}
7	1.3×10^{-7}
10	0.13

In the preceding sub-section, we concluded that if the S^{2-} ion concentration is maintained at 5.5×10^{-20} M, it is possible to separate the cations of the Group II from those of the Group IV by precipitation as their sulphides. Let us calculate the hydrogen ion concentration necessary to adjust the S^{2-} ion concentration to this value.

$$[H_3O^+]^2 = \frac{1.3 \times 10^{-21}}{[S^{2-}]}$$

$$= \frac{1.3 \times 10^{-21}}{5.5 \times 10^{-20}}$$

$$= 2.4 \times 10^{-2}$$

Hence, $[H_3O^+] = 0.15$ M

Thus, the concentration of H_3O^+ must be at least 0.15 M to prevent the precipitation of ZnS with the Group II sulphides. The concentration of H_3O^+ is maintained at 0.3 M to provide some margin of safety. However, when H_2S gas is passed into a solution of cations of Group IV, which has been buffered with aqueous NH_3 and NH_4Cl, a very high concentration of sulphide ions is provided. This is because the acid (H_2S) and the base (NH_3) react to form a salt $(NH_4)_2S$.

$$2NH_3(aq) + H_2S(aq) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$$

The sulphide ion concentration is sufficiently large so that the solubility products of ZnS, NiS, CoS and MnS are exceeded and these sulphides precipitate from the solution.

5.6.3 The Precipitation of Group III Cations

Group III consists of Al^{3+}, Fe^{3+} and Cr^{3+}. The precipitating reagent for these cations is ammonium hydroxide in the presence of a high concentration of ammonium chloride. To explain why only Al^{3+}, Fe^{3+} and Cr^{3+} precipitate as their hydroxides on addition of the group reagent, let us consider the solubility product constants of the hydroxides of the cations of Group III, IV, V and VI, which are given in Table 5.7.

Table 5.7 : Solubility Product Constants of the Hydroxides of Cations of Group III, IV, V and VI at 25° C

Formula	K_{sp}
$Fe(OH)_3$	6.3×10^{-38}
$Al(OH)_3$	1.9×10^{-33}
$Cr(OH)_3$	7.0×10^{-31}
$Zn(OH)_2$	4.5×10^{-7}
$Co(OH)_2$	2.0×10^{-16}
$Ni(OH)_2$	2.0×10^{-15}
$Mn(OH)_2$	2.0×10^{-13}
$Mg(OH)_2$	1.5×10^{-11}
$Ca(OH)_2$	7.9×10^{-6}
$Sr(OH)_2$	3.2×10^{-4}
$Ba(OH)_2$	5.0×10^{-3}

In the presence of a high concentration of ammonium chloride, the dissociation of the ammonium hydroxide is suppressed. As a result the concentration of hydroxide ions is reduced so much that the solubility products of only less soluble $Al(OH)_3$, $Cr(OH)_3$ and $Fe(OH)_3$ are exceeded and they are precipitated from the solution. In the first place, the above seems to be a plausible explanation. But the following discussion shows that this is not the whole truth, and some other factors as well must be at work to prevent the precipitation of $Ni(OH)_2$, $Co(OH)_2$ and $Zn(OH)_2$. Let us consider that the initial concentration of ammonium hydroxide is

0.1 M and x mol dm^{-3} of it dissociates into NH_4^+ and OH^- ions at equilibrium:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Initial concentration	0.1 M	0	0
At equilibrium	0.1 – x M	x M	x M

From the Law of Mass Action, $\frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} = K(NH_4OH) = 1.8 \times 10^{-5}$

Substituting the values in the above expression, we get,

$$\frac{x \cdot x}{0.1 - x} = 1.8 \times 10^{-5}$$

As NH_4OH is a very weak electrolyte, value of x will be very small and it can be ignored in the denominator. Hence,

$$\frac{x^2}{0.1} = 1.8 \times 10^{-5}$$

or $$x^2 = 1.8 \times 10^{-6}$$

or $$x = 1.34 \times 10^{-3}\ M$$

Thus the concentration of OH^- ions in a solution of 0.1 M NH_4OH is 1.34×10^{-3} M.

As you know that the ionic products of divalent and trivalent metal hydroxides can be written as

$$[M^{2+}]\,[OH^-]^2 = Q \text{ for } M(OH)_2 \text{ and}$$

$$[M^{3+}]\,[OH^-]^3 = Q \text{ for } M(OH)_3.$$

Assuming that the concentration of metal ions, $[M^{2+}]$ or $[M^{3+}]$, is 0.1 M, the ionic products, Q, of $M(OH)_2$ and $M(OH)_3$ in presence of 0.1 M NH_4OH will be

$$(0.1) \times (1.34 \times 10^{-3})^2 = 1.79 \times 10^{-7} \text{ for } M(OH)_2 \text{ and}$$

$$(0.1) \times (1.34 \times 10^{-3})^3 = 2.4 \times 10^{-10} \text{ for } M(OH)_3.$$

As you can see that the ionic products of $Zn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Mn(OH)_2$, $Mg(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ are higher than their solubility products. Hence, all the above should precipitate from the solution. The ionic products of $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ are lower than their solubility products and therefore, these should remain in solution. These will require a higher OH^- ion concentration for their precipitation.

Let us now find out, what happens to OH^- ion concentration and ionic products of $M(OH)_2$ and $M(OH)_3$ in a solution of 0.1 M NH_4OH in the presence of a high concentration of ammonium chloride.

In the presence of a high concentration of ammonium chloride the concentration of the NH_4^+ ion is raised to about 1.5 M, since NH_4Cl is a strong electrolyte and is completely dissociated into ions in solution:

$$NH_4Cl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

$$1.5\ M \rightleftharpoons 1.5\ M \qquad 1.5\ M$$

Hence, $[NH_4^+]$ = 1.5 M, since the NH_4^+ ions from the ammonium hydroxide can be neglected as compared with those from the strong electrolyte NH_4Cl. But

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K(NH_4OH)$$

$$\text{or } \frac{1.5 \times [OH^-]}{0.1} = 1.8 \times 10^{-5}$$

Hence, $[OH^-] = 1.2 \times 10^{-6}$ mol dm^{-3}.

Thus, in the presence of a high concentration of NH_4Cl, the concentration of OH^- ions in a solution of NH_4OH of concentration of 0.1 M is reduced to 1.2×10^{-6} M. Assuming that the concentration of metal ions, $[M^{2+}]$ or $[M^{3+}]$ is 0.1 M, the ionic products, Q, of $M(OH)_2$ and $M(OH)_3$ in presence of 0.1 M NH_4OH and 1.5 M NH_4Cl will be

$$(0.1) \times (1.2 \times 10^{-6})^2 = 1.4 \times 10^{-13} \text{ for } M(OH)_2 \text{ and}$$

$$(0.1) \times (1.2 \times 10^{-6})^3 = 1.7 \times 10^{-19} \text{ for } M(OH)_3.$$

You can see from the above that even in the presence of a high concentration of NH_4Cl, the ionic products of $Zn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ are higher than their solubility products. Hence, all these should precipitate from the solution even in the presence of 1.5 M NH_4Cl. Then why only $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ precipitate from the solution, whereas $Zn(OH)_2$, $Co(OH)_2$ and $Ni(OH)_2$ remain in the solution?

The answer to this conflict between experimental fact (that only $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ are precipitated) and theoretical prediction based upon the solubility product concept almost certainly lies in the formation of soluble complex ions with ammonia molecules. Ammonia molecules are in plenty in ammonium hydroxide solution. Actually the concentration of free ammonia molecules in ammonia solution far exceeds the concentration of ammonium hydroxide molecules.

$$Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}(aq),\ K_f = 2.9 \times 10^9$$

$$Co^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{2+}(aq),\ K_f = 1.3 \times 10^5$$

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq),\ K_f = 5.5 \times 10^8$$

As a result of the formation of soluble complex ions, the concentration of metal cations, i.e., Zn^{2+}, Co^{2+}, and Ni^{2+} is so reduced that the solubility products of their hydroxides are not exceeded in the presence of ammonium chloride and they remain in solution. However, the solubility products of ZnS, CoS, NiS and also MnS are much lower than those of their hydroxides and are easily exceeded on passing H_2S gas in presence of NH_4OH. Therefore, ZnS, CoS, NiS and MnS precipitate from the solution and constitute Group IV of the scheme of qualitative analysis.

5.6.4 The Precipitation of Group V Cations

Ba^{2+}, Sr^{2+} and Ca^{2+} constitute the analytical Group V. These are referred to as the insoluble carbonate group because they are precipitated as carbonates from a buffered solution of aqueous ammonia by the addition of ammonium carbonate.

It is important to note that these cations are derived from the metals of the same

group of the periodic table, their properties are similar. Therefore, separations of individual ions are more difficult than most separations in the earlier groups of cations. Mg^{2+} ions are not precipitated in the group because $MgCO_3$ has a much higher solubility product than those of $BaCO_3$, $SrCO_3$ and $CaCO_3$ (Table 5.8) and the aqueous ammonia solution is buffered to prevent the precipitation of $Mg(OH)_2$.

Table 5.8 : Solubility Products and Molar Solubilities of Group V Carbonates and $MgCO_3$

Compound	K_{sp}	Molar Solubility
$MgCO_3$	4.0×10^{-5}	6.6×10^{-3} M
$BaCO_3$	8.1×10^{-9}	9.0×10^{-5} M
$CaCO_3$	4.8×10^{-9}	6.9×10^{-5} M
$SrCO_3$	9.4×10^{-9}	3.1×10^{-5} M

The precipitating reagent of Group V, 1 M ammonium carbonate, contains the cation of a weak base and the anion of a weak dibasic acid. Both these hydrolyse in aqueous solution, but carbonate ion hydrolysès to a much greater extent than the ammonium ion as their dissociation constants show:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq), \quad K_a = 5.6 \times 10^{-10}$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq), \quad K_b = 2.1 \times 10^{-4}$$

Therefore, solutions of $(NH_4)_2CO_3$ do not contain sufficiently high concentrations of CO_3^{2-} ions to precipitate the Group V carbonates completely. Precipitation of the cations of Group V is, therefore, carried out in a buffered aqueous ammonia (ammonium hydroxide) solution:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$NH_4Cl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

The OH^- ions from aqueous ammonia suppress the hydrolysis of CO_3^{2-} ions. Thus, there are enough CO_3^{2-} ions to precipitate Ca^{2+}, Sr^{2+} and Ba^{2+}. The reactions by which the Group V cations are precipitated can be represented as following:

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \rightarrow SrCO_3(s)$$

These carbonates precipitate as white, dense, crystalline compounds, so there appears to be relatively less amount of the precipitate.

5.7 THE DISSOLUTION OF PRECIPITATES

After precipitation of cations of an analytical group, the next step in the analysis is the separation of individual cations. Separation of cations is achieved by selective dissolution of the precipitate. Dissolution of a precipitates is accomplished by reducing the concentrations of the constituent ions so that K_{sp} is no longer

exceeded, i.e., $Q < K_{sp}$. The dissolution of precipitates is based upon the following type of reactions.

5.7.1 By Converting Anion into a Weak Electrolyte

When anion part of the precipitate is converted into a weak electrolyte, the ionic product becomes lesser than the solubility product of the compound resulting into the dissolution of the precipitate. A few typical examples are:

a) Acidification of insoluble $Al(OH)_3$ in contact with its saturated solution converts OH^- ions to the weak electrolyte water. This shifts the solubility equilibrium to the right until $[Al^{3+}]\,[OH^-]^3 < K_{sp}$, and dissolution occurs:

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$$

$$3OH^-(aq) + 3H^+(aq) \rightarrow 3H_2O(l)$$

$$Al(OH)_3(aq) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$

b) Treatment of $Mg(OH)_2$ with NH_4^+ ions from a salt, such as NH_4Cl, converts OH^- ions (from saturated solution of $Mg(OH)_2$) to the weak electrolytes, NH_3 and H_2O. As a result, $[Mg^{2+}]\,[OH^-]^2 < K_{sp}$ and $Mg(OH)_2$ dissolves.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

$$2OH^-(aq) + 2NH_4^+(aq) \rightarrow 2NH_3(aq) + 2H_2O(l)$$

$$Mg(OH)_2(s) + 2NH_4^+(aq) \rightarrow Mg^{2+}(aq) + 2NH_3(aq) + 2H_2O(l)$$

c) Acidification of some metal sulphides such as ZnS and MnS, converts S^{2-} ions (from saturated solution of MS) into H_2S, a weak electrolyte. As a result, $[M^{2+}]\,[S^{2-}] < K_{sp}$ and the sulphide dissolves.

$$MS(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)$$

$$S^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g)$$

$$MS(s) + 2H^+(aq) \rightarrow M^{2+}(aq) + H_2S(g)$$

Highly insoluble sulphides, such as CuS, CdS, PbS, CoS, NiS, etc., do not produce sufficiently high concentrations of S^{2-} ions in their saturated solutions to react with even the strongest non-oxidising acids. They require oxidation of S^{2-} ions for their dissolution.

5.7.2 By Converting Anion into Another Species by Redox Reaction

Highly insoluble metal sulphides, such as those mentioned above, can be dissolved in hot nitric acid because the NO_3^- ions oxidise the S^{2-} ions to elemental sulphur, thereby removing S^{2-} ions from solution:

$$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)] \times 3$$

$$3S^{2-}(aq) + 2NO_3(aq) + 8H^+(aq) \rightarrow 3S(s) + 2NO(g) + 4H_2O(l)$$

$$3CuS(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 3S(s) + 2NO(g) + 4H_2O(l)$$

5.7.3 By Complex Ion Formation

Many insoluble compounds can be dissolved by converting them into soluble complex ions. For example, when a precipitate of AgCl and Hg_2Cl_2 is treated with

aqueous ammonia solution, AgCl passes into solution due to the formation of the complex ion, $[Ag(NH_3)_2]^+$:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$Ag^+(aq) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)$$

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

When a mixture of sulphides of Group II cations is treated with a solution of yellow ammonium sulphide, As_2S_3, Sb_2S_3 and SnS_2 dissolve due to the formation of soluble complex ions leaving behind a residue of other metal sulphides:

$$(NH_4)_2S_2(aq) \rightleftharpoons 2NH_4^+(aq) + S_2^{2-}(aq)$$

$$As_2S_3(s) + 4S_2^{2-}(aq) \rightarrow 2[AsS_4]^{3-}(aq) + S_3^{2-}(aq)$$

Tetrathioarsenate(V) ion

$$SnS_2(s) + S_2^{2-}(aq) \rightarrow [SnS_3]^{2-}(aq) + S(s)$$

Trithiostannate(IV) ion

5.8 SUMMARY

In this unit you studied solubility, solubility product constant and the relation between the two. You also studied the common ion effect, complex formation and the classification of cations into analytical groups. You studied how the cations of an analytical group are separated from those of the other analytical groups by selective precipitation. The cations of an analytical group are then separated from each other by selective dissolution of their precipitate.

5.9 ANSWERS

To Self-Assessment Questions

1. Cu^{2+} and Co^{2+} are precipitated as their sulphides on reaction with H_2S in acidic and basic medium, respectively. Therefore, they belong to two different analytical groups.

2. $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$

   $K_{sp}(Ag_2CO_3) = [Ag^+]^2 [CO_3^{2-}]$

   $Bi_2S_3(aq) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$

   $K_{sp}(Bi_2S_3) = [Bi^{3+}]^2 [S^{2-}]^3$

3. For a salt of A_xB_y type, the solubility product $K_{sp} = x^x \cdot y^y \cdot S^{x+y}$, where S is solubility of the salt.

   For CaF_2, $x = 1$ and $y = 2$

   Hence, $K_{sp} = 1^1 \cdot 2^2 \cdot S^{1+2}$

   or $4.0 \times 10^{-11} = 4S^3$

   or $S^3 = \dfrac{4.0 \times 10^{-11}}{4} = 1.0 \times 10^{-11}$

Hence, $S = (1.0 \times 10^{-11})^{1/3} = 2.15 \times 10^{-4}$ mol dm^{-3}

Hence, solubility of CaF_2 is 2.15×10^{-4} mol dm^{-3}.

UNIT 6 DETECTION OF THE CATIONS-II

Structure

6.1 INTRODUCTION

In the preceding unit, you studied the concepts of solubility, solubility product, the common ion effect and complex formation. You also studied that the cations are classified into seven analytical groups on the basis of similarities in the solubility behaviour of their sparingly soluble salts and also on the basis of similarities in their chemical behaviour. Also that the cations of each analytical group are separated from those of others by selective precipitation. The cations of individual groups are then separated from each other by selective dissolution of their precipitates and are identified by specific confirmatory tests. In this unit, you will study the details of the scheme of analysis and the chemistry of separation and identification of cations present in a mixture.

Objectives

After studying this unit, you should be able to:

- classify the cations into analytical groups,
- list the cations of each analytical group,
- separate cations into analytical groups by selective precipitation,
- identify the cations present in a mixture by performing the systematic tests for cations,
- discuss the chemistry of analysis of cations,

- write down the colour and the chemical formulae of the precipitate formed by each cation on reaction with group reagent, and
- if possible, perform the flame tests for certain cations present in the mixture.

6.2 PRELIMINARY INVESTIGATION OF THE SAMPLE

Observe the colour of the sample and the solution. It may provide a clue to the identity of cations and may help in performing subsequent successful analysis of the sample. The colours of some of the cations are listed below.

Cu^{2+}	blue green
Ni^{2+}	green
Mn^{2+}	faint pink (above 0.5 M)
Co^{2+}	pink-red
Cr^{3+}	violet-purple
Fe^{2+}	pale green
Fe^{3+}	yellow

The solution may acquire purple (MnO_4^-), pale green (CrO_4^{2-}) or orange ($Cr_2O_7^{2-}$) colour due to the presence of anions listed in the parenthesis.

Sometimes the colour of the solution may not represent the true identity of the ions because of the presence of more than one species. The concentration of the ion in solution is also very important. For example, an aqueous solution of Mn^{2+} salts may appear almost colourless unless present in a concentration above 0.5 M. Incidentally cobalt(II) salts are also pink. The presence of a complexing anion has also an important influence on the colour of the cations in solution. In the presence of high concentration of chloride ions, a cobalt salt in solution may appear deep blue in colour. Likewise, nickel(II) and copper(II) salts may appear either blue or green depending on the anion present. Iron(II) salts though generally pale green may appear almost colourless in aqueous solution. The observations with regard to the presence of coloured cations, therefore, may not be conclusive.

6.3 PREPARATION OF SOLUTION FOR THE ANALYSIS OF CATIONS

Cations are separated into analytical groups by selective precipitation as sparingly soluble salts from aqueous solution. Therefore, first of all the solid mixture should be brought into solution. Place 100 mg of the finely powdered material in a glass test tube and add the solvents in the following order:

Aqua regia consists of 3 parts of concentrated hydrochloric acid for every 1 part of concentrated nitric acid.

i) distilled water

ii) dilute HCl (6 M)

iii) concentrated HCl (12 M)

iv) dilute nitric acid (6 M)

v) concentrated nitric acid (16 M)

vi) aqua regia

Treat the sample first with distilled water. If the substance does not dissolve completely, keep in a boiling water bath for nearly 10 minutes and stir periodically. If the sample dissolves completely stop adding distilled water. If the substance does

not dissolve completely, treat the residue with dilute hydrochloric acid and heat gently. If a solid still remains, try dissolution in concentrated hydrochloric acid and proceed as before.

If a residue still remains, try dissolution in dilute nitric acid and then concentrated nitric acid. If the sample dissolves in any of the solvents, there is no need to test with the other solvents.

If the substance still does not dissolve in any of the solvents completely, add aqua regia and heat to near dryness in a china dish. Note the colour change, odour and colour of the gases evolved. This may sometimes be quite useful in the analysis of ions present in the substance.

Always drive off the volatile acid and carefully evaporate the solution to nearly 0.5 – 1.0 cm^3. Do not evaporate the solution to dryness as insoluble oxides may form, which are subsequently difficult to dissolve. Extract with a small volume of distilled water and add dilute hydrochloric acid before proceeding for cation analysis.

Use 500 mg to 1.0 g of the sample in a china dish or small beaker after making a proper choice of the solvent and proceed in the manner as described above for complete dissolution of the sample.

Water is a preferred solvent for most of the ionic substances. Many inorganic compounds which contain anions of weak acids are insoluble in water. These compounds are soluble in dilute strong acids like hydrochloric acid (6 M). Carbonates, sulphites, oxalates, borates, thiosulphates are soluble in dilute solutions of strong acids.

A concentrated solution of a non-oxidising strong acid such as hydrochloric acid (12 M) often provides a rich source of hydronium ions. Such a treatment may be necessary when the anion is derived from a strong acid.

Oxidising acid, like nitric acid attacks substances when hot and oxidises them. Finally when every other acid fails, aqua regia generally dissolves compounds because of its oxidising action or due to the formation of chloro complexes. All sulphides are soluble in aqua regia. Hot dilute nitric acid dissolves all the sulphides except HgS.

If still a residue remains, consult your Counsellor.

6.4 SEPARATION OF THE CATIONS INTO ANALYTICAL GROUPS

The cations of each successive group are precipitated as sparingly soluble compounds with anions supplied by the group reagents. The precipitate containing cations of one group is separated either by filtration or centrifugation. The centrifugate or solution remaining after filtration is similarly converted into a sparingly soluble precipitate by another group reagent. However, care must be taken that precipitation is complete before proceeding for the next group. Always add a slight excess of the precipitating agent to ensure complete precipitation.

The major classification of the analytical groups is as follows:

Cations of Analytical Group I: Pb^{2+}, Ag^{2+} and Hg_2^{2+}

These are precipitated as chlorides since the chlorides of Ag(I), Hg(I) and Pb(II) only are insoluble in the presence of 0.2 M HCl solution, other cations remain in solution since the chlorides of other cations being soluble.

Cations of Analytical Group II : Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{4+}

These are precipitated as sulphides from a solution of lower pH made 0.3 M in HCl

and saturating the solution with H_2S or using H_2S water. These cations precipitate as sulphides from solution of high H^+ ion concentration and require a low concentration of S^{2-} ions because the sulphides of these cations have very low solubility, i.e., the sulphides of the group are those with the smallest K_{sp} values. Therefore, they precipitate in the presence of sulphide ion concentration that is kept low enough to avoid precipitation of the more soluble sulphides of the cations of Group IV. The solution should, however, be diluted atleast 100 times and hydrogen sulphides should be passed before proceeding to the next group otherwise Cd^{2+} is likely to be missed. This group is further separated into subgroups by using yellow ammonium sulphide.

Cations of Analytical Group III : Fe^{3+}, Cr^{3+}, Al^{3+}

After boiling off H_2S, and oxidation of Fe^{2+}, these cations are precipitated as hydroxides by controlling the concentration of OH^- ions by addition of NH_4OH in the presence of NH_4Cl. All other cations remain in solution.

Cations of Analytical Group IV : Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}

The sulphides of cations of this group are more soluble than the sulphides of the cations of Group II. The cations of this group obviously require a higher concentration of S^{2-} ions, which is achieved by raising the pH in the presence of NH_4Cl–NH_4OH buffer solution, for precipitation to occur. All other cations of higher groups remain in solution.

Cations of Analytical Group V : Ba^{2+}, Sr^{2+}, Ca^{2+}

These cations are precipitated after boiling off H_2S and precipitating with ammonium carbonate in the presence of NH_4Cl and NH_4OH. Other cations remain in solution. This group is sometimes referred to as the 'insoluble carbonate group'.

Cation of Analytical Group VI: Mg^{2+}

Mg^{2+} belongs to this group which is precipitated as $Mg(NH_4)PO_4$ by the addition of $(NH_4)_2HPO_4$ in buffered aqueous ammonia solution.

Cations of Analytical Group Zero; NH_4^+, K^+ and Na^{2+}

Salts of Na^+, NH_4^+ and K^+ are soluble in water. Therefore, these cations are sometimes referred to as cations belonging to the soluble group. They are generally analysed before proceeding for the analysis of cations of Group I and therefore, are known as the cations of Group zero also.

This procedure divides the cations present in original mixture into various groups. Each group is then separated into individual ions, which are subjected to confirmatory tests.

The separation of cations into different analytical groups along with the group reagents, formulae and colours of the precipitates is given in Table 6.1. The procedure for separating the cations into analytical groups is summarised in Flow Chart 6.1.

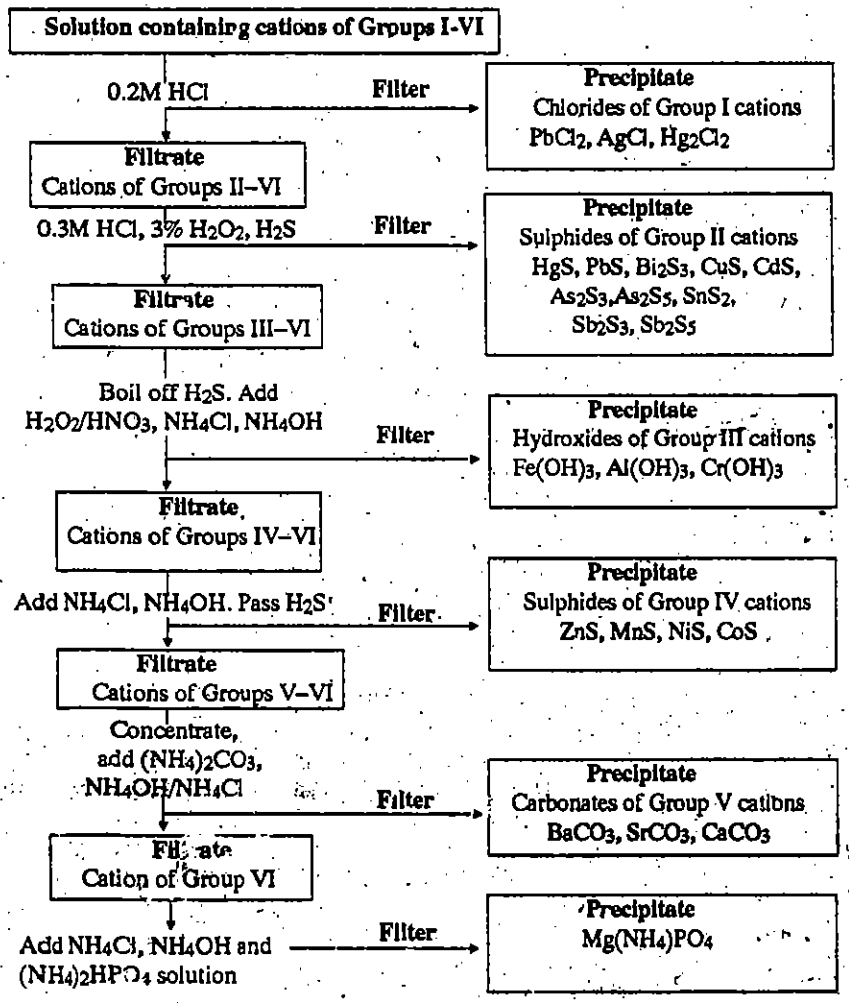
6.5 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP I

The cations of Group I are Pb^{2+}, Ag^+ and Hg_2^{2+}. The Group I cations are precipitated as chlorides. The K_{sp} values for AgCl and Hg_2Cl_2 are very small, while the K_{sp} for $PbCl_2$ is rather large. If enough hydrochloric acid is added to the aqueous solution

Table 6.1 : Separation of Cations into Analytical Groups

Analytical group	Group reagent	Ion	Product
I	0.2 M HCl	Pb(II)	$PbCl_2$ (white)
		Ag(I)	AgCl (white)
		Hg(I)	Hg_2Cl_2 (white)
II	0.3 M HCl, $+H_2S$	Hg(II)	HgS (black)
		Pb(II)	PbS (deep brown)
		Bi(III)	Bi_2S_3 (black)
		Cu(II)	CuS (black)
		Cd(II)	CdS (yellow)
		As(III)	As_2S_3 (yellow)
		As(V)	As_2S_5 (yellow)
		Sb(III)	Sb_2S_3 (orange)
		Sb(V)	Sb_2S_5 (orange)
		Sn(IV)	SnS_2 (yellow)
III	NH_4OH/NH_4Cl	Fe(III)	$Fe(OH)_3$ (brown)
		Al(III)	$Al(OH)_3$ (white)
		Cr(III)	$Cr(OH)_3$(gray blue)
IV	NH_4OH/NH_4Cl, H_2S	Co(II)	CoS (black)
		Ni(II)	NiS (black)
		Mn(II)	MnS (pink)
		Zn(II)	ZnS (white)
V	NH_4OH/NH_4Cl, $(NH_4)_2CO_3$	Ba(II)	$BaCO_3$ (white)
		Sr(II)	$SrCO_3$ (white)
		Ca(II)	$CaCO_3$ (white)
VI	$(NH_4)_2HPO_4$, NH_4OH/NH_4Cl	Mg(II)	$Mg(NH_4)PO_4$ (white)
Zero	None	NH_4^+, K^+, Na^+	–

Flow Chart 6.1 : Separation of Cations into Analytical Groups



of these ions so as to raise the $[Cl^-]$ to 0.2 M, very few Ag^+ or Hg_2^{2+} ions will remain in solution. The presence of hydrogen ion prevents the precipitation of the bismuth and the antimony oxychlorides, which would form in the absence of these ions:

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$$

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

$$Hg_2^{2+}(aq) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s)$$

$$Bi^3(aq) + Cl^-(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2H^+(aq)$$

$$Sb^3(aq) + + Cl^-(aq) + H_2O(l) \rightleftharpoons SbOCl(s) + 2H^+(aq)$$

A very large excess of the acid will contain an equally large excess of chloride ions. Silver and lead chlorides form soluble chloro complexes in the presence of a large excess of chloride ions. One consequence of chloro complex formation is that excess of chloride ions will cause this group precipitate to redissolve. Mercury(I) chloride does not dissolve because the chloro complexes of mercury(I) are unstable.

$$Ag^+(aq) + 2Cl^-(aq) \rightleftharpoons [AgCl_2]^-(aq)$$

$$Pb^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq)$$

A second consequence can be the formation of stable chloro complexes of some other cations, such as $[CdCl_4]^{2-}$. Since $PbCl_2$ is several times more soluble than AgCl or Hg_2Cl_2, it is impossible to avoid carrying some of Pb(II) into the solution after separation of AgCl and Hg_2Cl_2. Consequently Group II of cation analysis always contains some Pb(II) ions.

Separation and Identification of Cations of Analytical Group I

Once the cations of this group are precipitated as chlorides, we need to separate the ions so that individual tests can be performed for the identification of individual ions.

Separation of lead(II) from other members is rather easy because the solubility of lead(II) chloride in hot water is several times greater than that at room temperature. This fact is made use of in the separation of lead from other cations of this group. [Solubility of $PbCl_2$: 9.9 g dm^{-3} at room temperature and 33.4 g dm^{-3} at 100°C]. Though the solubilities of chlorides of silver(I) and mercury(I) also increase with temperature, but the solubilities are so low that their ions are not detected by the method of qualitative analysis. [Solubility of AgCl: 0.089 mg dm^{-3} at 20°C and 0.21 mg dm^{-3} at 100°C; solubility of Hg_2Cl_2: 0.21 mg dm^{-3} at 20°C and 1.0 mg dm^{-3} at 45°C.]

The precipitate of Group-I chlorides is boiled with water and filtered. The lead chloride passes into solution, whereas the silver chloride and mercury(I) chloride remain as solid.

$$PbCl_2(s) \underset{\text{hot water}}{\rightleftharpoons} Pb^{2+}(aq) + 2Cl^-(aq)$$

The hot filtrate deposits lead chloride on cooling. Consequently, the hot filtrate is used for confirmation of lead(II).

The precipitate of silver(I) and mercury(I) chlorides is thoroughly washed with hot water before addition of aqueous ammonia, otherwise a gray precipitate consisting of a mixture of basic lead(II) chloride, Pb(OH)Cl and lead(II) hydroxide, $Pb(OH)_2$ coats the precipitate of mercury(II) amido chloride, $HgNH_2Cl$.

$$PbCl_2(s) + NH_3(aq) + H_2O(l) \rightarrow Pb(OH)Cl(s) + Pb(OH)_2(s) + NH_4^+(aq) + 2Cl^-(aq)$$

Aqueous ammonia reacts with silver(I) chloride to form a colourless soluble ammine complex, $[Ag(NH_3)_2]^+$ while mercury(I) chloride undergoes disproportionation in the presence of excess ammonia solution to produce finely divided metallic mercury (black) and mercury(II) amidochloride (white) which stays as a precipitate.

$$Hg_2Cl_2(s) + 2NH_3(aq) \rightarrow Hg(l) + HgNH_2Cl(s) + NH_4^+(aq) + Cl^-(aq)$$

The black precipitate confirms that Hg(I) ions are present.

Identification of Lead(II)

Divide the hot solution of lead chloride into three parts and perform confirmatory tests for the presence of Pb(II).

i) Add potassium chromate when insoluble yellow $PbCrO_4$ is precipitated.

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

The precipitate of $PbCrO_4$ dissolves on addition of NaOH producing hydrogen plumbate(II) ion, $HPbO_2^-$. Lead chromate is reprecipitated when the solution is acidified with acetic acid as the excess hydroxide ion is neutralized and the equilibrium shifts to the left.

$$PbCrO_4(s) + 3OH^-(aq) \rightarrow HPbO_2^-(aq) + CrO_4^{2-}(aq) + H_2O(l)$$

ii) Add potassium iodide, when a yellow precipitate of PbI_2 forms. When this is warmed, the solution on cooling deposits crystals of PbI_2 as golden shining needles.

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

iii) Add dilute sulphuric acid to the solution when a white precipitate of $PbSO_4$ is obtained. $PbSO_4$ dissolves in excess of acetate ions due to the formation of tetraacetatoplumbate(II) complex ion.

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

$$PbSO_4(s) + 4CH_3COO^-(aq) \rightleftharpoons [Pb(CH_3COO)_4]^{2-}(aq) + SO_4^{2-}(aq)$$

Lead sulphate is also soluble in excess of alkali hydroxide, when colourless $[Pb(OH)_4]^{2-}$ is formed.

$$PbSO_4(s) + 4OH^-(aq) \rightleftharpoons [Pb(OH)_4]^{2-}(aq) + SO_4^{2-}(aq)$$

Further confirmation can be obtained by acidification with acetic acid and adding K_2CrO_4 solution when a yellow precipitate of $PbCrO_4$ is formed.

$$[Pb(OH)_4]^{2-}(aq) + 4H^+(aq) \rightleftharpoons Pb^{2+}(aq) + 4H_2O(l)$$

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons PbCrO_4(s)$$

Identification of Silver(I)

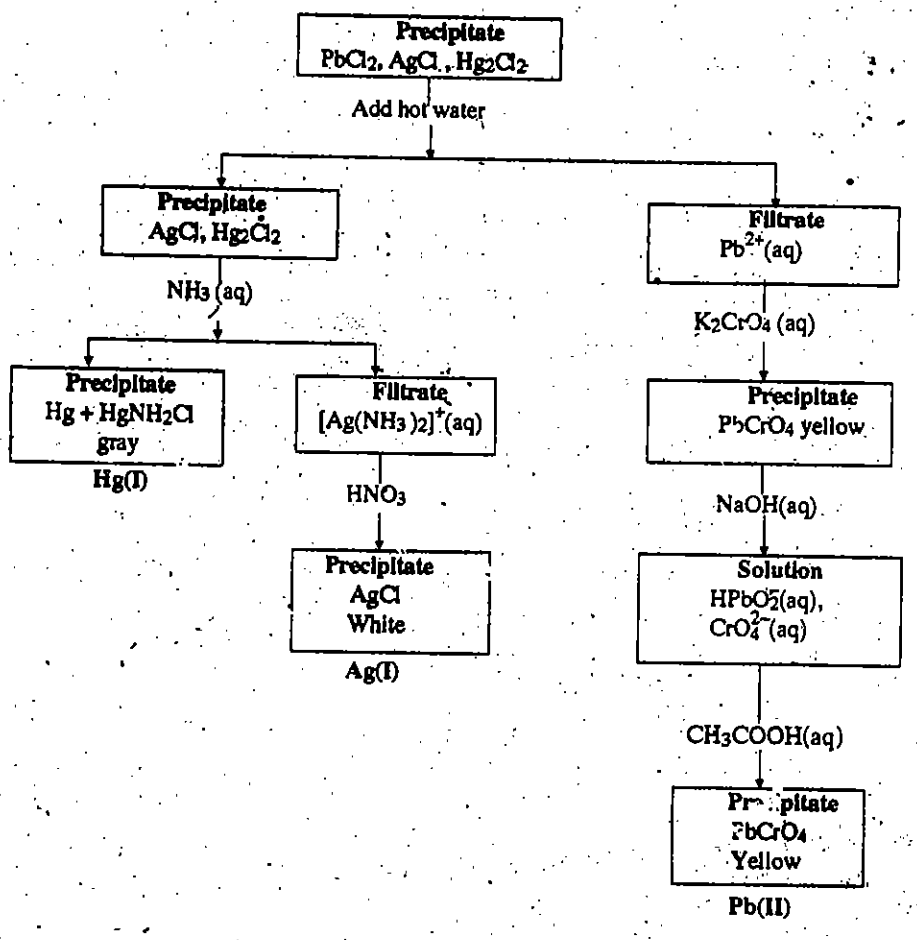
The presence of Ag^+ ions in the colourless solution is confirmed by the acidification with dilute nitric acid when a white precipitate of silver(I) chloride is formed.

$$[Ag(NH_3)_2]^+(aq) + Cl^-(aq) + 2H^+(aq) \rightarrow AgCl(s) + 2NH_4^+(aq)$$

The nitric acid converts NH_3 to NH_4^+ thereby destroying the complex ion. This

increases the concentration of free silver ions in the solution resulting into reprecipitation of AgCl. The procedure of analysis of the cations of Group I is summarised in Flow Chart 6.2.

Flow Chart 6.2 : Separation and Identification of Group I Cations



6.6 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP II

The cations of this group are Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{4+}. These cations of Group II are precipitated as sulphides from 0.3 M HCl solution saturated with H_2S. The sulphides of this group are the ones with the smallest K_{sp} values. At low pH, $[S^{2-}]$ is very low and only those cations which produce sparingly soluble sulphides with a very small K_{sp} will precipitate. Cations of other groups with relatively large K_{sp} values will not precipitate under these conditions. The key to the separation of cations of Group II and IV, therefore, lies in the difference between the K_{sp} values of sulphides of the cations of these groups. The real problem lies with the precipitation of CdS which has an intermediate K_{sp} value. Dilution of the solution decreases the concentration of H^+ ions and also releases Cd^{2+} from the $[CdCl_4]^{2-}$ complex. The slight increase in pH is enough to give a $[S^{2-}]$ sufficient to precipitate cadmium(II). Hydrogen peroxide is added to the solution to ensure oxidation of Sn(II) to Sn(IV) so that the much less soluble sulphide SnS_2 is produced.

$$Pb^{2+}(aq) + H_2S(aq) \rightarrow PbS(s) + 2H^+(aq)$$

$$Hg^{2+}(aq) + H_2S(aq) \rightarrow HgS(s) + 2H^+(aq)$$

$$2Bi^{3+}(aq) + 3H_2S(aq) \rightarrow Bi_2S_3(s) + 6H^+(aq)$$

$$Cu^{2+}(aq) + H_2S(aq) \rightarrow CuS + 2H^+(aq)$$
$$Cd^{2+}(aq) + H_2S(aq) \rightarrow CdS(s) + 2H^+(aq)$$
$$2As^{3+}(aq) + 3H_2S(aq) \rightarrow As_2S_3(s) + 6H^+(aq)$$
$$2Sb^{5+}(aq) + 5H_2S(aq) \rightarrow Sb_2S_5(s) + 10H^+(aq)$$
$$Sn^{4+}(aq) + 2H_2S(aq) \rightarrow SnS_2 + 4H^+(aq)$$
$$Sn^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow Sn^{4+}(aq) + 2H_2O(l)$$

6.6.1 Separation of Analytical Group II into Group IIA and Group IIB

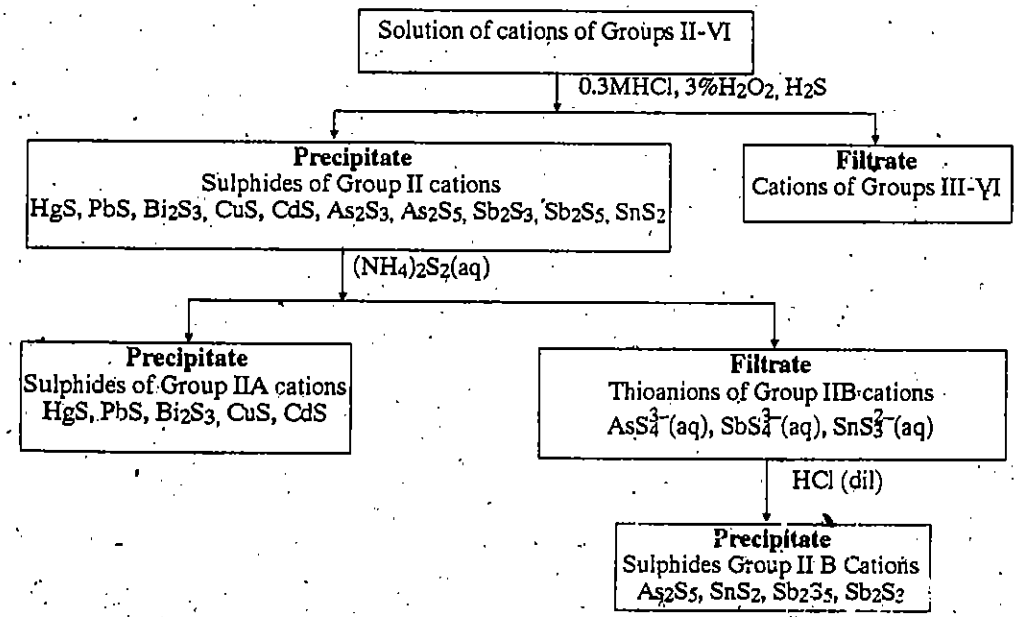
After precipitation the cations of Group II are separated into Group IIA and Group IIB by selective dissolution of the precipitate. The sulphides of arsenic, antimony and tin are separated from other members of the group by dissolving them in yellow ammonium sulphide.

$$As_2S_3(s) + 4S_2^{2-}(aq) \rightleftharpoons 2[AsS_4]^{3-}(aq) + S_3^{2-}(aq)$$
$$As_2S_5(s) + 6S_2^{2-}(aq) \rightleftharpoons 2[AsS_4]^{3-}(aq) + 3S_3^{2-}(aq)$$
$$Sb_2S_3(s) + 4S_2^{2-}(aq) \rightleftharpoons 2[SbS_4]^{3-}(aq) + S_3^{2-}(aq)$$
$$Sb_2S_5(s) + 6S_2^{2-}(aq) \rightleftharpoons 2[SbS_4]^{3-}(aq) + 3S_3^{2-}(aq)$$
$$SnS_2(s) + 2S_2^{2-}(aq) \rightleftharpoons [SnS_3]^{2-}(aq) + S_3^{2-}(aq)$$

The cations As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+} and Sn^{4+} constitute the Group IIB of the scheme.

The sulphides of Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+} and Cd^{2+} do not dissolve in yellow ammonium sulphide and are left behind. These constitute the Group IIA of the scheme. The procedure for precipitation of Group II cations and their separation into Group IIA and Group IIB is summarised in Flow Chart 6.3.

Flow Chart 6.3 : Precipitation of Group II Cations and Separation into Group IIA and Group IIB



6.6.2 Separation of Cations of Group IIA

The separation of HgS from other members of this group is based on the solubility of PbS, Bi_2S_3, CuS and CdS in dilute HNO_3 while HgS remains insoluble.

$$3PbS(s) + 8H^+(aq) + 2NO_3^-(Aq) \rightarrow 3Pb^{2+}(aq) + 2NO(g) + 4H_2O(l) + 3S(s)$$

$$3CuS(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l) + 3S(s)$$

$$Bi_2S_3(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow 2Bi^{3+}(aq) + 2NO(g) + 2H_2O(l) + 3S(s)$$

$$3CdS(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Cd^{2+}(aq) + 2NO(g) + 4H_2O(l) + 3S(s)$$

Mercury(II) sulphide dissolves in aqua regia due to the combined effect of very high oxidising action and complexing ability of aqua regia. This results in the formation of stable tetrachloromercurate(II) complex ion, $[HgCl_4]^{2-}$

$$3HgS(s) + 8H^+(aq) + 12Cl^-(aq) + 2NO_3^-(aq) \rightarrow 3[HgCl_4]^{2-}(aq) + 2NO(g) + 4H_2O(l) + 3S(s)$$

Lead(II) is separated from other members i.e., Cu(II), Cd(II), and Bi(III) by precipitation as $PbSO_4$. Nitric acid must be completely removed from the solution by fuming with concentrated H_2SO_4 since $PbSO_4$ is soluble in HNO_3. The evaporation must be carried out in a hood since the vapours of HNO_3, oxides of nitrogen and sulphur are extremely corrosive and toxic. The solution is diluted to reprecipitate $PbSO_4$.

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

Bismuth(III) is separated from the remaining members of the group, i.e., Cu(II) and Cd(II), by precipitation as $Bi(OH)_3$ by adding aqueous ammonia solution. Copper(II) and cadmium(II) stay in solution because they form tetraammine complexes, copper complex being deep blue in colour.

$$Bi^{3+}(aq) + 3NH_3(aq) + 3H_2O(l) \rightarrow Bi(OH)_3(s) + 3NH_4^+(aq)$$

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

$$Cd^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cd(NH_3)_4]^{2+}(aq)$$

The blue colour of the solution is a preliminary indication of the presence of Cu^{2+} ion.

6.6.3 Separation of Cations of Group IIB

The solution containing thioanions of arsenic, antimony and tin is acidified with dilute HCl. The sulphides of these cations are again precipitated along with sulphur in the colloidal form:

$$2[AsS_4]^{3-}(aq) + 6H^+(aq) \rightarrow As_2S_5(s) + 3H_2S(g)$$

$$2[SbS_4]^{3-}(aq) + 6H^+(aq) \rightarrow Sb_2S_5(s) + 3H_2S(s)$$

$$Sb_2S_5(s) \rightarrow Sb_2S_3(s) + S(s)$$

$$[SnS_3]^{2-}(aq) + 2H^+(aq) \rightarrow SnS_2(s) + H_2S(g)$$

$$S_2^{2-}(aq) + 2H^+(aq) \rightarrow H_2S(g) + S(s)$$

The separation of As_2S_5 from other members of this group is based on the dissolution of Sb_2S_3 and SnS_2 in concentrated HCl, due to the formation of tetrachloroantimonate(III) and hexachlorostannate(IV) ions:

$$Sb_2S_3(s) + 6H^+(aq) + 8Cl^-(aq) \rightarrow 2[SbCl_4]^-(aq) + 3H_2S(g)$$

$$SnS_2(s) + 4H^+(aq) + 6Cl^-(aq) \rightarrow [SnCl_6]^{2-}(aq) + 2H_2S(g)$$

The solution is boiled to expel H_2S and used to confirm the presence of antimony and tin ions in solution. The insoluble As_2S_5 is treated with aqueous ammonia and H_2O_2 or with nitric acid and the solution evaporated to near dryness. As a result arsenate ions are produced. Confirmation of arsenic is done using this solution.

$$As_2S_5(s) + 16NH_3(aq) + 20H_2O_2(aq) \rightarrow 2AsO_4^{3-}(aq) + 16NH_4^+(aq) + 5SO_4^{2-}(aq) + 12H_2O(l)$$

$$3As_2S_5(s) + 10H^+(aq) + 10NO_3^-(aq) + 4H_2O(l) \rightarrow 6H_3AsO_4(aq) + 10NO(g) + 15S(s)$$

The procedure for precipitation and separation of cations of Group II is summarised in Flow Chart 6.3.

6.6.4 Identification of the Cations of Group II

After separation of individual cations either by selective precipitation or by selective dissolution as discussed above, their presence is further confirmed by means of identification tests for each cation.

Identification of Mercury(II)

The precipitate of mercury(II) sulphide is black. Dissolve the precipitate in aqua regia and evaporate to near dryness. Add $1cm^3$ conc. HCl and heat again. Dilute with water and divide into three parts.

i) Add a few drops of $SnCl_2$ solution to one part, appearance of a white precipitate which turns gray confirms mercury(II):

$$2Hg^{2+}(aq) + 2Cl^-(aq) + Sn^{2+}(aq) \rightarrow Hg_2Cl_2(s) + Sn^{4+}(aq)$$

$$Hg_2Cl_2(s) + Sn^{2+}(aq) \rightarrow 2Hg^0(l) + Sn^{4+}(aq) + 2Cl^-(aq)$$

ii) Add a few drops of KI solution to another part. A yellow precipitate of HgI_2 is formed. The precipitate dissolves on adding excess KI due to the formation of tetraiodomercurate(II), $[HgI_4]^{2-}$, complex ion:

$$Hg^{2+}(aq) + 2I^-(aq) \rightarrow HgI_2(s)$$

$$HgI_2(s) + 2I^-(aq) \rightarrow [HgI_4]^{2-}(aq)$$

iii) Add a small piece of copper wire to the third part, when a shining deposit of mercury is obtained on the copper wire and the solution turns greenish blue.

$$Hg^{2+}(aq) + Cu^0(s) \rightarrow Hg^0(l) + Cu^{2+}(aq)$$

Identification of Lead(II)

The precipitate of lead sulphate is white. Divide the precipitate into two parts and perform the following tests :

i) Heat one part of the precipitate with excess of ammonium acetate solution. The precipitate will dissolve due to the formation of tetraacetatoplumbate(II) complex ion:

$$PbSO_4(s) + 4CH_3COO^-(aq) \rightleftharpoons [Pb(CH_3COO)_4]^{2-}(aq) + SO_4^{2-}(aq)$$

ii) Heat the other part of the lead sulphate precipitate with excess of sodium hydroxide. The precipitate will dissolve to give a colourless solution due to the formation of tetrahydroxoplumbate(II) ion:

$$PbSO_4(s) + 4OH^-(aq) \rightleftharpoons [Pb(OH)_6]^{2-}(aq) + SO_4^{2-}(aq)$$

Acidify the solution with acetic acid and add potassium chromate solution. A yellow precipitate of lead chromate will be formed.

$$[Pb(OH)_4]^{2-}(aq) + 4H^+(aq) \rightleftharpoons Pb^{2+}(aq) + 4H_2O(l)$$

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

Identification of Bismuth(III)

The precipitate of $Bi(OH)_3$ is transparent and gelatinous. Confirm bismuth(III) by addition of a freshly prepared sodium tetrahydroxostannate(II) reagent (sodium stannite) to $Bi(OH)_3$ when black metallic bismuth precipitates.

$$2Bi(OH)_3(s) + 3[Sn(OH)_4]^{2-}(aq) \rightarrow 2Bi^\circ(s) + 3[Sn(OH)_6]^{2-}(aq)$$

Alternatively, dissolve $Bi(OH)_3$ in dilute HCl and divide into two parts.

$$Bi(OH)_3(s) + 3H^+(aq) \rightarrow Bi^{3+}(aq) + 3H_2O(l)$$

i) Add distilled water to one part when white bismuth oxychloride precipitates.

$$Bi^{3+}(aq) + Cl^-(aq) + H_2O(l) \rightarrow BiOCl(s) + 2H^+(aq)$$

ii) Add potassium iodide reagent dropwise to the second part when a black precipitate of BiI_3 is obtained. The precipitate dissolves readily in excess reagent when orange coloured tetraiodobismuthate ions are formed.

$$Bi^{3+}(aq) + 3I^-(aq) \rightarrow BiI_3(s)$$

$$BiI_3(s) + I^-(aq) \rightarrow [BiI_4]^-(aq)$$

Identification of Copper(II)

The presence of copper is confirmed by making the solution acidic with acetic acid and adding potassium hexacyanoferrate(II) when a reddish brown precipitate of $Cu_2[Fe(CN)_6]$ forms.

$$[Cu(NH_3)_4]^{2+}(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 4NH_4^+(aq)$$

$$2Cu^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow Cu_2[Fe(CN)_6](s)$$

Cadmium ions under similar conditions produce a white precipitate.

$$2Cd^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightleftharpoons Cd_2[Fe(CN)_6](s)$$

When both copper(II) and cadmium(II) are present, copper ions are separated by reduction of the ammine complex with $Na_2S_2O_4$ (sodium dithionite). Under these conditions cadmium ions are not reduced and so after separation of metallic copper, the solution is saturated with H_2S when yellow CdS precipitates.

$$[Cu(NH_3)_4]^{2+}(aq) + S_2O_4^{2-}(aq) + 2H_2O(l) \rightarrow Cu^\circ(s) + 2SO_3^{2-}(aq) + 4NH_4^+(aq)$$

$$[Cd(NH_3)_4]^{2+}(aq) + S^{2-}(aq) \rightarrow CdS(s) + 4NH_3(aq)$$

Alternatively, acidify the solution containing Cu(II) and Cd(II) ions with dilute HCl and pass H_2S. Only black CuS precipitates. Separate the precipitate. Dilute the solution atleast 100 times and pass H_2S, a yellow precipitate of CdS will be formed:

$$[Cu(NH_3)_4]^{2+}(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 4NH_4^+(aq)$$

$$Cu^{2+}(aq) + H_2S(aq) \rightarrow CuS(s) + 2H^+(aq)$$

$$[Cd(NH_3)_4]^{2+}(aq) + 4H^+(aq) + 4Cl^-(aq) \rightleftharpoons [CdCl_4]^{2-}(aq) + 4NH_4^+(aq)$$

$$[CdCl_4]^{2-}(aq) \rightleftharpoons Cd^{2+}(aq) + 4Cl^-(aq)$$

$$Cd^{2+}(aq) + H_2S(aq) \rightleftharpoons CdS(s) + 2H^+(aq)$$

Dissolve copper sulphide by treating with dilute HNO_3 and evaporating to near dryness. Extract with water and neutralise with aqueous ammonia and confirm copper(II) by using $K_4[Fe(CN)_6]$ reagent.

Use of KCN to separate Cu(II) and Cd(II)

Solution containing $[Cu(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$ is treated with an excess of KCN prior to saturation with H_2S. Cu^{2+} is reduced to Cu^+ and a very stable complex $[Cu(CN)_3]^{2-}$ is produced ($K_f = 2.0 \times 10^{27}$).

$$2[Cu(NH_3)_4]^{2+}(aq) + 8CN^-(aq) \rightleftharpoons 2[Cu(CN)_3]^{2-}(aq) + (CN)_2(g) + 8NH_3(aq)$$

Consequently, concentration of Cu(I) ions in equilibrium with the complex is very low and K_{sp} of Cu_2S is not exceeded when the solution is saturated with H_2S.

Cadmium(II) ions form tetracyanocadmate(II) complex ions in the presence of cyanide ions. But the tetracyanocadmate(II) ions are much less stable ($K_f = 7.1 \times 10^{18}$)than the tricyanocuprate(I) ions, and they react with sulphide ions to form a yellow precipitate of cadmium sulphide:

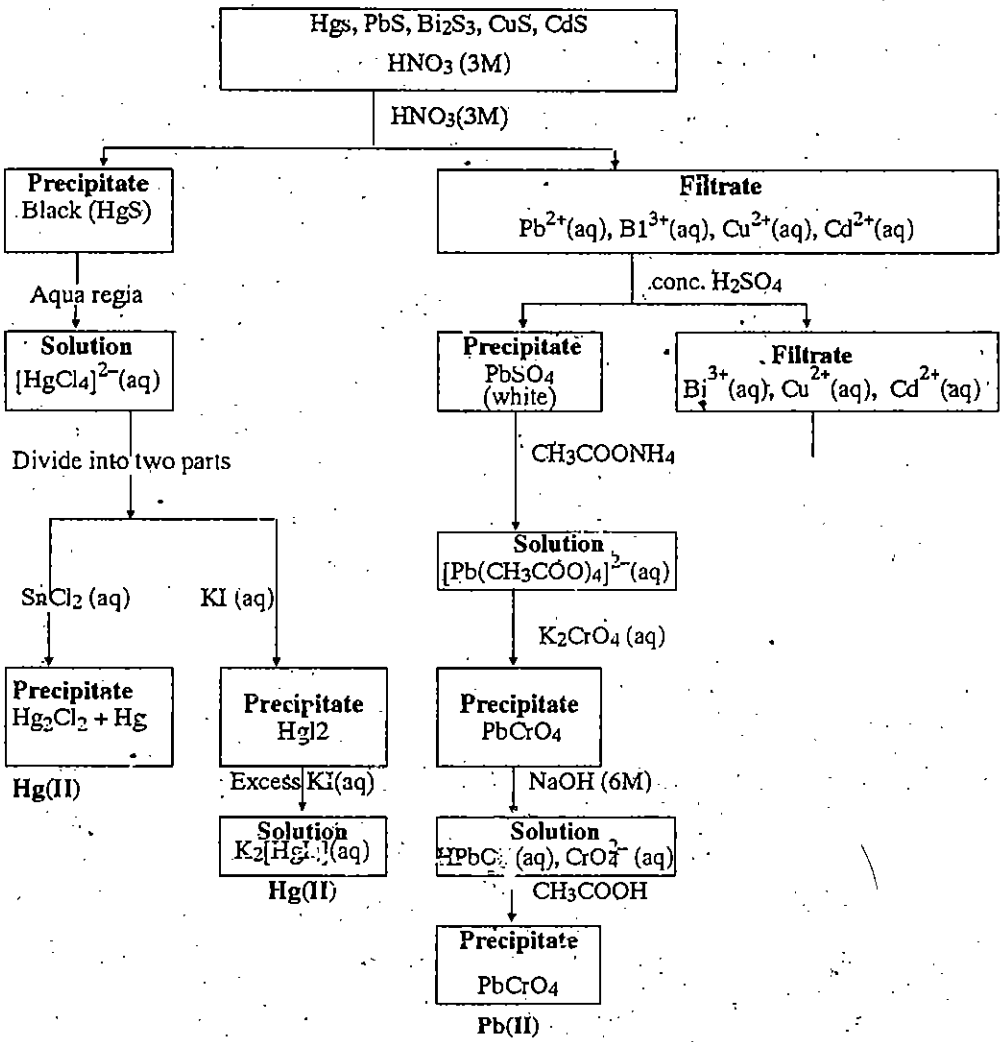
Potassium cyanide is a deadly poison. You may not have access to this chemical for performing the separation of copper and cadmium.

$$[Cd(NH_3)_4]^{2-}(aq) + 4CN^-(aq) \rightleftharpoons [Cd(CN)_4]^{2-}(aq) + 4NH_3(aq)$$

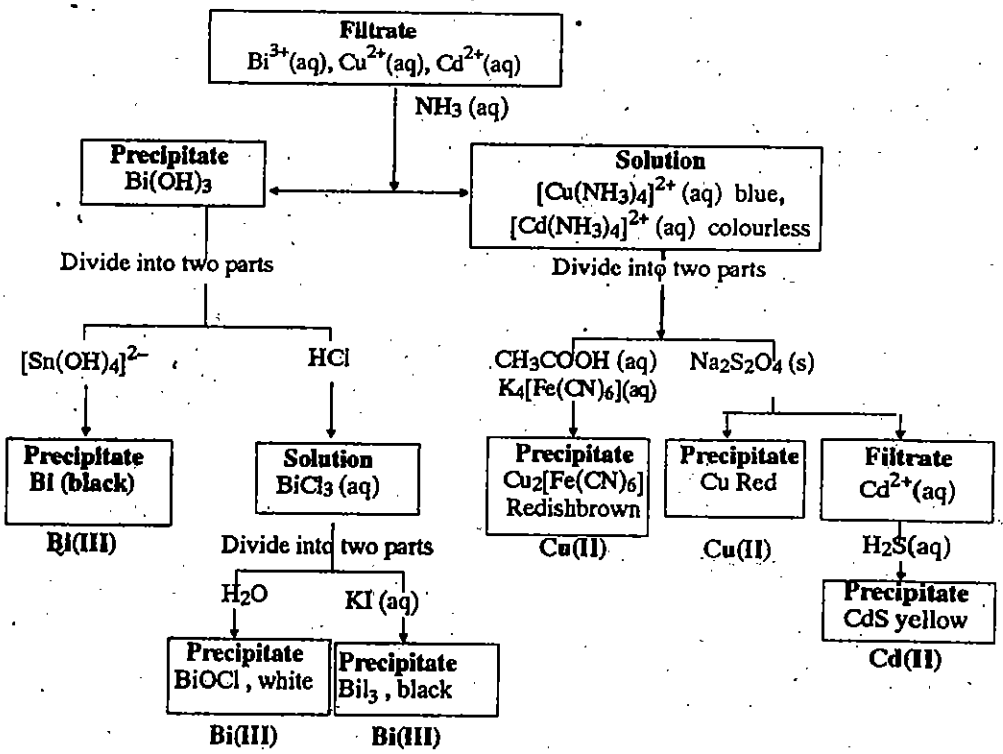
$$[Cd(CN)_4]^{2-}(aq) + S^{2-}(aq) \rightarrow CdS(s) + 4CN^-(aq)$$

The separation and identification of the cations of Group IIA is summarised in Flow Chart 6.4.

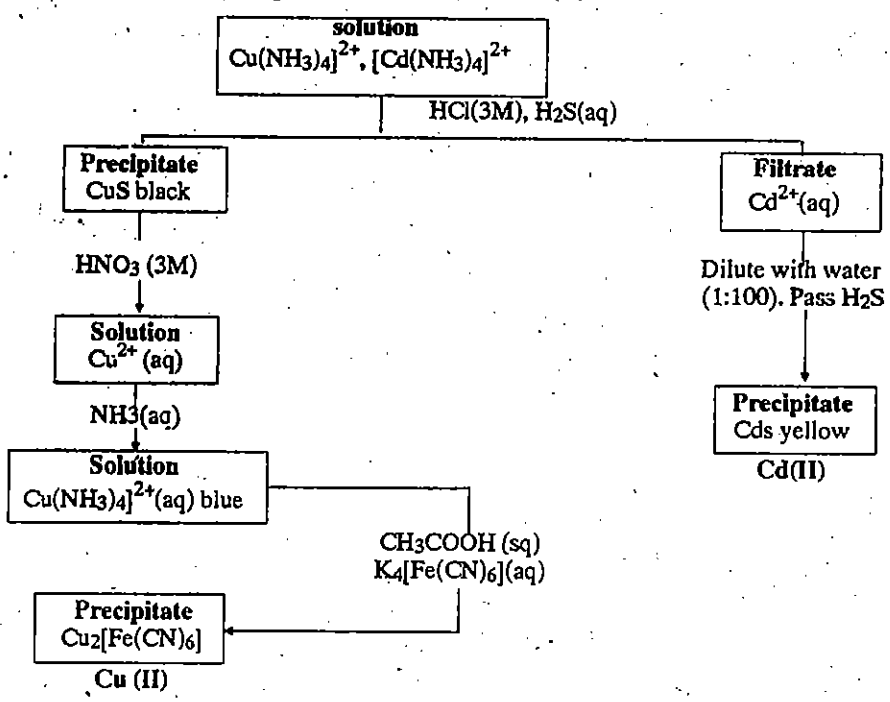
Flow Chart 6.4 : Separation and Identification of Group IIA Cations



Flow Chart 6.4 continued



Alternate Procedure for Separation of Cu(II) and Cd(II)



Identification of Arsenic(V)

Arsenate ion behaves very much like phosphate ion in its reactions. For example, when a solution of ammonium molybdate and nitric acid are added to a solution of arsenate ions, a yellow precipitate is formed:

$$AsO_4^{3-}(aq) + 12MoO_4^{2-}(aq) + 3NH_4^+(aq) + 24H^+(aq) \rightarrow (NH_4)_3[As(Mo_3O_{10})_4](s) + 12H_2O(l)$$

When magnesia mixture is added in the presence of ammonia, white insoluble magnesium ammonium arsenate precipitates :

$$AsO_4^{3-}(aq) + NH_4^+(aq) + Mg^{2+}(aq) + 6H_2O(l) \rightarrow MgNH_4AsO_4.6H_2O(s)$$

Further confirmation of arsenic(V) involves dissolution of the precipitate in acetic acid and addition of $AgNO_3$ solution in the presence of ammonia(aq) when red-brown Ag_3AsO_4 precipitates:

$$MgNH_4AsO_4.6H_2O(s) + 2CH_3COOH(aq) \rightarrow Mg^{2+}(aq) + NH_4^+(aq) + H_2AsO_4^-(aq) + 2CH_3COO^-(aq) + 6H_2O(l)$$

$$H_2AsO_4^-(aq) + 3Ag^+(aq) + 2NH_3(aq) \rightarrow Ag_3AsO_4(s) + 2NH_4^+(aq)$$

Identification of Tin(IV) and Atimony(III)

Sn(IV) and Sb(III) ions react with oxalic acid to form soluble complex compounds:

$$[SnCl_6]^{2-}(aq) + 3H_2C_2O_4(s) \rightarrow [Sn(C_2O_4)_3]^{2-}(aq) + 6Cl^-(aq) + 6H^+(aq)$$

$$[SbCl_4]^-(aq) + 3H_2C_2O_4(s) \rightarrow [Sb(C_2O_4)_3]^{3-}(aq) + 6H^+(aq) + 4Cl^-(aq)$$

For confirmation of tin(IV) in presence of antimony, add a piece of iron to the solution and heat on a water bath for 5 minutes. This reduces Sb(III) to Sb° and Sn(IV) to Sn(II). Filter the black deposit of antimony and add a few drops of $HgCl_2$ solution and wait. A white precipitate of Hg_2Cl_2 separates which turns gray on standing. If elemental iron is not available, a piece of aluminium wire may be substituted in the test.

$$2[SbCl_4]^-(aq) + 3Fe(s) \rightarrow 2Sb^\circ(s) + 3Fe^{2+}(aq) + 8Cl^-(aq)$$

$$[SnCl_6]^{2-}(aq) + Fe(s) \rightarrow [SnCl_4]^{2-}(aq) + Fe^{2+}(aq) + 2Cl^-(aq)$$

$$[SnCl_4]^{2-}(aq) + 2HgCl_2(aq) \rightarrow [SnCl_6]^{2-}(aq) + Hg_2Cl_2(s)$$

$$[SnCl_4]^{2-}(aq) + Hg_2Cl_2(s) \rightarrow [SnCl_6]^{2-}(aq) + 2Hg^\circ(l)$$

H_2S interferes with the test and must be boiled off before performing this test. High concentration of HCl should be avoided as it leads to the formation of stable $[HgCl_4]^{2-}$, which reduces the concentration of Hg^{2+} ions in solution. The separation and identification of the cations of Group IIB is summarised in Flow Chart 6. 5.

6.7 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP III

After the separation of cations of Group II, the filtrate from Group II is heated in a china dish to boil off H_2S gas. 5-6 drops of conc. HNO_3 are added and the solution again heated so as to oxidise iron(II) to iron(III), and H_2S, if any, to free sulphur:

$$3Fe^{2+}(aq) + 4H^+(aq) + NO_3^- \rightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$$

$$3H_2S(aq) + 2H^+(aq) + 2NO_3^-(aq) \rightarrow 3S(s) + 2NO(g) + 4H_2O(l)$$

The solution is buffered with $NH_4Cl - NH_4OH$ solution. The concentration of OH^- ion is controlled by adding NH_4^+ ions to the solution as a result of which only the hydroxides of Fe(III), Cr(III) and Al(III) are precipitated. The only remaining cation in the scheme that forms a precipitable hydroxide is Mg^{2+} ion. However, this hydroxide is much more soluble and would require a higher concentration of hydroxide ions than is available in the presence of NH_4^+ ions.

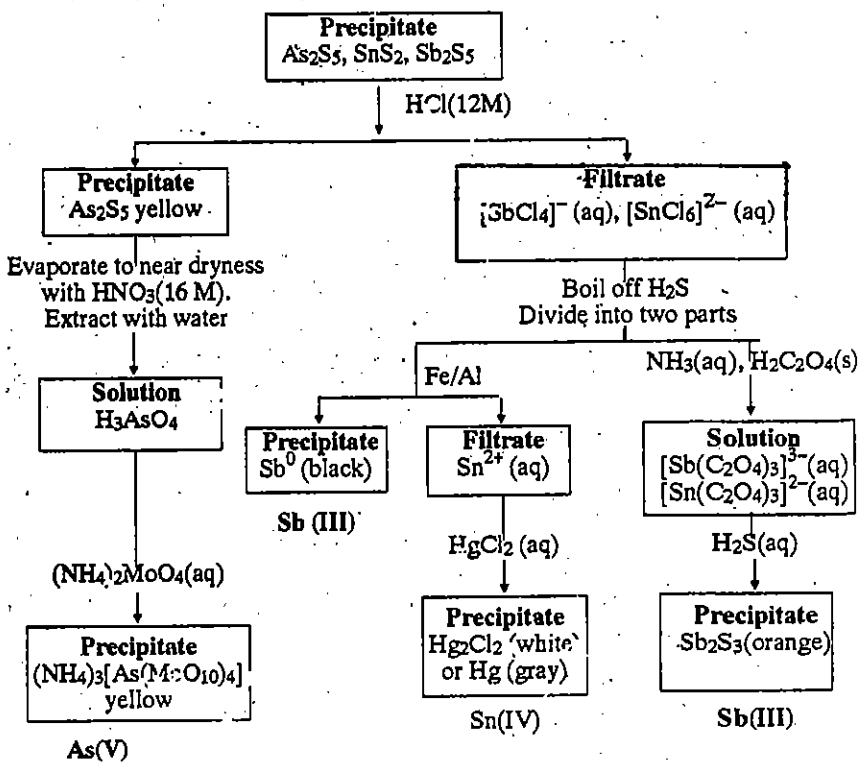
$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$

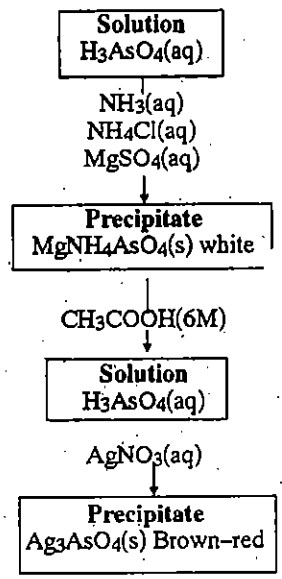
$$Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$$

$$Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$$

Flow Chart 6.5: Separation and Identification of Group IIB Cations



Identification of Arsenic(V)



Separation and Identification of the Cations of Analytical Group III

Aluminium and chromium hydroxides are amphoteric and readily dissolve in alkaline solution above pH 10.0 with the formation of $[Al(OH)_4(H_2O)_2]^-(aq)$ (colourless) and $[Cr(OH)_4(H_2O)_2]^-(aq)$ (green) complex species. Iron(III) hydroxide, however, does not dissolve in presence of excess alkali. Further the complex tetrahydroxochromate ion is easily oxidised to yellow chromate ion, $CrO_4^{2-}(aq)$ by heating with H_2O_2, which is a strong oxidising agent in alkaline solution.

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons [Al(OH)_4(H_2O)_2]^-(aq)$$

$$Cr(OH)_3(s) + OH^-(aq) \rightleftharpoons [Cr(OH)_4(H_2O)_2]^-(aq)$$

$$2[Cr(OH)_4(H_2O)_2]^-(aq) + 2OH^-(aq) + 3H_2O_2(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + 12H_2O(l)$$

Hence, separation of iron(III) from Al(III) and Cr(III) can be easily achieved.

Identification of Iron(III)

The brown coloured precipitate of $Fe(OH)_3$ is dissolved in dil. HNO_3 to give a light yellow solution containing $Fe^{3+}(aq)$. The presence of Fe^{3+} is confirmed by the formation of characteristic colour of Prussian blue, $KFe[Fe(CN)_6]$ or the blood red thiocyanatoferrate(III) iron, $[Fe(NCS)(H_2O)_5]^{2+}$:

$$Fe^{3+}(aq) + K^+(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow KFe[Fe(CN)_6](s)$$

$$[Fe(H_2O)_6]^{3+}(aq) + NCS^-(aq) \rightleftharpoons [Fe(NCS)(H_2O)_5]^{2+}(aq) + H_2O(l)$$

A large number of complexes exist in solution depending on the concentration of thiocyanate. However, these complexes dissociate on dilution with water. Therefore, a high concentration of thiocyanate should be maintained while performing this test.

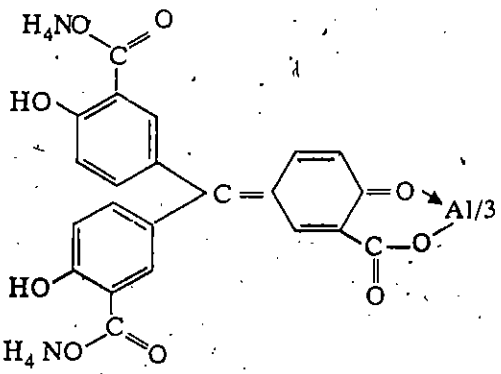
Identification of Aluminium(III)

The solution containing diaquotetrahydroxoaluminate(III), $[Al(OH)_4(H_2O)_2]^-$, on careful acidification or boiling with NH_4Cl reprecipitates aluminium hydroxide:

$$[Al(OH)_4(H_2O)_2]^-(aq) + H^+(aq) \rightarrow Al(OH)_3(s) + 3H_2O(l)$$

$$[Al(OH)_4(H_2O)_2]^-(aq) + NH_4^+(aq) \rightarrow Al(OH)_3(s) + NH_3(g) + 3H_2O(l)$$

The presence of aluminium ions in the solution can be further confirmed by addition of aluminon, the ammonium salt of aurinetricarboxylic acid, which gives an insoluble red coloured lake. Blue litmus solution can also be used in place of aluminon reagent.



In case of blue litmus solution, a blue floating lake is observed in the solution when ammonia is continuously added down the side of the test tube containing an acidified solution of aluminium(III). The dye gets adsorbed on the precipitate of gelatinous aluminium hydroxide.

$$Al^{3+}(aq) + 3NH_3(aq) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3NH_4^+(aq)$$

Identification of Chromium(III)

If the solution after oxidation is coloured yellow, it shows the presence of chromate ions, CrO_4^{2-}. This solution on acidification turns orange due to the existence of a pH dependent equilibrium :

$$2CrO_4^{2-}(aq) \underset{OH^-(aq)}{\overset{H^+(aq)}{\rightleftharpoons}} Cr_2O_7^{2-}(aq)$$

The presence of chromium is confirmed by the acidification of solution containing CrO_4^{2-} in the presence of H_2O_2, when a blue colour appears, which rapidly fades producing free oxygen. The colour can be stabilised if amyl alcohol or ether is added before adding H_2O_2:

$$Cr_2O_7^{2-}(aq) + 4H_2O_2(aq) + 2H^+(aq) \rightarrow 2CrO_5(aq) + 5H_2O(l)$$

$$4CrO_5(aq) + 12H^+(aq) \rightarrow 4Cr^{3+}(aq) + 7O_2(g) + 6H_2O(l)$$

Addition of either Pb^{2+} or Ba^{2+} to a solution of CrO_4^{2-} ions made acidic with acetic acid produces yellow precipitate of $PbCrO_4$ or $BaCrO_4$:

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons BaCrO_4(s)$$

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons PbCrO_4(s)$$

The yellow precipitate, however, dissolves in the presence of strong acid.

$$2BaCrO_4(s) + 2H^+(aq) \rightleftharpoons 2Ba^{2+}(aq) + Cr_2O_7^{2-}(aq) + H_2O(l)$$

The separation and identification of the cations of Group III is summarised in Flow Chart 6.6.

6.8 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP IV

The filtrate after separation of Group III cations contains ammine complexes of cobalt(II), nickel(II) and zinc(II) and $Mn(OH)_2$, which does not precipitate because the $[OH^-]$ is controlled by the NH_4^+ ion added as NH_4Cl.

$$Co^{2+}(aq) \xrightarrow{NH_3(aq)} Co(OH)_2(s) \xrightarrow{NH_3(excess)} [Co(NH_3)_6]^{2+} \text{ tan}$$

$$Ni^{2+}(aq) \xrightarrow{NH_3(aq)} Ni(OH)_2(s) \xrightarrow{NH_3(excess)} [Ni(NH_3)_6]^{2+} \text{ deep blue}$$

$$Zn^{2+}(aq) \xrightarrow{NH_3(aq)} Zn(OH)_2(s) \xrightarrow{NH_3(excess)} [Zn(NH_3)_4]^{2+} \text{ colourless}$$

The sulphides of this group have larger K_{sp} values than the sulphides of Group II and, therefore, would require higher concentration of S^{2-} ions for precipitation.

H_2S produces S^{2-} according to the reaction $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$. In the preceding unit, you have studied that the S^{2-} ion concentration can be controlled by controlling the H^+ ion concentration. If the $[H^+]$ decreases, then the $[S^{2-}]$ will increase as a new equilibrium will be established through an increased forward reaction. To produce the desired $[S^{2-}]$, a ammonium hydroxide controlled reaction is used to reduce $[H^+]$ by means of the strong forward reaction $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$. By decreasing the H^+ ion concentration still further, the S^{2-} concentration is increased as the reaction $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$ shifts still further to the right. The cations of this group are, therefore, precipitated from NH_4Cl–NH_4OH buffered solution as sulphides by passing H_2S:

$$[Co(NH_3)_6]^{2+}(aq) + S^{2-}(aq) \rightarrow CoS(s) + 6NH_3(aq)$$

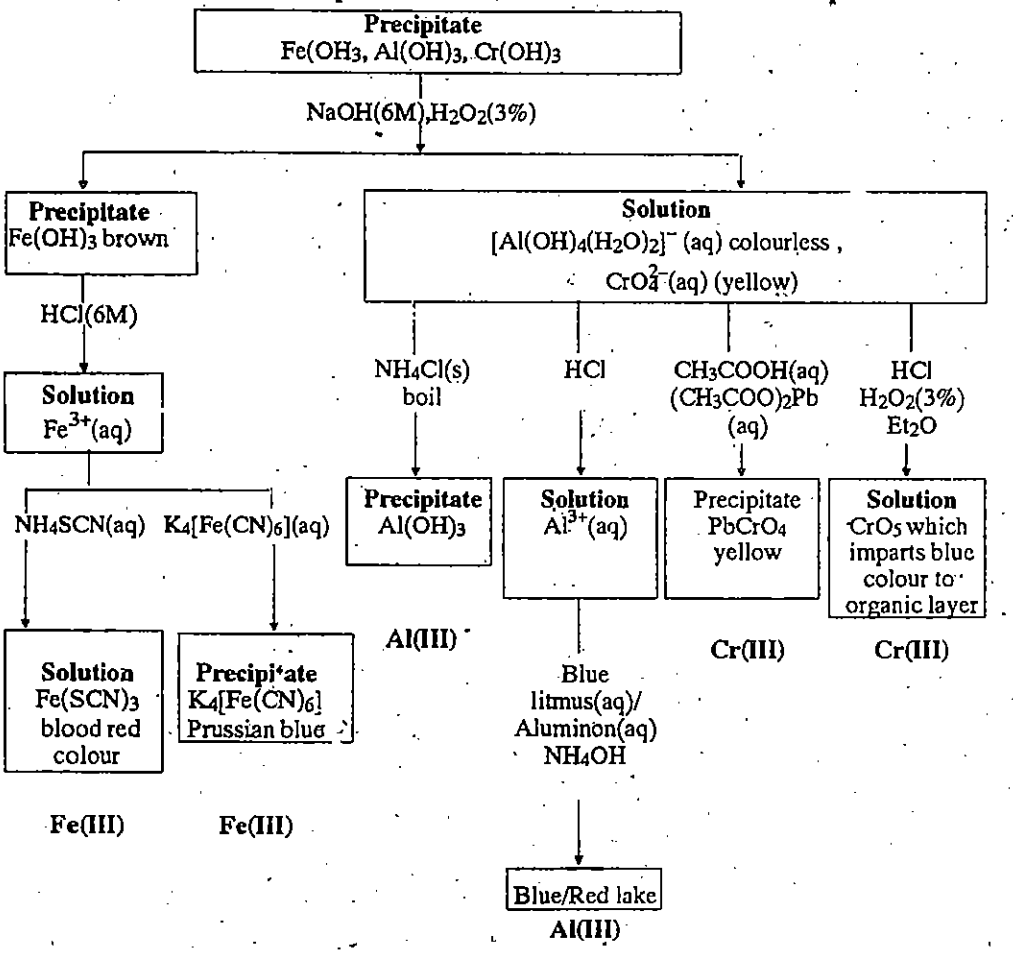
$$[Ni(NH_3)_6]^{2+}(aq) + S^{2-}(aq) \rightarrow NiS(s) + 6NH_3(aq)$$

$$Mn^{2+}(aq) + S^{2-}(aq) \rightarrow MnS(s)$$

$$[Zn(NH_3)_4]^{2+}(aq) + S^{2-}(aq) \rightarrow ZnS(s) + 4NH_3(aq)$$

Two forms of cobalt sulphide exist, α-CoS, which is readily soluble in HCl(6 M). However, the α-CoS on standing converts spontaneously to ß-CoS, which is slightly soluble in dilute HCl. Freshly precipitated NiS has a tendency to convert to colloidal form. Therefore, before filtration, it is desirable to add $NH_4Cl(s)$ and warm the solution in a water bath which not only flocculates the precipitate but also converts α-CoS to ß-CoS.

Flow Chart 6.6 : Separation and Identification of Cations of Group III



Separation and Identification of the Cations of Analytical Group IV

The cations of this group can be separated into nickel-cobalt and zinc-manganese subgroups. Zinc and manganese sulphides readily dissolve in dilute HCl, while cobalt and nickel sulphides are sparingly soluble. Therefore, the precipitate of the Group IV cations is treated with dil. HCl to separate them into two sub-groups. ZnS and MnS pass into solution, whereas CoS and NiS remain as residue which is separated by filtration.

$$MnS(s) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + H_2S(g)$$

$$ZnS(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2S(g)$$

The solution now contains Mn(II) and Zn(II). The solution is boiled to expel H_2S and Zn(II) is separated from Mn(II) by taking advantage of the amphoteric character of zinc hydroxide, which dissolves in presence of excess alkali. The solution, therefore, when boiled with NaOH converts zinc(II) to soluble

tetrahydroxozincate(II), $[Zn(OH)_4]^{2-}$, leaving a black-brown $MnO_2.xH_2O$. Oxidation of black MnO_2 by H_2O_2 in nitric acid brings Mn(II) into solution.

$$Zn^{2+}(aq) + 4OH^-(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$$

$$Mn^{2+}(aq) + 2OH^-(aq) \rightarrow Mn(OH)_2(s)$$

$$Mn(OH)_2 + H_2O_2(aq) \rightarrow MnO_2(s) + 2H_2O(l)$$

$$MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + O_2(g)$$

The residue of CoS and NiS is then dissolved in aqua regia.

$$CoS(s) + HNO_3(aq) + 3HCl(aq) \rightarrow Co^{2+}(aq) + S(s) + NOCl(g) + 2Cl^-(aq) + 2H_2O(l)$$

$$NiS(s) + HNO_3(aq) + 3HCl(aq) \rightarrow Ni^{2+}(aq) + S(s) + NOCl(g) + 2Cl^-(aq) + 2H_2O(l)$$

On longer heating the mixture becomes clear because sulphur gets oxidised to sulphate ions:

$$S(s) + 4NO_3^-(aq) \rightarrow SO_4^{2-}(aq) + 4NO_2(g)$$

Identification of Zinc(II)

The presence of zinc(II) can be confirmed either by reprecipitation of zinc sulphide or by production of a gray white precipitate of $K_2Zn_3[Fe(CN)_6]_2$ in acidic solution. Most other hexacyanoferrates are soluble in acidic solution, whereas the gray-white precipitate dissolves in basic solution.

$$Zn^{2+}(aq) + S^{2-}(aq) \rightleftharpoons ZnS(s)$$

$$3Zn^{2+}(aq) + 2K^+(aq) + 2[Fe(CN)_6]^{4-}(aq) \rightarrow K_2Zn_3[Fe(CN)_6]_2(s)$$

$$K_2Zn_3[Fe(CN)_6]_2(s) + 12OH^-(aq) \rightarrow 2K^+(aq) + 3[Zn(OH)_4]^{2-}(aq) + 2[Fe(CN)_6]^{4-}(aq)$$

Identification of Manganese(II)

When the brown precipitate of manganese(IV) oxide is dissolved in H_2O_2 containing nitric acid and the oxidation effected by a powerful oxidant like sodium bismuthate(V) or lead(IV) oxide, conversion to purple permanganate ion, MnO_4^-, takes place. This is an excellent confirmatory test for the detection of manganese(II).

$$MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + O_2(g) + 2H_2O(l)$$

$$2Mn^{2+}(aq) + 14H^+(aq) + 5NaBiO_3(s) \rightarrow 2MnO_4^-(aq) + 5Bi^{3+}(aq) + 7H_2O(l) + 5Na^+(aq)$$

Identification of Cobalt(II)

Cobalt is identified by the golden yellow colour of potassium hexanitritocobaltate(III) or by the blue colour of thiocyanato complex, $[Co(NCS)_4]^{2-}$ or by the red colour of 1-nitroso-2-naphtholate complex.

Add potassium nitrite to the solution and acidify with acetic acid when hexanitritocobaltate(II), $[Co(NO_2)_6]^{4-}$, forms which gets oxidised to hexanitritocobaltate(III) ion, $[Co(NO_2)_6]^{3-}$:

$$Co^{2+}(aq) + 6NO_2^-(aq) \rightarrow [Co(NO_2)_6]^{4-}(aq)$$

$$[Co(NO_2)_6]^{4-}(aq) + NO_2^-(aq) + 2H^+(aq) \rightarrow [Co(NO_2)_6]^{3-}(s) + NO(g) + H_2O(aq)$$

This in turn reacts with potassium ions in solution to precipitate golden yellow potassium hexanitritocobaltate(III).

$$3K^+(aq) + [Co(NO_2)_6]^{3-}(aq) \rightarrow K_3[Co(NO_2)_6](s)$$

The overall reaction can be expressed as follows:

$$Co^{2+}(aq) + 7KNO_2(s) + 2H^+(aq) \rightarrow K_3[Co(NO_2)_6](s) + NO(g) + 4K^+(aq) + H_2O(l)$$

Other tests may also be performed to confirm the presence of cobalt in the solution.

Add amyl alcohol or ether and solid ammonium thiocyanate, followed by concentrated hydrochloric acid. Deep blue colour in alcohol or ether layer confirms cobalt(II).

$$Co^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons [Co(SCN)_4]^{2-}$$

Tetrathiocyanatocobaltate(II)

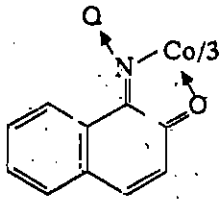
$$2H^+(aq) + [Co(SCN)_4]^{2-} \rightleftharpoons H_2[Co(SCN)_4]$$

Deep blue colour in amyl alcohol or ether

Since Fe(III) forms a blood red coloured complex, $[Fe(NCS)(H_2O)_5]^{2+}$, which would interfere with the test for cobalt. Addition of sodium fluoride prevents interference of Fe(III) due to formation of stable $[FeF_6]^{3-}$ complex ion.

$$[Fe(H_2O)_6]^{3+}(aq) + 6F^-(aq) \rightarrow [FeF_6]^{3-}(aq) + 6H_2O(l)$$

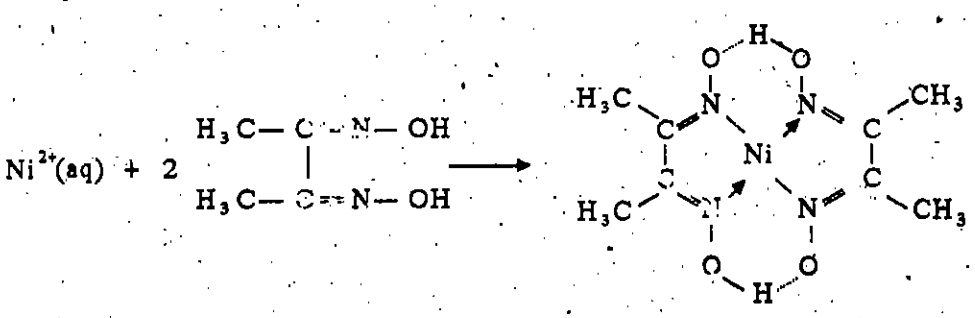
Add 1-nitroso-2-naphthol reagent. An orange red precipitate forms, which is extractable into chloroform. A number of other metal ions, like nickel(II), copper(II), iron(II) etc. also form insoluble precipitates with this reagent. Cobalt forms a complex, which is inert and is unaffected even in the presence of concentrated hydrochloric acid, other complexes dissociate and go back into aqueous phase.



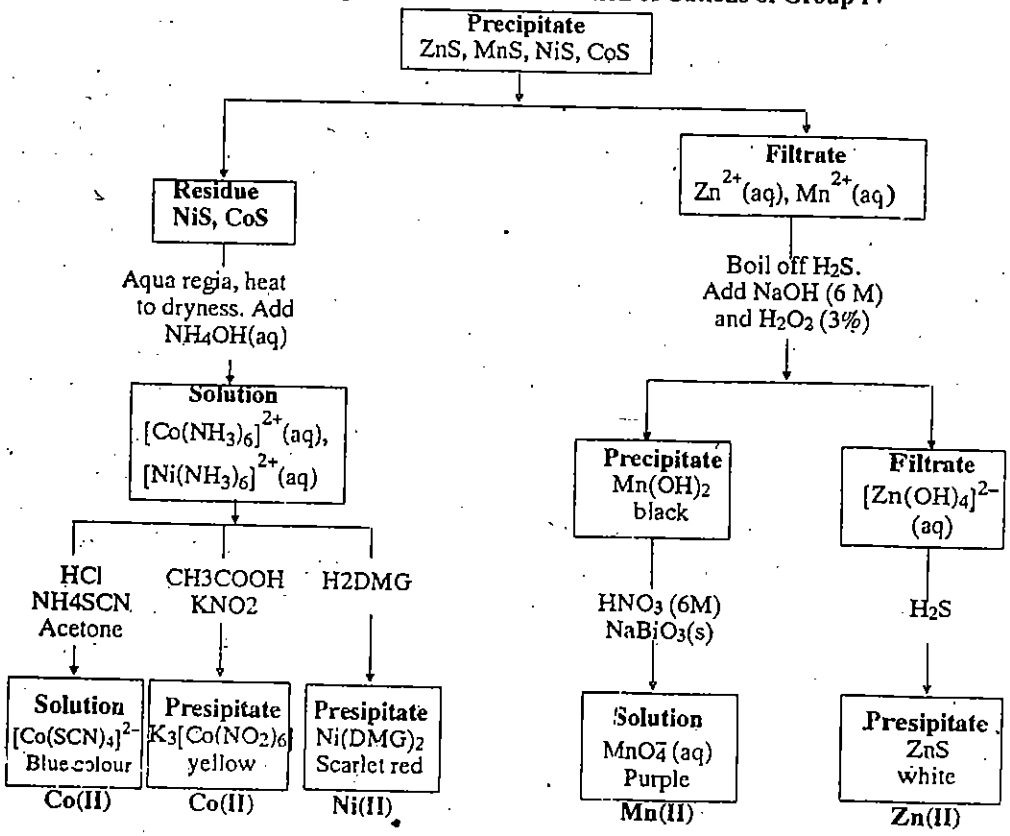
Identification of Nickel(II)

The presence of nickel in the solution is confirmed by addition of dimethyl glyoxime reagent when a scarlet red complex is formed. Cobalt(II) also complexes with the reagent but the complex does not precipitate and so cobalt does not interfere in the detection of nickel.

The separation and identification of the cations of Group IV is summarised in Flow Chart 6.7.



Flow Chart 6.7 : Separation and Identification of Cations of Group IV



6.9 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP V

The solution after separation of Group IV cations contains Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+} and K^+, besides a very high concentration of NH_4^+ salts. The solution is acidified with HCl and boiled to expel H_2S. Ammonium salts can be decomposed either by strong heating or heating with concentrated HNO_3 at elevated temperatures.

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

$$NH_4NO_3(s) \rightarrow NH_3(g) + HNO_3(g)$$

$$NH_3(g) + HNO_3(g) \rightarrow N_2O(g) + 2H_2O(l)$$

The cations of this group are precipitated as carbonates by addition of $(NH_4)_2CO_3$ from a $NH_4Cl - NH_4OH$ buffered solution.

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \rightarrow SrCO_3(s)$$

Separation and Identification of the Cations of Analytical Group V

The separation of the cations of this group is achieved by taking advantage of the analytically useful difference in the solubilities of chromates. Calcium chromate is soluble. Barium chromate can be precipitated. However, if the concentration of CrO_4^{2-} ions is high, $SrCrO_4$ can coprecipitate. The presence of acetic acid decreases the concentration of CrO_4^{2-} ions and allows only $BaCrO_4$ to precipitate leaving Sr(II) and Ca(II) in solution. Any possible coprecipitation of $SrCrO_4$ is further prevented by precipitation from hot solution.

The carbonates of this group are dissolved in acetic acid and barium chromate is precipitated by addition of K_2CrO_4.

$$BaCO_3(s) + 2H^+(aq) \rightarrow Ba^{2+}(aq) + H_2O(l) + CO_2(g)$$

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$$

$$SrCO_3(s) + 2H^+(aq) \rightarrow Sr^{2+}(aq) + H_2O(l) + CO_2(g)$$

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$$

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$$

Even though the K_{sp} values of $SrSO_4$ and $CaSO_4$ are also close to each other, only $SrSO_4$ precipitates when $(NH_4)_2SO_4$ is added to the solution. Possibly Ca(II) forms soluble sulphato complex, $[Ca(SO_4)_2]^{2-}$. So using a moderate concentration of SO_4^{2-} ions, $SrSO_4$ can be precipitated leaving Ca^{2+} in solution:

$$Sr^{2+}(aq) + SO_4^{2-}(aq) \rightarrow SrSO_4(s)$$

Identification of Barium(II)

The presence of barium in solution is confirmed by the precipitation of yellow $BaCrO_4$ on addition of potassium chromate. Strontium chromate may also precipitate if the concentration of CrO_4^{2-} ions is high enough. The presence of acetic acid decreases the concentration of CrO_4^{2-} ions so that $SrCrO_4$ does not precipitate. The pH of the solution is maintained at 7.0 by addition of ammonium acetate.

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$$

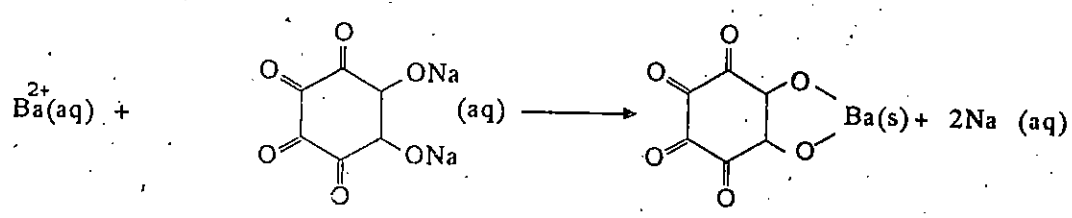
Further confirmation may be done by converting barium chromate to barium chloride by addition of hydrochloric acid and (i) performing the flame test or (ii) by precipitating white $BaSO_4$.

$$2BaCrO_4(s) + 2H^+(aq) \rightarrow 2Ba^{2+}(aq) + Cr_2O_7^{2-}(aq) + H_2O(l)$$

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Barium imparts a grassy green colour to the non-luminous flame.

Detection of barium can also be done by spotting a drop of solution containing Ba^{2+} ions on a filter paper and by adding a drop of sodium rhodizonate solution. Appearance of a red-brown spot confirms the presence of barium. The colour remains unaffected even on addition of dilute HCl.



Identification of Strontium(II)

The presence of strontium(II) ions in solution is confirmed by the addition of saturated $(NH_4)_2SO_4$ solution, when white $SrSO_4$ precipitates. Though the K_{sp} values for $SrSO_4$ and $CaSO_4$ are very close to each other, $CaSO_4$ does not precipitate, possibly due to the formation of calcate(II) ion, $[Ca(SO_4)_2]^{2-}$:

$$Sr^{2+}(aq) + SO_4^{2-}(aq) \rightarrow SrSO_4(s)$$

The precipitate of $SrSO_4$ is converted to $SrCO_3$ by transposition with sodium carbonate solution.

$$SrSO_4(s) + CO_3^{2-}(aq) + 2Na^+(aq) \rightleftharpoons SrCO_3(s) + 2Na^+(aq) + SO_4^{2-}(aq)$$

Finally perform flame test after converting $SrCO_3$ to $SrCl_2$ by addition of hydrochloric acid.

$$SrCO_3(s) + 2H^+(aq) + 2Cl^- \rightarrow Sr^{2+}(aq) + 2Cl^-(aq) + CO_2(g) + H_2O(l)$$

A red or scarlet colour is imparted to the flame. The colour is visible through single cobalt blue glass, but is not visible while seen through multilayers of blue glasses (distinction from K^+).

Further confirmation can be done using neutral solution and spotting on a filter paper and adding a drop of sodium rhodizonate when a red-brown spot is obtained. Strontium rhodizonate is, however, soluble in dilute HCl (distinction from barium) and the colour disappears on addition of dil. HCl.

Identification of Calcium(II)

The presence of calcium in solution is detected by precipitating calcium oxalate from neutral or slightly alkaline solution. The precipitate is insoluble in acetic acid medium. It, however, precipitates slowly and, therefore, the concentration of the acid should be suitably adjusted by addition of ammonium hydroxide to enhance precipitation.

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$$

Perform flame test after dissolving CaC_2O_4 in hydrochloric acid. A brick-red colour is imparted to the flame.

$$CaC_2O_4(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq) + 2H^+(aq) + C_2O_4^{2-}(aq)$$

Confirmation of Ba^{2+}, Sr^{2+} and Ca^{2+} by Flame Tests

Chlorides of barium, strontium, calcium, sodium, potassium and some other metals, when fed into a non-luminous Bunsen burner flame, impart a characteristic colour to the flame. The colour of the flame is then used to identify the metal chloride fed into the flame. This type of test is known as the flame test.

When the chlorides of above mentioned metals are fed into the flame, they are volatilised and dissociated into metal and the chlorine atoms. The burner flame is hot enough to promote electrons in metal atoms to higher energy levels. As these excited metal atoms move out of the hot region of the flame, electrons drop back to their ground state energy levels and energy is liberated. When the energy liberated is emitted as visible light, the atoms impart characteristic colours to the flame because the differences between energy levels are very specific and correspond to light of specific wavelengths in the visible region. The electronic transitions which take place during a flame test can be represented as shown in Fig. 6.1.

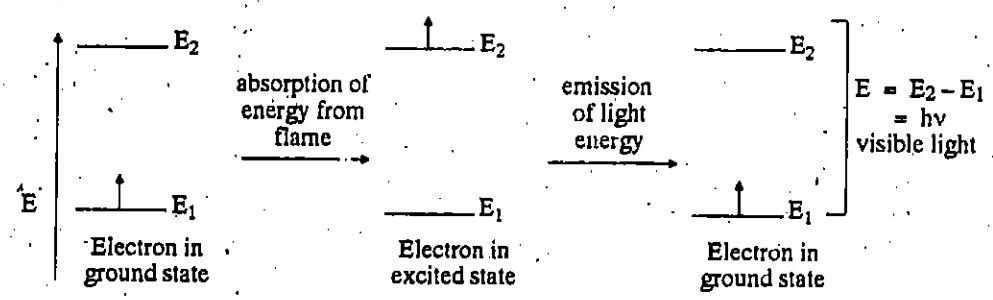


Fig. 6.1 : Electronic Transitions in a Flame Test

Flame tests are performed with a piece of platinum wire sealed into the end of a glass tubing or stuck into a small cork. Flame tests are very sensitive, therefore, the wire must be perfectly clean before a flame test is performed. The end of the wire is

bent into a small loop so that, when it is dipped into a solution, a film of liquid covers the loop. The burner flame is adjusted so that it is as hot as possible and there is a well defined blue cone with very little colour in the outer part of the flame. The wire loop is dipped in dilute HCl (6 M), brought slowly up to the outer edge of the blue cone, and held there until the loop is red hot. The hot loop is dipped in dilute HCl again and the operation is repeated until the wire imparts no colour to the flame (Fig. 6.2).

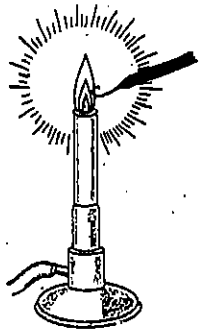


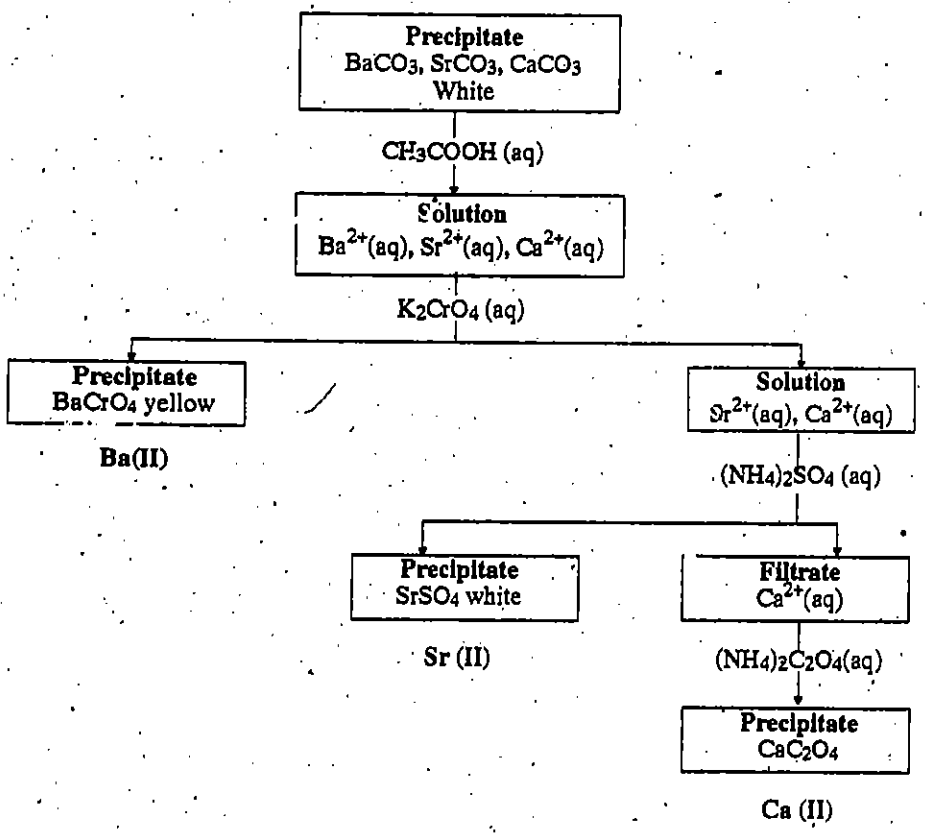
Fig. 6.2 : Performing a Flame Test

The clean wire is then dipped into the solution to be flame-tested and brought up to the outer edge of the blue cone. The cations of Group V and Group zero impart the following colours to flame:

Ba^{2+}	apple-green
Sr^{2+}	crimson-red
Ca^{2+}	brick-red
Na^{2+}	intense yellow
K^{+}	violet

The separation and identification of the cations of Group V is summarised in Flow Chart 6.8.

Flow Chart 6.8 : Separation and Identification of Cations of Group V



6.10 ANALYSIS OF THE CATION OF ANALYTICAL GROUP VI

Magnesium(II) is the only cation left in solution along with potassium and NH_4^+. It is convenient to analyse NH_4^+ and K^+ ions prior to the analysis of Group I cations. Magnesium precipitates from ammonical solution by addition of diammonium or disodium hydrogen phosphate as white magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$.

$$Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) + 6H_2O(l) \rightarrow MgNH_4PO_4.6H_2O(s)$$

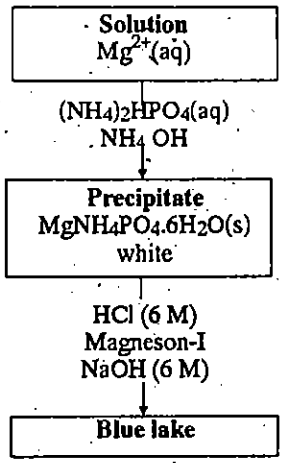
The precipitate dissolves readily in dilute HCl

$$MgNH_4PO_4.6H_2O(s) + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + H_2PO_4^-(aq) + 6H_2O(l)$$

Identification of Cation of Group VI

Treat the solution containing magnesium ions with magneson-I reagent (p-nitrobenzeneazoresorcinol) and sodium hydroxide. A blue solid lake containing the adsorbed dye on the surface of $Mg(OH)_2$ precipitate forms (the reagent is orange-red in solution). Identification of magnesium(II) is summarised in Flow Chart 6.9.

Flow Chart 6.9 : Identification of Mg(II)



6.11 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP ZERO

The cations, which are not precipitated as chlorides, hydroxides, sulphides, carbonates or phosphates comprise the members of this group, sometimes called the 'soluble group'. Sometimes the cations of this group are also referred to as 'Zero Group' cations, since it is advisable to identify these cations prior to the analysis of Group I cations. The members of this group include sodium, potassium, rubidium, caesium and ammonium etc. Here we will discuss the identification of NH_4^+ and K^+ ions only.

Solubility behaviour of NH_4^+ and K^+ salts is almost similar because of similar ionic radii (K^+ = 133pm, NH_4^+ = 143pm). For this reason removal of NH_4^+ ion before detection of K^+ ion by precipitation is essential to avoid any possible interference.

Separation of these cations is not necessary since independent tests are available for their identification. It is, therefore, advisable to perform tests directly with the original sample or its aqueous extract rather than with the solution obtained after the analysis of Group VI cations.

Identification of Ammonium ion (NH_4^+)

Heating ammonium salts with a stronger base (OH^- ion) liberates ammonia which can be detected by the following tests:

i) its characteristic odour (do not sniff the vapour directly)

ii) dense white fumes with HCl

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$

$$NH_3(aq) \rightleftharpoons NH_3(g)$$

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(g)$$

iii) the change in colour of the moist red litmus to blue when exposed to NH_3 vapour.

iv) its reaction with alkaline Nessler's reagent which turns brown.

$$4NH_3(g) + 2[HgI_4]^{2-}(aq) \xrightarrow{OH^-(aq)} Hg_2NI(s) + 7I^-(aq) + 3NH_4^+(aq)$$

v) formation of a yellow precipitate with sodium hexanitritocobaltate(III), $Na_3[Co(NO_2)_6]$.

$$2NH_4^+(aq) + Na_3[Co(NO_2)_6](aq) \rightarrow (NH_4)_2Na[Co(NO_2)_6](s) + 2Na^+(aq)$$

Diammonium sodium hexanitritocobalte(III)

In the following section, you will learn that potassium ions also give a yellow precipitate with $Na_3[Co(NO_2)_6]$.

Identification of Potassium (K^+)

Potassium is detected in aqueous solution by addition of sodium hexanitritocobaltate(III), $Na_3[Co(NO_2)_6]$, when yellow coloured dipotassium sodium hexanitritocobaltate(III), $K_2Na[Co(NO_2)_6]$, precipitates:

$$2K^+(aq) + 3Na^+(aq) + [Co(NO_2)_6]^{3-}(aq) \rightarrow K_2Na[Co(NO_2)_6](s) + 2Na^+(aq)$$

The presence of strong acid destroys the nitrite ion. Therefore, sodium nitrite(s) should invariably be added to the reagent solution before performing this test. Preferably use a freshly prepared reagent solution. Presence of oxidising agents and OH^- ions changes the composition of the reagent and renders it ineffective.

$$3NO_2^-(aq) + 2H^+(aq) \rightarrow 2NO(g) + NO_3^-(aq) + H_2O(l)$$

It is convenient to perform the flame test using the yellow precipitate since the precipitate concentrates K^+ ions. Potassium ions give a crimson-violet colour when seen through multilayers of blue cobalt glasses. No other ion interferes even if the test is performed with the mixture of salts.

Identification of Potassium(K^+) and Ammonium (NH_4^+) Ions When Present Together

The presence of NH_4^+ ions can be detected by the distinctive reaction resulting in the evolution of ammonia when heated with a strong base. [See test under identification of NH_4^+ ion.]

Since both the cations give yellow precipitates with $Na_3[Co(NO_2)_6]$, ammonium salts must be destroyed before testing for K^+ ion in the solution. A convenient method is to heat the ammonium salts with concentrated nitric acid (5-10 drops) to dryness, extracting the residue with water and testing for the absence of ammonium ions with alkaline Nessler's reagent.

$$NH_4^+(aq) + NO_3^-(aq) \xrightarrow{H^+(aq)} N_2O(g) + 2H_2O(g)$$

Once the absence of NH_4^+ ion is confirmed in solution, K^+ ions can be detected with $Na_3[Co(NO_2)_6]$. Alternatively, a flame test may be done using the mixture of salts. Further confirmation for K^+ ions may be obtained by addition of sodium tetraphenylboron reagent, $Na[B(C_6H_5)_4]$, when a white precipitate of potassium tetraphenylboron is formed:

$$K^+(aq) + Na[B(C_6H_5)_4] \rightarrow K[B(C_6H_5)_4](s) + Na^+(aq)$$

6.12 SUMMARY

In this unit you studied the scheme of qualitative analysis of the cations present in an inorganic mixture. You studied the separation of the cations into seven analytical groups by selective precipitation. Selective precipitation is performed by the addition of the group reagents in a sequential manner. You also learnt the confirmatory tests for identification of various cations. The procedure for analysis of the cations is given in Schemes 6.1 to 6.8 in the Appendix.

6.13 FURTHER READING

Vogel's Qualitative Inorganic Analysis, G. Svehla, Orient Longman, Sixth edition, 1987.

APPENDIX

Scheme 6.1 : Separation of Cations into Analytical Groups

Take original solution in a test tube. Add dilute HCl dropwise and with stirring. If a precipitate forms, allow it to settle. Add more acid and check if precipitation is complete.Filter.

Precipitate: **(Group I)** $PbCl_2$, $AgCl$, Hg_2Cl_2. Follow Scheme 6.2 for analysis of individual cations.

Filtrate:
Add 3% H_2O_2 and warm in a water bath. Add enough dilute HCl to make the solution acidic. Warm the solution and pass H_2S. Allow the precipitate to settle and filter. Dilute the filtrate with distilled water (check with only a small portion and dilute 100 times, if no precipitate forms, there is no need to pass H_2S) and pass H_2S through the warm solution until precipitation is complete. Filter.

Precipitate: **(Group II)** Sulphides of Hg(II), Pb(II), Bi(III), Cu(II), Cd(II), As(III), As(V), Sb(III), Sb(V) & Sn(IV). Follow Scheme 6.3-6.5 for analysis of individual cations.

Filtrate:
Acidify with dil. HCl and boil off H_2S. Heat to near dryness. Add 5-10 drops of concentrated HNO_3 and heat. Add 1 cm^3 distilled water and remove any sulphur that separates by filtration or centrifugation. Add NH_4Cl and make the solution basic by addition of dilute NH_4OH dropwise. Add a few drops of NH_4OH in excess. Heat in a boiling water bath for 1-2 minutes. Filter.

Precipitate: **(Group III)** $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$. Follow Scheme 6.6 for analysis of individual cations.

Filtrate:
Add 1 cm^3 of dilute NH_4OH and pass H_2S. Warm on a water bath and allow to stand for 2-3 minutes. Filter.

Precipitate: **(Group IV)** CoS, NiS, ZnS, MnS. Follow Scheme 6.7 for analysis of individual cations.

Filtrate:
Acidify with dilute HCl and boil off H_2S. Add 5-10 drops of concentrated HNO_3 and heat to dryness. Cool and add 1 cm^3 distilled water. Add NH_4Cl and ammonia (6M) till the solution is basic. Add $(NH_4)_2CO_3$, stir well and filter.

Precipitate: **(Group V)** $BaCO_3$, $SrCO_3$, $CaCO_3$. Follow Scheme 6.8 for analysis of individual cations.

Filtrate:
Mg^{2+}, K^+, NH_4^+. Refer to Sections 6.9 and 6.10 for analysis of these cations.

Scheme 6.2 : Separation and Identification of Group I Cations

To the solution of the cations add dropwise and with stirring dilute HCl (0.2 M) till no more precipitate is formed. The precipitate may contain $PbCl_2$, AgCl, Hg_2Cl_2. Stir well and filter. Add a drop of HCl to check for complete precipitation. Wash the precipitate with cold water containing a few drops of HCl and discard the washings. Add boiling water to the precipitate, heat in a boiling water bath for 5 minutes with periodic stirring. Filter while hot.

Precipitate: White ($AgCl$, Hg_2Cl_2). Thoroughly wash with hot water. Treat with ammonia (aq). Stir well and filter.		**Filtrate:** Colourless. Contains Pb^{2+} ions. Lead chloride precipitates on cooling. Divide into three parts and perform confirmatory tests while hot. i) Add K_2CrO_4 solution–a yellow precipitate of $PbCrO_4$ soluble in NaOH solution. On acidification with acetic acid $PbCrO_4$ precipitates ii) Add KI solution–a yellow precipitate of PbI2. The precipitate dissolves on boiling. On cooling deposits golden shining spangles. iii) Add dilute H_2SO_4– a white precipitate of $PbSO_4$. **Pb(II) confirmed**
Precipitate: Black ($Hg + HgNH_2Cl$) **Hg(I) confirmed**	**Filtrate:** Colourless. Contains $[Ag(NH_3)_2]^+Cl^-$. Divide into two parts. i) Acidify with dilute HNO_3 till acidic to litmus paper–a white precipitate of AgCl. ii) Add K_2CrO_4 solution – a brick red precipitate of Ag_2CrO_4. **Ag(I) confirmed**	

Scheme 6.3 : Precipitation and Separation of the Cations of Group II into Group IIA and Group IIB

The filtrate from Group I may contain cations belonging to Group II to VI. Acidify with dil. HCl (0.3 M). Add 1 cm^3 3% H_2O_2 and saturate with H_2S. Dilute the filtrate and pass H_2S again to ensure complete precipitation of Group II cations. Heat in a boiling water bath for 5 minutes to coagulate the sulphides. Filter. The precipitate may consist of HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_5, Sb_2S_3, Sb_2S_5, SnS_2. Wash the precipitate with water. Treat the washed precipitate with minimum volume of yellow ammonium sulphide. Heat in a boiling water bath for 2-3 minutes and filter.

Precipitate:	**Filtrate:**
May contain HgS, PbS, Bi_2S_3, CuS, CdS. Group IIA present. Follow Scheme 6.4.	May contain thioanions, AsS_4^{3-}, SbS_4^{3-}, SnS_3^{2-}. Add dilute HCl till just acidic and warm gently. A yellow or orange precipitate, which may contain As_2S_5, Sb_2S_3, , Sb_2S_5 and SnS_2, indicates the presence of Group IIB. Follow Scheme 6.5 .

The precipitate may contain HgS, PbS, Bi_2S_3, CuS, CdS. Wash the precipitate with water. Treat the precipitate with minimum amount of dilute HNO_3(3M) and heat in a water bath for 4-5 minutes. Filter.

Precipitate:
Black (HgS). Dissolve in aqua regia and evaporate to near dryness. Add 1 cm^3 of conc. HCl and heat again. Dilute and divide into three parts.

i) Add a few drops of $SnCl_2$ - white precipitate turning gray.

ii) Add KI solution - an orange precipitate of HgI_2 soluble in excess of KI.

iii) Add copper wire - a silvery white deposit of mercury on the wire.

Hg(II) confirmed

Filtrate
May contain nitrates of Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}. Add a few drops of conc. H_2SO_4 and evaporate until a dense white cloud of SO_3 is produced showing that HNO_3 has decomposed. Cool and dilute with water. Filter.

Precipitate:
White ($PbSO_4$). Dissolve the precipitate in hot ammonium acetate containing aceatic acid and divide into two parts.

i) Add K_2CrO_4 - a yellow precipitate of $PbCrO_4$.

ii) Add KI – a yellow precipitate of PbI_2, soluble in hot water. Golden spangles on cooling.

Pb(II) confirmed

Filtrate:
May contain Bi^{3+}, Cu^{2+}, Cd^{2+}. Add NH_4OH dropwise till in slight excess. Filter.

Precipitate:
White ($Bi(OH)_3$). Divide the precipitate into three parts.

i) Add freshly prepared sodium stannite solution - a black deposit of Bi.

ii) Dissolve the precipitate in dilute HCl and drop into water– a white precipitate of BiOCl.

iii) Dissolve the precipitate in acetic acid and add KI solution– a black precipitate of BiI_3 dissolves in excess of KI producing orange colour.

Bi(III) confirmed

Filtrate:
Blue($[Cu(NH_3)_4]^{2+}$), colourless ($[Cd(NH_3)_4]^{2+}$.) Divide into three parts.

i) Add acetic acid and $K_4[Fe(CN)_6]$ solution - a reddish brown precipitate of $Cu_2[Fe(CN)_6]$.
Cu(II) present.

ii) Add $Na_2S_2O_4$(s). Heat in a water bath for 1-2 minutes till all the blue colour of copper is gone. Observe and filter.
(a) brown red precipitate. Cu(II) present.
(b) pass H_2S through the filtrate - a yellow precipitate. **Cd(II) present.**

iii) Acidify with dilute HCl and pass H_2S. Filter.

Pricipitate:
Black(CuS)

Cu(II) confirmed

Filtrate:
May contain Cd(II). Dilute and pass H_2S- a yellow preciptate.

Cd(II) confirmed

Scheme 6.5 : Separation and Identification of Group IIB Cations

The precipitate may contain As_2S_5, Sb_2S_3, Sb_2S_5 and SnS_2. Wash with hot water, boil with concentrated HCl and filter.

Precipitate:	**Filtrate:**
Yellow, may contain As_2S_5. Wash with hot water. Dissolve in minimum amount (5 drops) of concentrated HNO_3 by warming. Dilute and divide the solution into two parts.	Colourless, may contain $[SbCl_4]^-$ and $[SnCl_6]^{2-}$. Divide into two parts.
i) Add ammonia (aq) to neutralise H_3AsO_4. Add magnesia mixture–a white precipitate of $MgNH_4AsO_4$. Dissolve the precipitate in acetic acid and add $AgNO_3$ solution–a brown red precipitate of Ag_3AsO_4.	i) Add NH_4OH, oxalic acid and pass H_2S– an orange precipitate **confirms Sb(III).**
ii) Add ammonium molybdate solution and warm–a yellow precipitate of $(NH_4)_3AsO_4.12MoO_3$. **As(V) confirmed**	ii) Add Fe/Al wire. Filter and add a few drops of $HgCl_2$–a white precipitate turning gray **confirms Sn(IV).**

Scheme 6.6 : Analysis of Group III Cations

The precipitate may contain $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$. Wash it well with a little ammonia solution (6 M). Treat the precipitate with 3 cm^3 NaOH solution and 1cm^3 3% H_2O_2. Stir well and allow the reaction to proceed till evolution of O_2 ceases. Boil for 2 minutes in a water bath. Extract the residue with a little distilled water and filter.

Precipitate :	**Filtrate:**
May contain $Fe(OH)_3$ (brown). Dissolve in 0.5-1.0 cm^3 dilute HNO_3. Warm in a water bath and divide the solution into two parts.	May contain $[Al(OH)_4(H_2O)_2]^-$ (colourless) and CrO_4^{2-} (yellow). The solution, if yellow indicates the presence of Cr(III). Divide the solution into four parts and perform tests for Al(III) and Cr(III).
i) To first part, add 2-3 drops of KSCN solution– a blood red colour.	**Tests for Al (III)**
ii) To second part, add one drop of $K_4[Fe(CN)_6]$ solution - a Prussian blue precipitate.	i) Add NH_4Cl (s) and boil– a gelatinous white precipitate of $Al(OH)_3$ reappears.
Fe(III) confirmed:	ii) Acidify with dilute HCl. Add aluminon reagent (or blue litmus solution). Add dilute NH_4OH (6M) from the side of the test tube–a red/(blue) floating lake due to adsorption of dye on $Al(OH)_3$.
	Al (III) confirmed

Tests for Cr (III)

i) Acidify with acetic acid and add $BaCl_2$/ $Pb(CH_3COO)_2$ solution–a yellow precipitate of $BaCrO_4$/$PbCrO_4$.

ii) Acidify with HCl, add amyl alcohol (or ether) and 1-2 cm^3 H_2O_2 (3%) and shake–blue colour in non-aqueous layer.

Cr (III) confirmed

Scheme 6.7 : Analysis of Group IV Cations

The precipitate may contain CoS, NiS, ZnS, MnS. Wash the precipitate with H_2S water containing 1% NH_4Cl. Treat the precipitate with dilute HCl. Stir for a minute and filter.

Precipitate:
May contain NiS, CoS. Dissolve the precipitate in aqua regia, followed by heating to near dryness. Extract with 2 cm^3 water and make basic by addition of dilute NH_4OH solution (6 M). Divide the solution into four parts and perform tests for Co(II) and Ni(II).

Filtrate:
May contain $MnCl_2$and $ZnCl_2$. Boil to expel H_2S. Add 1 cm^3 H_2O_2 (3%), 1 cm^3 NaOH solution and warm in a water bath for 2 minutes. Dilute with distilled water and filter.

Test for Cobalt(II)

i) Add acetic acid and KNO_2(s). Wait for 1-2 minutes– a golden yellow precipitate.

ii) Acidify with concentrated HCl (if HCl is added in great excess, the solution may turn blue due to the formation of $[CoCl_4]^{2-}$) till just acidic. Add 0.5 g NaF(s). Stir and add NH_4SCN (s) and amyl alcohol. Shake. Blue-green colour in amyl alcohol layer.

iii) Add 1-nitroso-2-naphthol reagent solution–an orange red precipitate extractable in $CCl_4/CHCl_3$, unaffected by addition of HCl (12M).

Co(II) confirmed

Test for Nickel (II)

iv) Add 1% alcoholic solution of dimethyl glyoxime-scarlet red precipitate.

Ni(II) confirmed

Precipitate:

$MnO_2.xH_2O$ (brown). Dissolve the precipitate in dilute nitric acid and add 1 cm^3 H_2O_2 (3%). Warm in a water bath for 2 minutes. Cool and add $NaBiO_3$(s) or PbO_2(s). Stir and allow the solid to settle–purple/pink colour in aqueous layer.

Mn(II) confirmed

Filtrate:

$[Zn(OH)_4]^{2-}$ (colouress). Divide into two parts.

i) Pass H_2S through the solution–a dirty white precipitate.

ii) Acidify with acetic acid and add $K_4[Fe(CN)_6]$ solution–a grayish white precipitate soluble in NaOH solution.

Zn(II) confirmed

Scheme 6.8 : Analysis of Group V Cations

The precipitate may contain $BaCO_3$, $SrCO_3$, $CaCO_3$. Dissolve it in minimum volume (1 cm^3) of dilute acetic acid. Add K_2CrO_4 solution and 0.5 to 1 cm^3 ammonium acetate. (Excess K_2CrO_4 will cause $SrCrO_4$ to precipitate.) Stir and filter.

<table>
<tr><td>Precipitate :
$BaCrO_4$ (yellow). Dissolve in 0.5 cm^3 of concentrated HCl.

i) Perform flame test–green or yellow green flame.

ii)Dilute with water and place one drop on a strip of Whatman filter paper No. 1 and add sodium rhodizonate reagent–red to brown spot.

Ba(II) confirmed</td><td colspan="2">Filtrate:
Sr^{2+}(aq), Ca^{2+}(aq), CrO_4^{2-}(aq). Concentrate the solution to 1 cm^3 and add saturated solution of $(NH_4)_2SO_4$. Heat in a boiling water bath with stirring. Cool and filter.

Precipitate :
$SrSO_4$ (white). Wash the precipitate with water containing $(NH_4)_2SO_4$.

Dissolve it in 0.5 cm^3 of concentrated HCl.

i) Perform flame test–crimson red colour.

ii) Dilute with water and add NH_4OH. Boil to expel NH_3. Place a drop of neutral solution on a strip of filter paper. Add sodium rhodizonate reagent–red brown spot, disappears on addition of dilute HCl.

Sr(II) confirmed</td><td>Filtrate
Ca^{2+}(aq): Make basic with NH_4OH and add $(NH_4)_2C_2O_4$ solution. Stir vigorously for 1 minute–a white precipitate of CaC_2O_4.
Dissolve it in 0.5 cm^3 HCl (12 M) and perform flame test–brick red colour is imparted to the flame.

Ca(II) confirmed</td></tr>
</table>