Indira Gandhi National
Open University
School of Sciences

BCHCL-132
CHEMISTRY LAB-I: ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS

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CHEMISTRY LAB I: ATOMIC STRUCTURE, BONDING, GENERAL ORGANIC CHEMISTRY AND ALIPHATIC HYDROCARBONS

Welcome to the first laboratory course in chemistry. This manual gives the procedural details of various experiments you are required to perform in the course of this lab work. 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 is known as analytical experiments. These deal with analysing various materials to find the nature and the amount of components constituting them. The other type of experiments deals with the synthesis of substances.

Broadly, analytical experiments are further 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 this course we begin by explaining the basic concepts involved in titrimetric analysis under the quantitative type. In Unit 1 you would be introduced first to the basic skills, such as, how to weigh a sample, measure volumes and prepare a solution for titrimetric analysis. Perhaps you might have learnt these skills in your previous classes. This unit is an important review and extension. You will also learn the handling of lab reagents and safety measures to be observed while working in the laboratory. After the unit there are a number of quantitative experiments given with procedural details. The 1st experiment is based on a neutralisation type of titration. Experiment 2, 3 and 4 are based on redox titrations and the 5th experiment is based on iodometry.

Under the qualitative type of analysis you will detect extra elements in organic compounds in Experiment 6. Experiment 7 and 8 deal with a separation technique called paper chromatography where you will separate and identify components in a given mixture of amino acids and a mixture of sugars.

Expected Learning Outcomes

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

- explain the basic concepts involved in titrimetric analysis,
- explain the principles of acid-base, redox and iodometric titrations,
- work out the stoichiometric relations based on the reactions involved in the above,
- take observations and calculate results after performing the experiments,

- carry out the physical examination of organic compounds,
- determine the elements (N, S, X) present in the given organic compound, and
- separate and identify the mixture of compounds by paper chromatography.

Study Guide

In this lab course, you would be doing eight experiments that involve the qualitative as well as the quantitative analytical techniques.

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.

The section/sub-section, '**Requirements'** gives you an idea of the apparatus and chemicals you would need 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 section/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 the last section/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 the preparation of standard solution, (c) in taking the burette readings, 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. 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 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. Purchase a 30-40 page chemistry notebook for this laboratory course.

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 note book.

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.

IMPORTANT

- **Attendance** is compulsory in the Laboratory Course work held generally at the Study Centre.
- The Laboratory Course is worth **2 credits** to be completed over **7 days** duration:
  - **6 days** of **Guided** Laboratory work
  - **1 day** for the **Unguided** Laboratory work
- To successfully complete the laboratory course you will have to pass (at least **35% marks**) in the Guided and Unguided components separately.

UNIT 1

TITRIMETRY: AN INTRODUCTION

Structure

1.1 INTRODUCTION

In the very first laboratory course of the first semester, there are five experiments based on the titrimetric analysis besides the elemental analysis of organic compounds and experiments based on chromatography. The introductory unit of the laboratory course has been designed to familiarise you with the apparatus which will be used in performing the titrimetric experiments and some of the basic concepts on which the experiments are based.

You might have studied in your previous classes that in titrimetry we estimate a substance in solution by titrating it against the standard solution of an appropriate substance. The whole process involves the use of specific apparatus that you need to be thoroughly familiar with. Therefore, first of all we 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. The weighing of chemicals being a part and parcel of these experiments, the correct use of analytical balance has been dealt in detail. Finally, we introduce you to the common safety measures one should observe in a Chemistry laboratory.

Expected Learning Outcomes

After studying this unit, you should be able to:

- measure and deliver sample volumes by selecting and using appropriate apparatus 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;
- list and explain different types of titrations; and
- explain the safety measures as applied to a chemistry laboratory.

1.2 APPARATUS COMMONLY USED

Titrimetric analysis involves reliable and accurate measurement 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

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

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

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.

CAUTION!

Do not suck corrosive liquids like strong acids and alkalies by mouth. You can use a rubber teat for this purpose.

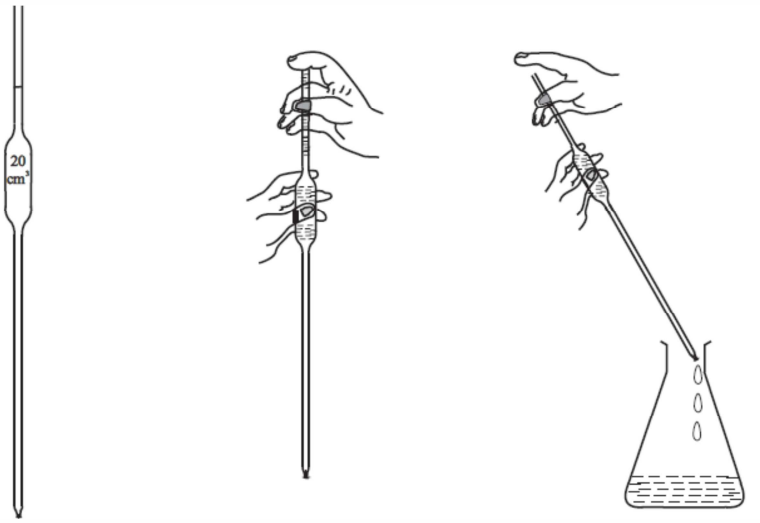


Fig. 1.1: (a) Pipette. (b) Handling of a pipette. (c) Correct way to drain out the solution.

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 pipette is calibrated to include the liquid column trapped at the tip. Further, blowing makes it dirty and CO_2 in the breath may react with the solution being pipetted. The volume of the liquid thus transferred through the pipette is equal to the volume marked on the pipette.

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.

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 marking 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.

Fig. 1.2: Graduated Pipette.

SAQ 1

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

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 with 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.

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.

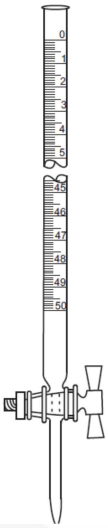


Fig. 1.3: Burette.

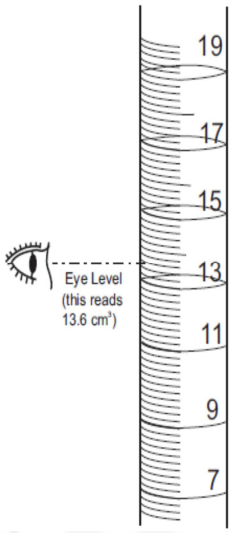


Fig. 1.4: Eye level for burette reading.

Fig. 1.5: Reading the burette with the use of the parallax card.

PRECAUTION!

No standard apparatus is to be heated above 298 K.

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.

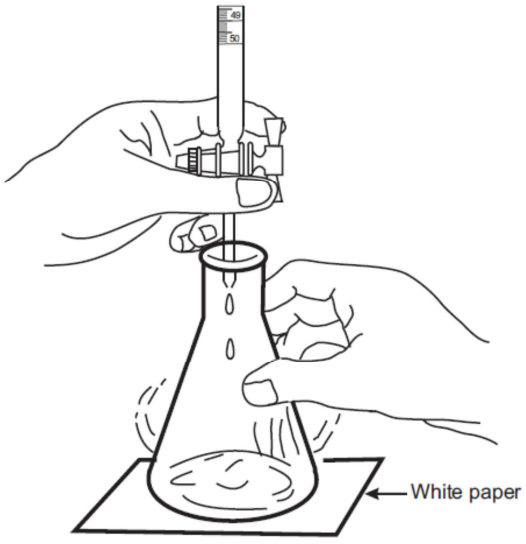


Fig. 1.6: Delivery of liquid from a burette.

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.

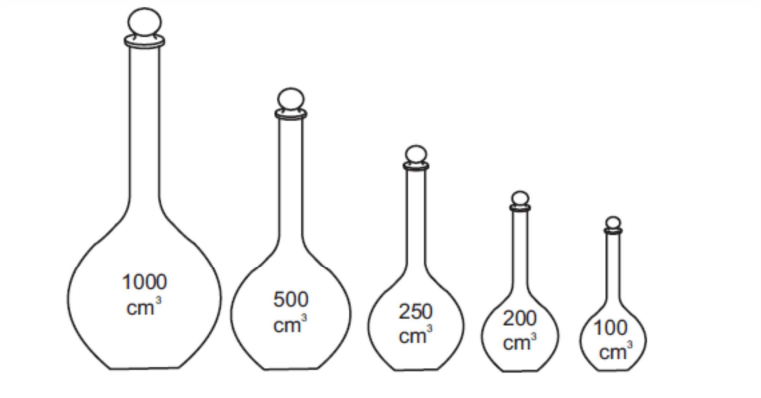


Fig. 1.7: Volumetric Flasks.

You will be using volumetric flasks of 100 cm^3 and 250 cm^3 capacity. The flask, before use, is cleaned thoroughly, washed with a detergent and plenty of 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.

Generally two types of analytical balances are used in chemical laboratories. These are:

(i) Double pan analytical balance

(ii) Single pan electronic analytical balance

Double pan analytical balance is now outdated but still some of our laboratories do not have electronic analytical balance and may have only double pan balance. A commonly used double pan analytical balance is shown in Fig. 1.8. The various parts of the balance are labeled 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.

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.

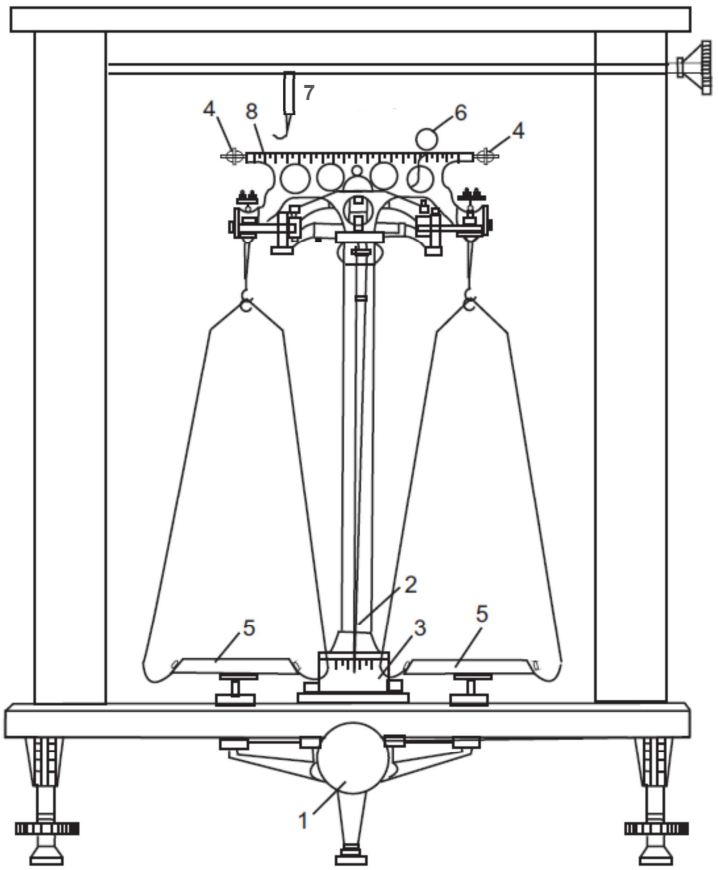


Fig 1.8: Analytical balance.

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 and the mid or zero of the scale should be the same.

	Reading on the left		**Reading on the Right**	
1. 2. 3. 4.	– 5.0 – 4.0 – 3.0 – 2.0		+ 5.0 + 4.0 + 3.0	
	– 14.0		+ 12	

$$\text{Average} = \frac{-14.0}{4} = -3.5 \qquad \frac{12.0}{3} = 4.0$$

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

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.

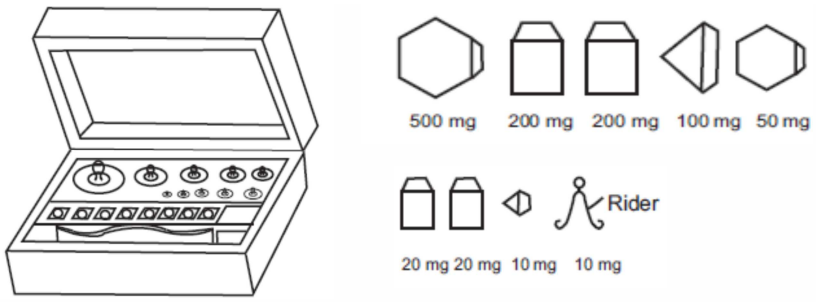


Fig. 1.10: Weight box and weights.

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

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.

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

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 3 on the subdivisions after 2 main divisions.

Then the mass of the object

= 15.00 g + (240 × 0.001) g + (2 × 0.001) g + (3 × 0.0002) g = 15.2426 g

Mass of the substance (m g) = Mass of the bottle with substance (m_1 g) – Mass of the bottle after transferring the substance (m_2 g)
$m = m_1 - m_2$ g

You have, so far, seen how to weigh an object accurately. If we want to weigh 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).

1.2.5 Single-Pan Electronic Analytical Balance

In case of electronic balance also known as **digital balance**, the mass of the object being weighed will be digitally displayed. In electronic balances (Fig.1.11), substance can be added to or removed from the balance without any problem.

Handling of Electronic Balance

Balances of all types should never be subjected to harsh treatment of any description. Always make adjustments smoothly and carefully. You will need to ensure that the balance reads zero before you start to weigh. However, if you are using a balance with a tare facility, it is not necessary to zero the balance.

Fig.1.11: Single-pan electronic analytical balance.

The tare facility allows you to cancel out the mass of the container so that you can weigh the required mass of material without having to take into account the mass of the container. Even if you cannot tare out the complete mass of the container, the tare facility can still be used to adjust the mass indicated by the scale to a convenient whole number.

For example, suppose you are using a balance that can only tare out 10 g, but your container weighs 22.45 g and you require to weigh 8.70 g of material. In such a case instead of

(1) weighing the container,

(2) adding its mass to the required mass of material, and

(3) adding material to the container until the balance reads the calculated mass,

you can use the tare facility to adjust the displayed mass of the container to read 20.00 g and then add material to the container until the balance reads 28.70 g. This avoids errors in weighing that arise due to miscalculations! Of course, when you have finished weighing, you should remove any tare and adjust the balance to read zero.

An important point to note here is that you should always use a container for weighing any material. Even a piece of filter paper is not very satisfactory as solid chemicals can easily spill onto the balance pan. As already mentioned small glass or plastic weighing bottles are available and these are most useful. For very accurate weighing, e.g. in the preparation of a standard solution it may be necessary to use a weighing bottle.

Never weigh anything (apart from the container) directly on the balance pan.

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

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 liquid 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:

Relative molecular mass being relative is unitless.

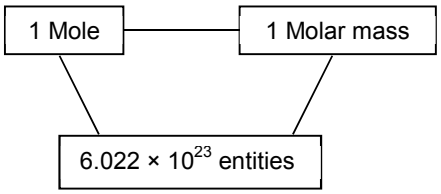
$$[12 + (16 \times 2)] = (12 + 32) = 44$$

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 dehydrate 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,

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

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

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

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

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.**

1 ml = 1.000028 cm^3

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,

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

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:

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

m_1 = mass of the solute

m_2 = mass of 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, the mole fraction can be given as follows:

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

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

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

Here *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:

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

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

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

ppm = mg dm^{-3}

= μ g cm^{-3}

= 10^{-3} g dm^{-3}

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}).

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}).

1.4 STANDARD SOLUTION

The concentration terms being clear to you, you must know about a standard solution which is a significant part of all the titrimetric experiments.

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:

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

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.

Few available primary standards for acid-base, redox and complexometric titrations are given in Table 1.1.

Table 1.1: List of primary standards used in acid-base, redox and complexometric titration

Name of the primary standard	Formula	Molecular mass	Type of titration
Potassium hydrogen phthalate	(KHP) $C_8H_5O_4K$	204.23	Acid-base
Anhydrous sodium carbonate	Na_2CO_3	106	Acid-base
Potassium dichromate	$K_2Cr_2O_7$	294.19	Redox
Arsenic (III) oxide	As_2O_3	197.85	Redox
Potassium iodate	KIO_3	214.00	Redox
Sodium oxalate	$Na_2C_2O_4$	134.00	Redox
Sodium Salt of EDTA	$C_{10}H_{16}N_2O_8$	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

According to the criteria given in the text, on what criteria do (a) sodium hydroxide and (b) benzoic acid fail as primary standards?

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**. The steps in a titrimetric estimation are depicted in Fig. 1.12.

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

We have stated 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 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.

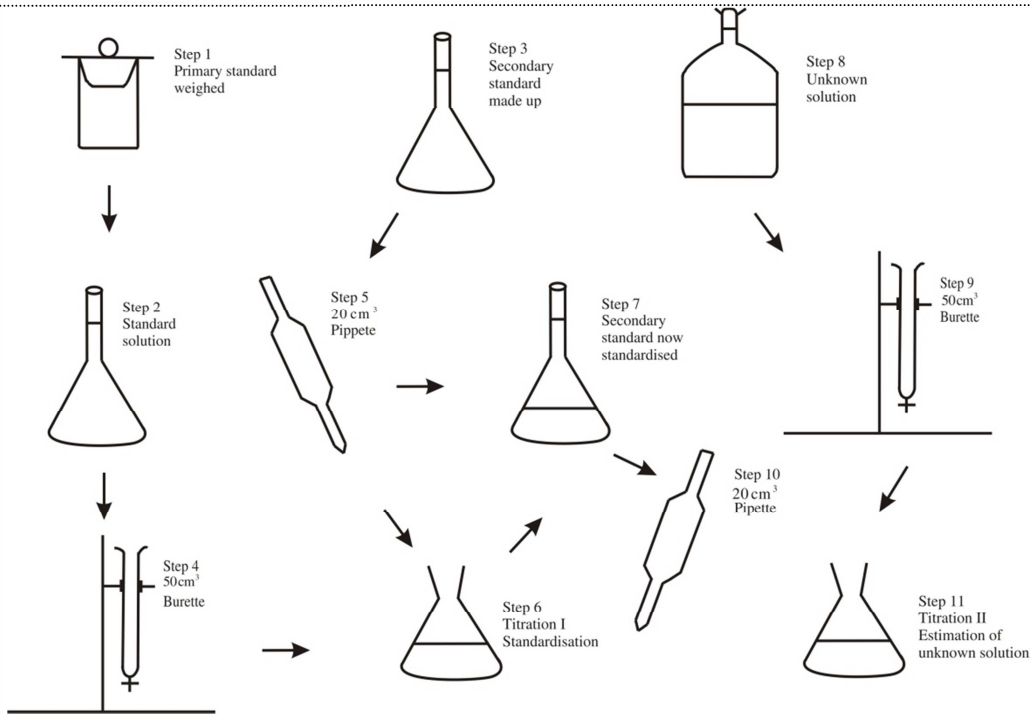


Fig. 1.12: Steps in a titrimetric estimation.

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 as shown below.

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

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 reaction, 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 this case, potassium permanganate gets reduced to Mn^{2+} while oxalic acid gets oxidized 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 p**recipitation 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 Titratons:** 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 metal ion are known as **ligands**, **L**.

$$M(H_2O)n + nL \rightleftharpoons ML_n + nH_2O$$

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 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. These are conductometer, potentiometer and colorimeter which measure the conductance, the potential and the colour intensity of the solution, respectively. Accordingly, these are named as conductometric titrations, potentiometric titrations and colorimetry. Instrumental methods are quicker and more accurate. Let us briefly understand these types.

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. 1.13).

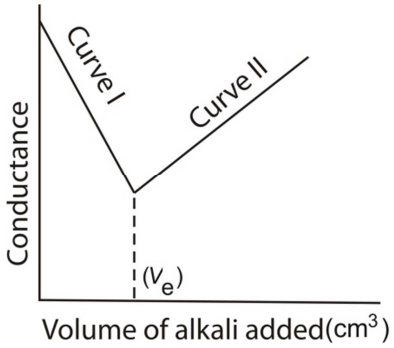


Fig. 1.13: Conductance curve: Titration of NaOH against HCl.

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.

Potentiometric Titrations

In potentiometric titrations, the solution with unknown concentration 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. A special case of potentiometry where hydrogen ion concentration, i.e. pH is measured is referred to as 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 (Fig. 1.14).

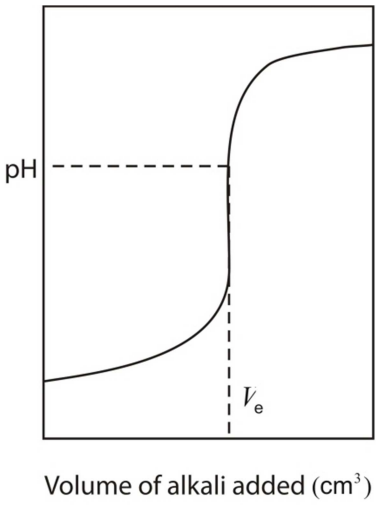


Fig. 1.14: pH metric titration of HCl vs. NaOH.

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 in your other courses. 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.

In the next section you will learn about another important aspect of a Chemistry laboratory that applies to all kind of laboratory work. Before proceeding further, you would like to assess what you have learnt about the instrumental determination of equivalence point. So, try answering the SAQ given below:

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.

1.7 SAFETY MEASURES IN THE LABORATORY

You will be using a number of reagents and chemicals while doing the experiments. There are laboratory 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.

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.

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 do's and don'ts in the laboratory would help you to avoid accidents.

The Do's:

- Wear a laboratory coat or an apron when working in the laboratory.
- Keep the test tubes pointing away from yourself and others while heating 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 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 laboratory.

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 especially 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 unauthorized 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. A list of hazardous chemicals and their effects is given in Table 1.2.

Table 1.2: List of hazardous chemicals and their effects

Hazardous Chemicals	Effects
Salts of Ag, As, Ba, Cu, Hg, Ni, Pb, Sb, Ti, 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.

Let us know the first-aid that should be given to a student or any person working in the laboratory, when such a mishap occurs.

i) **Cuts:** The most common accidents in the chemistry laboratory 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.

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 technique during the experiment can lead to an explosion. 'You should work with highly oxidizing or explosive chemicals only under strict supervision'.

Table 1.3 gives the remedies for a few common chemical reagents used in the laboratory.

Table 1.3: Remedies for a few chemical reagents

Chemical	Neutralising wash
Acid like HNO_3, H_2SO_4, HCl	Initial action should be a thorough washing with cold water. Then $NaHCO_3$ or 2*M* ammonium carbonate (leaves no residue on clothes), 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 wood pad

1.8 ANSWERS

Self-Assessment Questions

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) × 0.001 g + 8 × 0.001 g + 2 × 0.0002 g.

   = 8 g + 0.350 g + 0.008 g + 0.0004 g

   = 8.3584 g

3. From Eq. 1.1, $M = \frac{1000\ m}{M_m V}$ mol dm^{-3}

   Where M_m = 40 g mol^{-1}

   m = 4.000 g

   V = 500 cm^3

   Therefore,

   $$M = \frac{1000 \times 4.000}{40 \times 500} \text{ dm}^{-3} = 0.200 \text{ mol dm}^{-3}$$

   Thus, molar concentration = 0.200 *M*

4. Again consider Eq. 1.1,

$$M = \frac{1000\ m}{M_m V}\ \text{dm}^{-3}$$

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

$$m = \frac{0.1 \times 169.87 \times 1000}{1000}$$

$= 16.987\ \text{g}$

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) ✓

EXPERIMENT 1

DETERMINATION OF SODIUM CARBONATE AND SODIUM HYDROGEN CARBONATE PRESENT IN A MIXTURE

Structure

1.1 INTRODUCTION

You might be familiar with the basic principle of acid-base titrations. In this experiment we are expanding acid-base titration methods further for the analysis of a mixture of sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) or sodium bicarbonate. This method of titration will help you in understanding the basic principle of some important industrial analyses such as that of soda ash (anhydrous sodium carbonate), washing soda (hydrated sodium carbonate, $Na_2CO_3.10H_2O$), baking soda (sodium hydrogen carbonate), mixture of sodium carbonate–sodium hydroxide, commercial caustic soda (NaOH), etc. All these commercial products have a tendency to absorb moisture and carbon dioxide from atmosphere. This phenomenon of absorption of moisture and carbon dioxide by these chemicals is called weathering. After such weathering soda ash and washing soda contain appreciable moisture and sodium hydrogen carbonate and caustic soda has appreciable amount of moisture and sodium carbonate. Therefore, it becomes necessary to analyse the purity of these chemicals before using them for any fine use. The procedures, such as, conductometry, potentiometry or acid-base indicator methods 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 hydrogen carbonate.

Procedure used for the titration of a mixture of sodium carbonate and sodium hydrogen carbonate is basically the same as that of the acid-base titration which you have performed in your earlier classes, except that there are two analytes in our sample.

Expected Learning Outcomes

After performing the experiment given, 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 hydrogen carbonate mixture;
- prepare a standard solution of sodium carbonate;
- standardise the given solution of hydrochloric acid and use it in estimating the strength of basic solutions; and
- determine the strength of sodium carbonate and sodium hydrogen carbonate in a given solution.

1.2 PRINCIPLE

During an acid-base titration, the pH changes in a characteristic way. The pH changes during titration can be understood by plotting a pH curve. A pH curve is formed, if the pH of the solution being titrated is plotted against the volume of solution added. The titration of sodium carbonate with a strong acid such as HCl produces the titration curve shown in Fig. 1.1.This titration curve has two equivalence points. You may like to ask, why does sodium carbonate solution behave this way? To answer this question we should study the behaviour of sodium carbonate in aqueous solution.

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-}. The equilibrium, which is often called hydrolysis, is given by the reaction:

$$\underset{\text{(carbonateion)}}{CO_3^{2-}} + H_2O \rightleftharpoons \underset{\text{(hydrogen carbonate ion)}}{HCO_3^-} + OH^- \quad ...(1.1)$$

The hydrogen carbonate ion is furtherhydrolysed to carbonic acid:

$$HCO_3^- + H_2O \rightleftharpoons \underset{\text{(carbonic acid)}}{H_2CO_3} + OH^- \quad ...(1.2)$$

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 reaction is completed in two steps. First, the carbonate ions are converted to the hydrogen carbonate 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.

$$\underset{(Na_2CO_3)}{CO_3^{2-}} + \underset{(HCl)}{H^+} \rightarrow HCO_3^- \quad ...(1.3)$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \quad \text{... (1.4)}$$
(HCl)

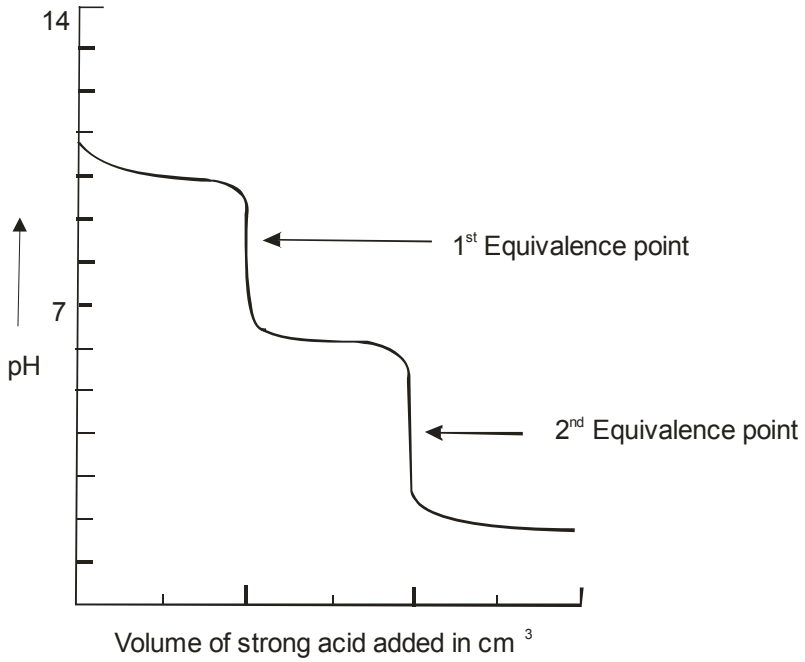


Fig. 1.1: The titration of sodium carbonate with hydrochloric acid.

As neutralisation takes place in two steps (it is indicated by reactions in Eqs. 1.3 and 1.4), we observe two regions of sharp pH change in the titration curve (Fig. 1.1) and thus two equivalence points at pH 8.31 and pH 3.69. As shown in Fig. 1.1, at the first equivalence point (in the pH range 9-7) CO_3^{2-} is neutralised to HCO_3^- and at the second equivalence point (in the pH range 5-3) HCO_3^- is neutralised to H_2CO_3.

Combining both the above equations we can write complete neutralisation reaction of sodium carbonate as

$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3 \quad \text{…(1.5)}$$

Finally, the carbonic acid produced as a result of these titrations can decompose into carbon dioxide (CO_2)

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O$$

In this experiment, we will utilise this behaviour of sodium carbonate in the estimation of a mixture of sodium carbonate and sodium hydrogen carbonate. Let us now understand the behavior of a mixture of sodium carbonate and sodium hydrogen carbonate during titration with hydrochloric acid.

The titration curve for a sodium carbonate and hydrogen carbonate mixture is shown in Fig. 1.2. As you can see, it has two equivalence points. The first equivalence point indicates half neutralisation of the carbonate in the given sample, i.e., its conversion to hydrogen carbonate (cf Eq. 1.3). The second equivalence point indicates neutralisation of the hydrogen carbonate in the initial sample mixture and the hydrogen carbonate just generated from the half neutralisation of carbonate (cf Eq. 1.4). In this experiment we will be using acid base indicators to detect both the equivalence points.

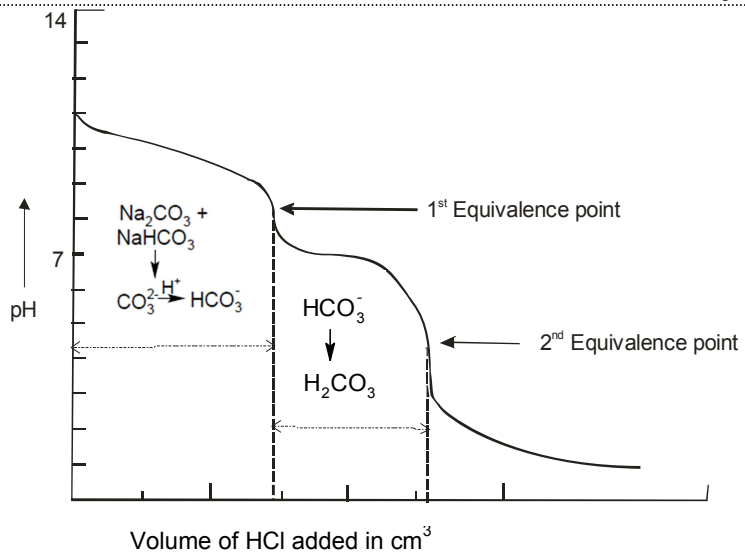
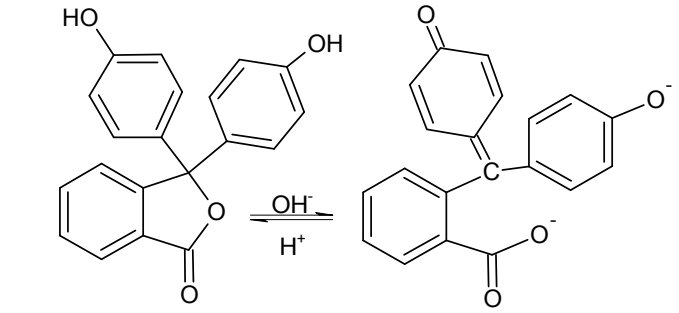


Fig.1.2:Titration curve for sodium carbonate and sodium hydrogen carbonate titrated with hydrochloric acid.

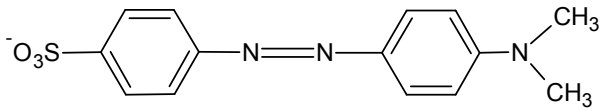
As you know, acid-base indicators are organic dyes which change colour as pH changes. This is because the indicator has two forms, one is acid form in lower pH medium and other is base form in higher pH medium and having two different structures. For example, phenolphthalein has two forms, one is benzenoid form (I) in low pH medium (pH < 8) and thus, it is colourless. Its second form has quinonoid structure (II) in high pH medium (pH > 10) which has a pink colour. Similarly, methyl orange exists in quinonoid form (III) in lower pH medium (pH < 3.2) and benzenoid form (IV) in higher pH medium (pH > 4.4). The colour of its benzenoid form is yellow while that of quinoniod form is red.



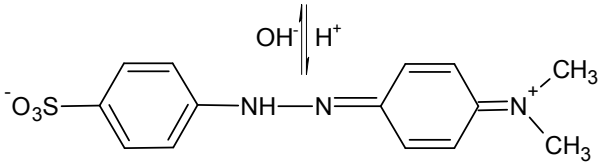
Benzenoid form in acidic solution (colourless) (I)

Quinonoid form in basic solution (pink) (II)

Phenolphthalein



Benzenoid form in basic solution (yellow) (III)



Quinonoid form in acidic solution (red) (IV)

Methyl orange

Equivalence point so obtained using indicators is called an **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 colour change, and other factors. Ideally end point and equivalence point should be as close as possible.

In general acid-base indicators show colour change in a pH range of ±1 pH unit. The colour change and the pH range of some common indicators are tabulated below to guide you for selecting appropriate indicator for any acid base titration.

The pH range is termed as the colour-change interval of the pH 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 the equivalence point. For example, pH indicator phenolphthalein shows colour change in pH range 8-10 and methyl orange in the pH range 3.1-4.4. Therefore, for detection of end points in the pH range of 8-10, phenolphthalein will be the suitable indicator. Similarly for detection of the end point in pH range of 3-4, methyl orange will be the suitable indicator.

Table 1.1: Colour changes and pH ranges of acid-base indicators

Name	Acid Colour	pH Range of Colour Change	Base Colour
Methyl violet	Yellow	0.0 - 1.6	Blue
Thymol blue	Red	1.2 - 2.8	Yellow
Methyl orange	Red	3.2 - 4.4	Yellow
Bromocresol green	Yellow	3.8 - 5.4	Blue
Methyl red	Red	4.8 - 6.0	Yellow
Litmus	Red	5.0 - 8.0	Blue
Bromothymol blue	Yellow	6.0 - 7.6	Blue
Thymol blue	Yellow	8.0 - 9.6	Blue
Phenolphthalein	Colourless	8.2 - 10.0	Pink

Using Fig. 1.2 and Table 1.3, you can select phenolphthalein and methyl orange as most suitable indicators for the detection of the first and the second end points, respectively for the titration of mixture of sodium carbonate and sodium hydrogen carbonate. Once, these two end points are detected, the volume of HCl used to titrate sodium carbonate and sodium hydrogen carbonate in the mixture can be determined. This can be further illustrated by considering Fig. 1.3.

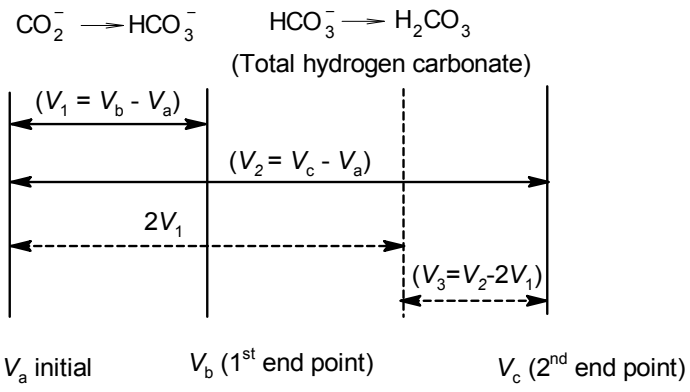


Fig. 1.3: Volumes of HCl used during titration of a mixture of sodium carbonate and sodium hydrogen carbonate.

In this diagram V_a, V_b and V_c refer to burette readings–initial, at the 1st end point with phenolphthalein and at the 2nd end point with methyl orange, respectively. These values of V_a, V_b and V_c are also used in calculating the volumes of HCl required for neutralizing Na_2CO_3 and $NaHCO_3$ present in mixture. Thus, for the first end point we need $V_b - V_a = V_1\,cm^3$ and for the second end point $V_c - V_a = V_2\,cm^3$ of hydrochloric acid. Thus, V_1 is the volume of HCl needed to titrate half of the sodium carbonate initially present in the mixture ($CO_3^{2-} + H^+ \rightarrow HCO_3^-$) and $2V_1$ will be the volume of HCl needed to neutralise whole sodium carbonate in the mixture ($CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$). V_2 is the volume of HCl required to neutralize both sodium carbonate and sodium hydrogen carbonate in the given solution. On subtraction of $2V_1$ from this volume, V_2, we can find out the volume of HCl, V_3, needed to neutralise initially present sodium hydrogen carbonate in the mixture, $V_3 = (V_2 - 2V_1)$.

The corresponding chemical reactions may be summarised as:

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

end point with phenolphthalein,
Volume of HCl = $V_1 = V_b - V_a$

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

($NaHCO_3$ + HCO_3^- of sodium carbonate)

end point with methyl orange,
Volume of HCl = $V_2 = V_c - V_a$

Using volume V_1, V_2, V_3 and molarity equations we can calculate amount of sodium carbonate and sodium hydrogen carbonate in the mixture.

Using reaction of Eq. 1.3, we can write molarity equation for the half neutralisation of sodium carbonate, here sodium carbonate reacts with hydrochloric acid in 1:1 molar ratio to gives hydrogen carbonate. Thus the molarity equation for this step will be:

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

i.e. $M_{Na_2CO_3}\,V_{Na_2CO_3} = M_{HCl}\,V_{HCl}$ …(1.6)

Where $M_{Na_2CO_3}$ the molarity of sodium is carbonate solution and $V_{Na_2CO_3}$ is the volume of sodium carbonate used in titration. M_{HCl} is the molarity of hydrochloric acid and V_{HCl} is the volume of the hydrochloric acid used in the titration of sodium carbonate up to hydrogen carbonate stage.

As indicated by the final reaction (Eq. 1.5), complete sodium carbonate reacts with hydrochloric acid in 1:2 molar ratios. Hence, molarity equation can be written as

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

i.e. $2 M_{Na_2CO_3} V_{Na_2CO_3} = M_{HCl} V_{HCl}$ …(1.7)

Where $M_{Na_2CO_3}$ is the molarity of sodium carbonate solution and $V_{Na_2CO_3}$ is the volume of sodium carbonate used in titration. M_{HCl} is the molarity of hydrochloric acid and V_{HCl} is the volume of the hydrochloric acid used in the complete titration of sodium carbonate (i.e. volume of HCl used up to methyl orange end point for standard sodium carbonate solution)). Eq. 1.7 will be used for the calculation of the strength of hydrochloric acid in the titration of standardisation of hydrochloric acid.

Chemical reaction of the neutralisation of sodium hydrogen carbonate with HCl can be written as:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \quad ...(1.8)$$

Here sodium hydrogen carbonate reacts with hydrochloric acid in 1:1 molar ratios. Hence, molarity equation can be written as

$$M_{NaHCO_3} V_{NaHCO_3} = M_{HCl} V_{Hcl} \quad ...(1.9)$$

Where M_{NaHCO_3} is the molarity of sodium hydrogen carbonate solution and V_{NaHCO_3} is the volume of sodium hydrogen carbonate used in titration. M_{HCl} is the molarity of hydrochloric acid and V_{HCl} is the volume of the hydrochloric acid used in the titration.

Hydrochloric acid used for titration of the mixture solution is not a primary standard. Therefore, 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 shown by Eq .1.5 and molarity equation used for calculating the molarity of hydrochloric acid is shown by Eq. 1.7. 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 or sharp pH change(s) which will be 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. 1.4 given below, suggest suitable indicators for the titration of ethanedioic acid or oxalic acid ($H_2C_2O_4$) against strong base.

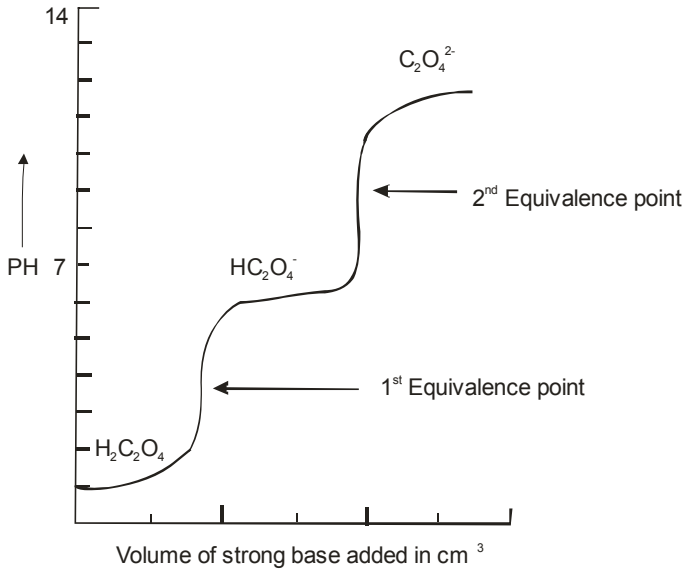


Fig. 1.4: Titration of ethanedioic acid (oxalic acid) with strong base like NaOH.

1.3 REQUIREMENTS

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

Apparatus		Chemicals
Beaker (250 cm^3)	2	Hydrochloric acid
Burette (50 cm^3)	1	Methyl orange
Burette stand with clamp	1	Phenolphthalein
Conical flask (250 cm^3)	1	Sample: Mixture of sodium carbonate and sodium hydrogen carbonate or baking soda
Funnel	1	Sodium carbonate (AR grade)
Pipette (20 cm^3)	1	
Volumetric flasks (250 cm^3)	2	
Weighing bottle	1	

Solutions provided

Sample solution: Prepare a sample solution by dissolving a mixture of sodium carbonate and sodium hydrogen carbonate (8.5 g Na_2CO_3+5.4 g $NaHCO_3$) or commercial baking soda (15 g) in 2 dm^3 distilled water.

Phenolphthalein indicator solution: It is prepared by dissolving 0.1 g of the reagent in 80 cm^3 of ethanol and adding adequate distilled water to make it 100 cm^3. If a precipitate is formed, it is filtered.

Methyl orange indicator solution: It is prepared by dissolving 0.1 g of free acid/sodium salt of the indicator in 80 cm^3 of distilled water and adds 20 cm of ethanol to make it 100 cm^3.

Hydrochloric acid solution (~ 0.1 *M):* This solution is prepared by taking 8.5 cm^3 conc. HCl (37%) in a 1 dm^3 volumetric flask and diluting the acid up to the mark with distilled water.

1.4 PROCEDURE

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 during titration.

Before using burette and pipette you should know how to use them.

Your apparatus should by dry and clean.

First collect 0.1 *M* hydrochloric acid in a 250 cm^3 beaker. 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 exact 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. Find the exact mass of sodium carbonate transferred by subtracting the mass of empty weighing bottle from the mass of the weighing bottle plus sodium carbonate. Dissolve sodium carbonate in volumetric flask in distilled water 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 background till a redcolour 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 sample solution (mixture of sodium carbonate and sodium hydrogen carbonate) against standardised hydrochloric acid:

i) Now collect sample solution in a 250 cm^3 beaker. Pipette out 20 cm^3 of the sample solution in a conical flask. Add 1-2 drops of phenolphthalein indicator 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 a 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 the titration with both the indicators to get two concordant sets of readings.

1.5 OBSERVATIONS

Mass of the weighing bottle ..... = m_1 g =……..g

Mass of weighing bottle + sodium carbonate . = m_2 g =……..g

Amount of sodium carbonate transferred ..... = $m_2 - m_1$ = mg =……..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 = $M_{Na_2CO_3}$ = ?

$$M_{NaCO_3} = \frac{m \times 1000}{M_m \times 250} \text{ mol dm}^{-3}$$

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

M_{NaCO_3} = ... mol dm^{-3}

Observation Table I

Sodium carbonate vs. Hydrochloric acid

S. No.	Volume of Na_2CO_3 in cm^3 ($V_{Na_2CO_3}$)	Burette reading		Volume of HCl in cm^3 (Final – Initial) (V_{HCl})
		Initial	final	

Observation Table II

Sample solution (Mixture of Na_2CO_3 and $NaHCO_3$) vs. Hydrochloric acid

S. No.	Volume of sample solution in cm^3	Burette reading			Volume of HCl used in titration of half of Na_2CO_3 ($CO_3^{2-} \rightarrow HCO_3^-$) in cm^3	Volume of HCl used in titration of total CO_3^{2-} + HCO_3^- in cm^3	Volume of HCl used in titration of initially present $NaHCO_3$ in cm^3
		Initial	With phenolphthalein	With methyl orange			
	V_s	V_a	V_b	V_c	($V_1 = V_b - V_a$)	($V_2 = V_c - V_a$)	($V_3 = V_2 - 2V_1$)

1.6 CALCULATIONS

a) **Standardisation of hydrochloric acid solution:**

Molarity of sodium carbonate solution = $M_{Na_2CO_3}$ = ...mol dm^{-3}

Volume of sodium carbonate solution = $V_{Na_2CO_3}$ = 20cm^3

Volume of hydrochloric acid = V_{HCl} = ...cm^3

(from Observation Table I)

Molarity of HCl solution = M_{HCl} = M_{std}= ?

Using Eq. 1.7, Molarity of HCl solution,

$$M_{std} = \frac{2M_{Na_2CO_3}V_{Na_2CO_3}}{V_{HCl}} \quad = \text{..... mol dm}^{-3} \qquad \text{...(1.10)}$$

b) **Estimation of sodium carbonate and sodium hydrogen carbonate in the sample solution**: This can be done as follows:

i) **Estimation of sodium carbonate in the Sample Solution**:

The molarity of the sodium carbonate in the given sample can also be calculated using molarity Eq. 1.10. But in this case the volume of HCl used in titration will be $2V_1$.

Volume of hydrochloric acidusedin the titration of half of sodium carbonate in the given sample (from Observation Table II)

V_1 = ... cm^3

Molarity of hydrochloric acid solution M_{HCl} = M_{std} =..... mol dm^{-3}

(From standardisation of HCl solution, Eq. 1.10)

Volume of the sample solution V_s cm^3 = 20cm^3

Molarity of Na_2CO_3 in the given sample solution = M_{sc} = ?

Using Eq. 1.6, substituting values from above:

$$M_{sc}V_s = M_{std}V_1$$

$$M_{sc} = \frac{M_{std}V_1}{V_s}$$

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

Strength of sodium carbonate present in the

given sample solution = $M_{sc}\times$ Molar mass of sodium carbonate

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

ii) **Estimation of sodium hydrogen carbonate in the Sample Solution**:

Volume of hydrochloric acid used in the titration of sodium hydrogen carbonate in the given sample

(from Observation Table II) = V_3 = ...cm^3

Molarity of hydrochloric acid solution = $M_{HCl} = M_{std}$ = ...mol dm^{-3}

(From standardisation of HCl solution, Eq. 1.10)

Volume of the sample solution V_s = 20 cm^3

Molarity of sodium hydrogen carbonate in the given sample solution = M_{shc}= ?

Similar to Eq. 1.8 neutralisation reaction of sodium hydrogen carbonate and HCl can be written as:

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

Here sodium hydrogen carbonate reacts with hydrochloric acid in 1:1 molar ratio. Hence, molarity equation can be written as

$$M_{HCO_3^-} V_{HCO_3^-} = M_{HCl} V_{Hcl}$$

Therefore, on substitution of the values from above:

$$M_{shc} = \frac{M_{std} V_3}{V_s}$$

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

Strength of sodium hydrogen carbonate in the given Sample Solution = $M_{sch} \times$ Molar mass of sodium hydrogen carbonate (Molar mass of $NaHCO_3$ = 84 g mol^{-1})

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

1.7 RESULTS

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

Molarity of $NaHCO_3$ in the given solution = ...mol dm^{-3}

ii) Strength of Na_2CO_3 in the given solution = ...g dm^{-3}

Strength' of $NaHCO_3$ in the given solution = ...g dm^{-3}

Compare the results with the correct values for the given sample solution of the mixture of sodium carbonate and sodium hydrogen carbonate.

Using the experimental technique mentioned above, you can also design an experiment to determine the percentage purity of commercial soda ash, washing soda, etc. For analysing mixture of sodium carbonate and sodium hydroxide, and commercial caustic soda, there is need of modification in the calculation of the volume of HCl needed to neutralise them. In this analysis, NaOH and half of the Na_2CO_3 is neutralised at the phenolphthalein end point and remaining half of sodium carbonate i.e. hydrogen carbonate at methyl orange end point. Calculation is carried out using following equations:

$$M_{Na_2CO_3} = \frac{2(V_{mo} - V_{phth}) M_{HCl}}{2V_s}$$

Sodium hydroxide and commercial caustic soda absorb moisture and CO_2 from the air and get converted into

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

$$M_{NaOH} = \frac{[V_{phth} - 2(V_{mo} - V_{phth})]M_{HCl}}{V_s}$$

Where, $M_{Na_2CO_3}$ and M_{NaOH} are the molarities of sodium carbonate and sodium hydroxide in the sample, respectively. V_s is the volume of the sample used in titration. V_{phth} and V_{mo} are the volumes used in titration of HCl up to phenolphthalein end point and methyl orange end point, respectively. M_{HCl} is the strength of standardized HCl used in this titration.

1.8 ANSWERS

Self-Assessment Questions

1. a) Basic
   b) Neutral
   c) Basic
   d) Basic
   e) Basic
2. a) One
   b) One
   c) Two
3. Methyl orange for the first pH break and phenolphthalein for second pH break (See Fig 1.4). As methyl orange remains coloured after the first end, point therefore, pH meter is preferred.

EXPERIMENT 2

ESTIMATION OF OXALIC ACID BY REDOX TITRATION

Structure

2.1 INTRODUCTION

You have learnt about the theory and applications of acid-base titrations in Experiment 1. A large number of analytical determinations make use of another important kind of titrations, namely, redox titrations. 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 experiment we will make use of 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 important types of titrations are **permanganatometry** using potassium permanganate, $KMnO_4$ and **chromatometry** using potassium dichromate, $K_2Cr_2O_7$ as the oxidizing agents. In the present experiment you will estimate oxalic acid using permanganatometry and in Experiment 3 the same oxidising

agent would be used to estimate water of crystallization in the Mohr's salt. Experiment 4 deals with the estimation of iron using another oxidising agent i.e. potassium dichromate.

Expected Learning Outcomes

After performing the experiment, you should 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,
- state and explain the principle involved in permanganatometry, and
- apply the redox titration method, viz., permanganatometry for estimating oxalic acid in the given solution.

2.2 OXIDATION-REDUCTION: REDOX POTENTIAL

Let us first 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.,

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad \text{... (2.1)}$$

An oxidising agent is the one which gains electrons and gets reduced, e.g., Cl_2 in Eq. 2.2 and a reducing agent is the one which loses electrons and gets oxidised, e.g., Fe^{2+} in Eq. 2.1.

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.,

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \quad \text{… (2.2)}$$

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:

Oxidising agent (I) + Reducing agent (II) $\rightarrow$ Reducing agent (I) + Oxidising agent (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 potentials** of the oxidising/reducing agents. The redox potential is a quantitative characteristics of the oxidising/ reducing power of a reagent. Let us try to understand the significance of redox potential.

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 the equilibrium. If the system tends to act as an oxidising agent, $Fe^{3+} \rightarrow Fe^{2+}$; it will take electrons from the platinum electrode leaving the latter positively charged. On the other hand, if the system has reducing properties ($Fe^{2+} \rightarrow Fe^{3+}$), electrons will be given 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 0.00 *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 on Celcius scale is taken as zero.

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+}, Mn_2^{7+}/Mn^{2+}, etc., rather than of the individual oxidant or reductant potentials.

For a simple reduction reaction,

$$\text{Oxidised form} + ne^- \longrightarrow \text{Reduced form}$$

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

$$E = E^o + \frac{RT}{nF} \log \frac{[\text{Ox}]}{[\text{Red}]} \qquad \ldots(2.3)$$

where R = Gas constant (= 8.314 J mol^{-1} K^{-1})

T = Absolute temperature (K)

F = Faraday's constant (= 96,500 C)

E^o = Standard redox potential

n = number of electrons gained or lost

When [Ox] = [Red], the log term in Eq. 2.3 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. 2.3, we get the following.

$$E = E^o + \frac{0.059}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \qquad \ldots (2.4)$$

Thus, 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's 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 molecules to form oxide ions

2.3 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.

2.3.1 Redox Titration Curves

We can see from Eq. 2.4 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 ions and potassium permanganate solution.

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:

$$[Fe^{2+} \rightleftharpoons Fe^{3+} + e^-] \times 5 \qquad \ldots(2.5)$$

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad \ldots(2.6)$$

Adding Eq. 2.5 and Eq. 2.6,

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \qquad \ldots(2.7)$$

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. 2.3. The values of *n* can be obtained from Eq. 2.5 and Eq. 2.6.

Thus:

$$E = 0.77 + \frac{0.059}{1} \log \frac{[5Fe^{3+}]}{[5Fe^{2+}]} \quad \ldots(2.8)$$

$$E = 1.51 + \frac{0.059}{1} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]} \quad \ldots(2.9)$$

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. 2.1, 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. 2.8) also goes on increasing gradually. At a stage just before the equivalence point, say about 0.1 cm^3 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. 2.1.

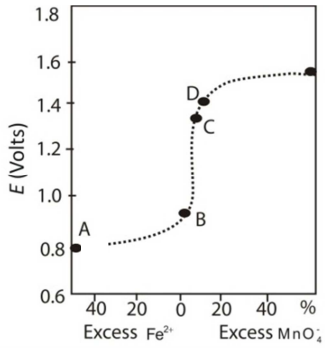


Fig. 2.1: Redox titration curve for $FeSO_4$ – $KMnO_4$ titration.

At equivalence point, point C in Fig. 2.1, the potential is given by the following general equation:

$$E = \frac{aE_a^0 + bE_b^0}{a + b} \quad \ldots(2.10)$$

where E_a^0 and E_b^0 are the standard potentials of the reducing and the oxidising agent, respectively and a and b are the corresponding stoichiometric coefficients. In the present case E_a^0 = 0.77V, E_b^0 = 1.51V, a=1, b = 5 and E =1.387V.

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. 2.1. 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 cm^3 of $FeSO_4$ solution at $[H^+] = 1M$ with permanganate solution of the same molarity is given in Table 2.1. You would notice that Eq. 2.9 for determining the potential of MnO_4^-/Mn^{2+} couple contains $[H^+]$ term. The concentration of $[H^+]$ is kept 1*M* so that in the effective equation we need only the amounts of MnO_4^- and Mn^{2+} ions. 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 1*M* 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 add), bromide is oxidised, but chloride is still unaffected. The latter is oxidised only at a much higher hydrogen ion concentration.

Table 2.1: Variations of the redox potential during titration of 100 cm^3 of 0.1*M* $FeSO_4$ solution with 0.02*M* $KMnO_4$ solution at $[H^+] = 1M$

$KMnO_4$ added (cm^3)	Excess cm^3		$\frac{[Fe^{3+}]}{[Fe^{2+}]}$	$\frac{[MnO_4^-]}{[Mn^{2+}]}$	Calculation *E* =	Oxidation potential *E* (V)
	$FeSO_4$	$KMnO_4$				
50	50	—	50:50=1	—	0.77+0.059 log1	0.770
91	9	—	91:9≈10	—	0.77+0.059 log10	0.829
99	1	—	99:1≈100	—	0.77+0.059 log100	0.888
99.9	0.1	—	99.9:0.1 ≈1000	—	0.77+0.059 log 1000	0.947
100 (equiv. pt.)	0.0	0.0	100:0	—	$\frac{0.77 + 5 \times 1.51}{5.1}$	1.387*
100.1	—	0.1	—	0.1:100 =0.001	$1.51 + \frac{0..59}{5} \log 0.001$	1.475
101.0	—	1.0	—	1:100 =0.01	$1.51 + \frac{0..059}{5} \log 0.001$	1.487
110.0	—	10	—	10:100 =0.1	$1.51 + \frac{0..059}{5} \log 0.001$	1.498
150	—	50	—	50:100 =0.5	$1.51 + \frac{0..059}{5} \log 0.5$	1.507

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

Redox potential of a redox system remains unaffected by dilution, this is because dilution affects both the oxidised and the reduced species equally. This is justified because in the Nenst equation also, the relative concentrations and

not the absolute concentrations of the two forms are required. On the other hand, in the region beyond the equivalence point, the actual potential would be slightly different from the calculated one, since $[H^+]$ ions are involved in the calculations and their concentration does depend upon dilution. This error, however, does not affect the general conclusions and can, therefore, be neglected.

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

2.3.2 Redox Indicators

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

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

In redox titrations, indicators are used in three different ways. These have already been discussed briefly in the introductory Unit 1. Let us recall it here. In certain titrations, e.g., those involving $KMnO_4$, one of the reacting species itself changes colour at the equivalence point and is called a **self indicator.** In some cases the indicator needs to be added to the solution, as phenolphthalein or methyl orange in the case of acid-base titrations, or, diphenylamine in case of chromatometry. Such indicators are called **internal indicators.** In yet some other cases, redox indicator may be replaced by a reagent which is used as a spot test reagent for the ion being determined. Such indicators are not added into the solution but are used externally. At various stages of the titration, a drop of the reaction mixture is taken out and tested for the ion by mixing with the indicator 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, you will perform the following experiment based on the principle of redox titrations.

2.4 PERMANGANATOMETRIC ESTIMATION OF OXALIC ACID

As stated above, 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 oxalic acid solution. Let us learn the principle of this determination.

2.4.1 Principle

Potassium permanganate is an oxidising agent and gets reduced in the presence of a suitable reducing agent, for example, oxalate ions ($C_2O_4^{2-}$) 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. 2.6, and to Mn^{4+} in neutral and alkaline media, as shown in Eq. 2.11.

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

$$\underset{\text{+ 7 state}}{MnO_4^- + 8H^+ + 5e^-} \rightleftharpoons \underset{\text{+2 state}}{Mn^{2+} + 4H_2O}, \quad E^0 = 1.51\,V \qquad \ldots(2.6)$$

$$\underset{\text{+7 state}}{MnO_4^- + 2H_2O + 3e^-} \rightleftharpoons \underset{\text{+4 state}}{MnO_2 + 4OH^-}, \quad E^0 = 0.57\,V \qquad \ldots(2.11)$$

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, $C_2O_4^{2-}$ gets oxidised to carbon dioxide as per the following equation

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \qquad \ldots(2.12)$$

The overall ionic equation for the titration of oxalic acid and permanganate in acidic medium can be obtained by adding Eq. 2.12 and Eq. 2.6 after balancing the number of electrons between them as follows:

$$[C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5 \qquad (2.12)$$

$$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \qquad \ldots (2.6)$$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2 \qquad \ldots (2.13)$$

We see from Eq. 2.13, that two moles of permanganate ions react with 5 moles of oxalate ions. Therefore, substituting the values in the molarity equation, the molarities are related as per the following equation:

$$\frac{M_{KMnO_4} V_{KMnO_4}}{M_{H_2C_2O_4} V_{H_2C_2O_4}} = \frac{2}{5} \Rightarrow 5M_{KMnO_4} V_{KMnO_4} = 2V_{H_2C_2O_4} M_{H_2C_2O_4} \qquad \ldots(2.14)$$

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. You can use Eq. 2.14 as the molarity equation to find out the molarity of the oxalic acid.

The Mohr's salt is preferred to ferrous sulphate because it has better shelf-life.

The solution of $KMnO_4$ is not stable and 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 for standardisation of potassium permanganate. The equation for the titration is given by Eq. 2.7.

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

The corresponding molarity equation for the titration would be:

$$5\ M_K V_K = M_F V_F$$

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 ferrous sulphate solution in presence of dilute H_2SO_4.

[Hint: Two steps are involved in the reaction]

SAQ 3

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

2.4.2 Requirements

Apparatus		**Chemicals**
Burette (50 cm^3)	1	Ferrous ammonium sulphate, FAS $FeSO_4.(NH_4)_2SO_4.6H_2O$, also known as Mohr's salt
Pipette (20 cm^3)	1	Sulphuric acid (1 *M*)
Conical flasks (250 cm^3)	2	Oxalic acid
Test Tube	1	Potassium permanganate
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	

Solutions Provided

Oxalic acid solution: About M/100, prepared by dissolving 0.35 g of oxalic acid dihydrate in water and making up the volume to 250 cm^3 in a volumetric flask.

Approximately *M*/250 solution of potassium permanganate, prepared by dissolving 0.20 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.

2.4.3 Procedure

As indicated above, you are provided with approximately *M*/250 potassium permanganate solution, and a solution of oxalic acid which is to be estimated. You are required to prepare a standard solution of ferrous ammonium sulphate, which is also known as Mohr's salt.

There are three steps in the experiment as follows:

1. Preparation of a standard solution of ferrous ammonium sulphate
2. Standardisation of given $KMnO_4$ solution by titrating against the standard ferrous ammonium sulphate solution
3. Titration of given oxalic acid solution with the standardised $KMnO_4$ solution

1. 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 (1 *M*) 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 added acid is not sufficient. Discard this solution. Do the whole exercise again using more H_2SO_4.

2. 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 the standard Mohr's salt solution (20 cm^3) in a conical flask and add an equal volume of dil. sulphuric acid (5M). **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 against $KMnO_4$ till a light but permanent pink colour is obtained. 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.

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

3. Titration of given oxalic acid solution against standardised $KMnO_4$ solution

Pipette out the given oxalic acid solution (20 cm^3), add equal volume of dil. H_2SO_4, heat to 60°C-70° C and titrate against $KMnO_4$ solution as above. Repeat the titration till two concordant readings are obtained. 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.

2.4.4 Observations

Approximate mass of the weighing bottle $= m_1 =$……..g

Mass of bottle + Mohr's salt $= m_2 =$……..g

Mass of bottle (after transferring the Mohr's salt) $= m_3 =$…….g

Mass of Mohr's salt transferred $= m_2 - m_3 = m =$ …...g

Molar mass of Mohr's salt $= 392.15$ g mol^{-1}

Volume of Mohr's salt solution prepared (V) $= 250$ cm^3

Molarity of Mohr's salt solution (M_1)

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

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

Observation Table I: Titration of standard Mohr's salt solution vs. Potassium permanganate solution

Sl. No.	Volume of Mohr's salt solution (cm^3)	Burette reading		Volume of $KMnO_4$ (cm^3) (Final – Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II: Titration of given Oxalic acid solution vs. Potassium permanganate solution

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

2.4.5 Calculations

Estimation of the strength of potassium permanganate

Molarity of Mohr's salt solution $= M_1 = \ldots\ldots\ldots \text{mol dm}^{-3}$

Vol. of Mohr's salt solution used $= V_1 = \ldots\ldots\ldots 20\ \text{cm}^3$

Vol. of $KMnO_4$ solution used (from Table I) $= V_2 = \ldots\ldots\ldots \text{cm}^3$

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

Using the molarity equation,

$$M_1V_1 = 5\ M_2\ V_2$$

Molarity of $KMnO_4$ solution, $M_2 = \dfrac{M_1V_1}{5V_2} = \ldots\ldots\ldots\ldots \text{mol dm}^{-3}$

Estimation of strength of given oxalic acid solution

Molarity of $KMnO_4$ $= M_3 = M_2 = \ldots\ldots\ldots \text{mol dm}^{-3}$ or M

Vol. of $KMnO_4$ solution used $= V_3 = \ldots\ldots\ldots\ldots \text{cm}^3$

Vol. of oxalic acid solution taken $= V_4 = 20\,\text{cm}^3$

Molarity of oxalic acid $= M_4 = ?$

Using the molarity equation,

$$2M_4V_4 = 5\ M_3V_3$$

Molarity of oxalic acid solution, $M_4 = \dfrac{5M_3V_3}{5V_4} = \text{mol dm}^{-3}$

Strength of oxalic acid solution $M_4 \times 126\ \text{g dm}^{-3}$

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

2.4.6 Result

The strength of given oxalic acid solution $= \ldots\ldots\ldots\ldots\ \text{g dm}^{-3}$

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

2.5 ANSWERS

Self-Assessment Questions

1) i) $H_2 \rightarrow 2H^+ + 2e^-$

ii) $S^{-2} \rightarrow S + 2e^-$

iii) $Cl_2 + 2e \rightarrow 2Cl^-$

iv) $Cu^+ \rightarrow Cu^2 + e^-$

v) $O_2 + 2e \rightarrow 2O^{-2}$

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

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

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

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

EXPERIMENT 3

ESTIMATION OF WATER OF CRYSTALLISATION IN MOHR'S SALT

Structure

3.1 INTRODUCTION

In the previous experiment you have learnt about and performed a redox titration based on permanganatometry. In that titration you determined the strength of a reducing agent- oxalic acid by titrating against $KMnO_4$ in the acidic medium. The $KMnO_4$ solution was standardised by titrating against a standard solution of Mohr's salt-another reducing agent. In the third experiment you are going to perform another titration based on permanganatometry to determine the number of water of crystallisation in Mohr's salt. In the next experiment you would learn about and perform another type of redox titration namely, chromatometry in which you would be using $K_2Cr_2O_7$ as the oxidising agent.

Expected Learning Outcomes

After performing the experiment, you should be able to:

- ❖ state and explain the principle involved in permanganatometry;
- ❖ prepare a standard solution of oxalic acid;
- ❖ standardise the given solution of potassium permanganate; and
- ❖ determine the number of water of crystallisation in Mohr's salt by permanganatometry.

3.2 PRINCIPLE

In the determination of the water of crystallisation in Mohr's salt (hydrated ferrous ammonium sulphate) we first prepare its solution of known concentration (g dm^{-3}). Then we estimate it as anhydrous ferrous ammonium sulphate by permanganatometry. The strength (g dm^{-3}) so obtained and actually taken is then used to determine the water of crystallisation as follows.

Let there be 'x' number of water of hydration in Mohr's salt, the molar mass of Mohr's salt can be written as follows:

Molar mass of Mohr's salt = Molar mass of the anhydrous salt + 18x

= 284 +18x

Let the amount of Mohr's salt taken to prepare the solution = A g

Let the amount of anhydrous salt determined by permanganatometry = B g

Then we can write the equation as follows:

$$\frac{A}{B} = \frac{284 + 18x}{284} \qquad \ldots(3.1)$$

By knowing A and B, the equation can be solved to get the value of x, the number of water of hydration in Mohr's salt. Let us now take up the determination of water of crystallisation in Mohr's salt by permanganatometry.

As discussed in the previous experiment, potassium permanganate is an oxidising agent and gets reduced in the presence of a suitable reducing agent. In this experiment we would be titrating it with Mohr's salt –a reducing agent. Permanganate ions, MnO_4^- get reduced in acidic, neutral or alkaline medium. In acidic medium, it gets reduced to Mn^{2+} ion as per the following equation.

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad \ldots(3.2)$$

On the other hand, the Fe (II) ions provided by Mohr's salt (ferrous ammonium sulphate) get oxidised to Fe (III) as per the following equation

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \ldots(3.3)$$

The overall ionic equation for the titration of Mohr's salt and permanganate ion in acidic medium can be obtained by adding Eq. 3.2 and Eq. 3.3 after balancing the number of electrons between them as follows:

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

$$\underline{MnO_4^- + 8H^+ + 5\,Fe^+ \rightarrow Mn^{2+} + 4H_2O}$$

$$MnO_4^- + 8H^+ + 5\,Fe^+ \rightarrow Mn^{2+} + 4H_2O \qquad \ldots(3.4)$$

As per equation 3.4, one mole of permanganate ions oxidises 5 moles of ferrous ions in the acidic medium. The corresponding molarity equation would be as given below:

$$\frac{M_{KMnO_4} V_{KMnO_4}}{M_{Fe(II)} V_{Fe(II)}} = \frac{1}{5} \qquad \ldots(3.5)$$

$$M_{KMnO_4} V_{KMnO_4} = M_{Fe(II)} V_{Fe(II)} \quad \ldots(3.6)$$

As you know, $KMnO_4$ is a secondary standard and has to be standardised against a primary standard. We would use oxalic acid as the primary standard in this experiment. The oxalate ions get oxidized to CO_2 as per the following equation:

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \quad \ldots(3.7)$$

The overall reaction between permanganate ion and oxalate ion can be obtained by combining Eq. 3.2 and Eq. 3.7 with suitable balancing of electrons as follows:

$$[MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O] \times 2$$
$$[C_2O_4^{2-} \rightleftharpoons 2CO_2 + 2e^-] \times 5 \quad \ldots(3.8)$$
$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightleftharpoons 2Mn^2 + 10CO_2 + 8H_2O$$

As per equation 3.8, two moles of permanganate ions oxidise 5 moles of oxalate ions in the acidic medium. The corresponding molarity equation would be as given below:

$$\frac{M_{Permanganate}\ V_{Permanganate}}{M_{oxalate}\ V_{oxalate}} = \frac{2}{5} \quad \ldots(3.9)$$

$$5M_{Permanganate}\ V_{Permanganate} = 2M_{oxalate}\ V_{oxalate} \quad \ldots(3.10)$$

3.3 REQUIREMENTS

Apparatus		Chemicals
Burette (50 cm^3)	1	Ferrous ammonium sulphate
Pipette (20 cm^3)	1	Oxalic acid
Conical flasks (250 cm^3)	2	Potassium permanganate
Test tube	1	Sulphuric acid (1 *M*)
Volumetric flask (250 cm^3)	1	
Beaker (250 cm^3)	1	
Weighing bottle	1	
Funnel (small)	1	
Wash bottle	1	
Burette stand and clamp	1	

Solutions Provided

Mohr's salt solution (8 g dm^{-3}): Prepared by taking accurately weighed about 8 g of Mohr's salt and transferring it to a volumetric flask of 1 dm^3 capacity. To this about 10 cm^3 of dilute H_2SO_4 (1 *M*) and about 50 cm^3 of distilled water is added to

dissolve the salt completely. The volume is then made up by adding more distilled water to the volumetric flask.

Approximately *M*/250 solution of potassium permanganate: Prepared by dissolving 0.16 g of potassium permanganate in distilled water and making up the volume of 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:

$$4KMnO_4 + 2H_2O \rightarrow 4KMnO_2 \downarrow + 4KOH + 3O_2$$

Indicator

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

3.4 PROCEDURE

As indicated above, you are provided with approximately *M*/250 potassium permanganate solution, and a solution of Mohr's salt which is to be estimated. You are required to prepare a standard solution of oxalic acid

There are three steps in the experiment.

1. Preparation of a standard solution of oxalic acid
2. Standardisation of given $KMnO_4$ solution by titrating against the standard solution of oxalic acid
3. Titration of given Mohr's salt solution with the standardised $KMnO_4$ solution

1. Preparation of standard oxalic acid solution (*M*/20)

Take approximate mass of a glass weighing bottle. Then weigh it accurately with about 0.32 g of oxalic acid. Transfer it 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 oxalic acid. The difference between the two masses gives the actual amount of oxalic acid transferred. Record these values in your observation note book. To the contents of the volumetric flask add about 30-40 cm^3 of distilled water, dissolve the acid completely; add more water, if necessary. Finally, make the volume upto the mark by adding distilled water carefully.

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

2. 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 the standard oxalic acid solution (20 cm^3) in a conical flask and add an equal volume of dil. sulphuric acid (1*M*) heat to 60°-70° C. **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 against $KMnO_4$ till a light but permanent pink colour is obtained. 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.

3. Titration of given Mohr's salt solution against standardised $KMnO_4$ solution

Pipette out the given Mohr's salt solution (20 cm^3), add equal volume of dil. H_2SO_4 and titrate against $KMnO_4$ solution as above. Repeat the titration till three concordant readings are obtained. Record the readings in Observation Table II.

3.5 OBSERVATIONS

Approximate mass of the weighing bottle $= m_1 =$……..g

Mass of bottle + oxalic acid (before transferring) $= m_2 =$……..g

Mass of bottle (after transferring the oxalic acid) $= m_3 =$…….g

Mass of oxalic acid transferred $= m_2 - m_3 = m =$ …...g

Molar mass of oxalic acid $= 126.06\ g\ mol^{-1}$

Volume of oxalic acid solution prepared (V) $= 250\ cm^3$

Molarity of oxalic acid solution (M_1)

$$= \frac{m \times 1000}{\text{Molar mass} \times 250} \text{mol dm}^{-3} = \frac{m \times 4}{126.06} \text{mol dm}^{-3}$$

Observation Table I: Titration of standard oxalic acid solution vs. Potassium permanganate

Sl. No.	Volume of Oxalic acid 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: Titration of given Mohr's salt solution vs. Potassium permanganate

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

3.6 CALCULATIONS

Estimation of the strength of potassium permanganate

Molarity of oxalic acid solution $= M_1 =$ ……..mol dm^{-3}

Vol. of oxalic acid 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. 3.10),

$$5M_{\text{Permanganate}}\, V_{\text{Permanganate}} = 2M_{\text{oxalate}}\, V_{\text{oxalate}}$$

$5M_2V_2 = 2\ M_1V_1$

Molarity of $KMnO_4$ solution

$$M_2 = \frac{2M_1V_1}{5V_2} \text{ =……..mol dm}^{-3}$$

Estimation of strength of given Mohr's salt solution

Molarity of $KMnO_4$ $= M_3 = M_2 =$ …… mol dm^{-3} or M

Vol. of $KMnO_4$ solution used $= V_3 =$ …… cm^3

Vol. of Mohr's salt solution taken $= V_4 = 20$ cm^3

Molarity of Mohr's salt $= M_4 =$?

Using the molarity equation (3.6),

$$5M_{\text{Permanganate}}\, V_{\text{Permanganate}} = M_{\text{Mohr's salt}}\, V_{\text{Mohr's salt}}$$

$5M_3\ V_3 = M_4\ V_4$

Molarity of Mohr's salt solution

$$M_4 = \frac{5M_3V_3}{V_4} = \text{..... mol dm}^{-3}$$

Strength of Mohr's salt (anhydrous) = $M_4 \times 284$ g dm^{-3}

= B = _____ g dm^{-3}

Determination of number of water of crystallisation

The amount of Mohr's salt taken to prepare the solution = A g

(Your counsellor would tell you the amount of Mohr's salt actually taken)

The amount of anhydrous salt determined by permanganatometry = B g

According to Eq.3.1

$$\frac{\text{A}}{\text{B}} = \frac{284 + 18x}{284} \qquad \ldots(3.1)$$

Substitute the values of A and B and solve for x.

3.7 RESULT

The number of water of hydration in Mohr's salt = …….

The above value can be compared with the actual one given on the bottle of Mohr's salt.

EXPERIMENT 4

ESTIMATION OF IRON(II) IONS BY CHROMATOMETRY USING INTERNAL INDICATOR

Structure

4.1 INTRODUCTION

You have studied about the concept of redox titrations and performed one such type of titration called permanganatometry in Experiment 2. In permanganatometric titration you used potassium permanganate as the oxidising agent to estimate the strength of given oxalic acid solution. In the fourth experiment you will perform another redox titration which makes use of potassium dichromate as the oxidising agent. This type of titration is called chromatometry. Dichromate acts as an oxidising agent only in the acidic medium. The general theory behind chromatometry is the same as that 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 in the following sections. The theory behind the colour change of indicators is also explained.

Expected Learning Outcomes

After performing the experiment, you should be able to:

- define chromatometry as a redox titration;
- state and explain the principle of chromatometry;
- list the apparatus and chemicals required for the estimation of Fe(II) ions in the given solution by chromatometry;

- ❖ record the observations of the titration performed;
- ❖ calculate the molarity and the strength of the given Fe(II) solution; and
- ❖ report the result of the titration performed.

4.2 PRINCIPLE

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

$$\underset{(+6\,\text{state})}{Cr_2O_7^{2-}} + 14H^+ + 6e^{-+} \rightleftharpoons \underset{(+3\,\text{state})}{2Cr^{3+}} + 7H_2O, \quad (E^0 = 1.33\,V) \qquad \ldots(4.1)$$

Fe^{2+} ions when titrated with dichromate get oxidised to Fe^{3+} as per the following equation.

(cf. Eq. 2.1 in Experiment 2):

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \quad (E^0 = 0.77\,V) \qquad \ldots(2.1)$$

The overall ionic equation of the titration can be obtained by adding Eq. 4.1 and Eq. 2.1 after balancing the number of electrons between them as follows:

$$[Fe^{2+} \rightleftharpoons Fe^{3+} + e^-] \times 6 \qquad \ldots(4.2)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad \ldots(4.1)$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad \ldots(4.3)$$

We see from Eq. 4.3 that one mole of potassium dichromate reacts with 6 moles of iron (II) ions in solution. Therefore, substituting the values of *p* and *q* in the molarity equation, the molarities are related as:

$$\frac{M_D V_D}{M_{Fe} V_{Fe}} = \frac{1}{6}$$

or $$6M_D V_D = M_{Fe} V_{Fe} \qquad \ldots(4.4)$$

where M_D and M_{Fe} represent the molarities of potassium dichromate and iron (II) solutions and V_D and V_{Fe} 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).

$$1\,\text{mole}\ K_2Cr_2O_7 = 6\ \text{moles}\ Fe(II)$$

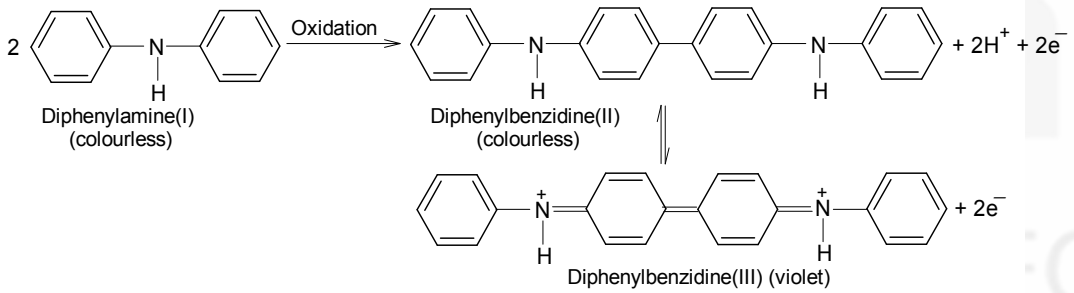
Potassium dichromate does not oxidise HCl, whereas $KMnO_4$ oxidises it to Cl_2. Hence, $KMnO_4$ cannot be used as an oxidising agent in estimating metal ions where the solution is made using HCl, whereas $K_2Cr_2O_7$ can be used in such cases too. Since, metals are leached out from their minerals with 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. 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 1

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].

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

SAQ 2

In the following put a tick mark ($\surd$) on the correct and cross ($\times$) on the wrong statements.

$K_2Cr_2O_7$ is superior to $KMnO_4$ because:

i) $K_2Cr_2O_7$ 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*M* or 2*M*.

iv) $K_2Cr_2O_7$ can be easily weighed.

4.3 REQUIREMENTS

Apparatus		Chemicals
Burette (50 cm^3)	1	Ferrous ammonium sulphate
Pipette (20 cm^3)	1	Sulphuric acid, dilute (1 *M*)
Conical flask (250 cm^3)	1	Phosphoric acid (85%)
Beaker (250 cm^3)	1	
Weighing bottle	1	
Funnel (small)	1	
Volumetric flask (250 cm^3)	1	
Wash bottle	1	
Burette stand	1	

Solutions Provided

Ferrous ammonium sulphate solution (unknown concentration): Prepared by dissolving about 8.0 g of ferrous ammonium sulphate in distilled water and dilute H_2SO_4 and making up the volume to 1 dm^3.

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).

4.4 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 about *M*/300 solution of $K_2Cr_2O_7$, which would act as an intermediate and needs to be standardised with a standard solution of ferrous ammonium sulphate.

This experiment has three steps as given below:

1. Preparation of standard solution of ferrous ammonium sulphate
2. Standardisation of given solution of potassium dichromate with standard solution of ferrous ammonium sulphate
3. Titration of given solution of ferrous ammonium sulphate with the standardised solution of potassium dichromate

1. Preparation of *M*/50 ferrous ammonium sulphate solution

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 (1*M)* 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.

2. 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 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.

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

3. Titration of the given ferrous ammonium sulphate 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 ferrous ammonium sulphate solution instead of standard ferrous ammonium sulphate solution. Record the observations in Observation Table II.

4.5 OBSERVATIONS

Approximate mass of the weighing bottle $= m_1 =$……..g

Mass of bottle + ferrous ammonium sulphate (before transferring 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)

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

$$= \frac{M \times 4}{392.15} \text{mol dm}^{-3} = ... \text{mol dm}^{-3}$$

Observation Table I: Titration of standard FAS solution vs. Potassium dichromate solution

Sl. No.	Volume of FAS solution (cm^3)	Burette reading		Volume of $K_2Cr_2O_7$ (cm^3) (Final — Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II: Titration of given FAS solution vs. Potassium dichromate solution

Sl. No.	Volume of FAS solution (cm^3)	Burette reading		Volume of $K_2Cr_2O_7$ (cm^3) (Final — Initial)
		Initial	Final	
1	20			
2	20			
3	20			

4.6 CALCULATIONS

Standardisation of $K_2Cr_2O_7$

Molarity of FAS solution = M_1 = …… mol dm^{-3}

Volume of FAS solution taken = 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,

$M_1V_1 = 6\ M_2V_2$

Molarity of $K_2Cr_2O_7$

$$M_2 = \frac{M_1V_1}{6V_2} = ... \text{ mol dm}^{-3}$$

Estimation of strength of given Iron (II) solution (FAS)

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

Volume of $K_2Cr_2O_7$ solution used = V_3 = 20 cm^3

Volume of iron(II) solution taken = V_4 = 20 cm^3

Molarity of iron(II) solution = M_4 =?

Using the molarity equation,

$$M_4 = \frac{6M_3V_3}{V_4}$$

Molarity of Fe(II) ions = …….. mol dm^{-3}

Strength of iron(II) ions in the given FAS solution

= Molarity of iron (II) ions in the given solution × molar mass

= $M_4 \times 392.15$ g dm^{-3}

= …… gdm^{-3}

4.7 RESULT

The strength of Fe(II) ions in the given FAS solution is found to be = … g dm^{-3}

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

4.8 ANSWERS

Self-Assessment Questions

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

$[2FeSO_4 + H_2SO_4 + (O) \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3$

$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$

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

2) i) √

ii) ×

iii) √

iv) ×

EXPERIMENT 5

ESTIMATION OF COPPER(II) IONS IODOMETRICALLY

Structure

5.1 INTRODUCTION

In the previous three experiments, you have performed two types of redox titrations, namely, permanganatometry and chromatometry. In this experiment, you would estimate the amount of copper (II) ions in a given sample solution using iodine as the reducing agent. You will realise that this experiment is also based on the principle of redox reactions. The redox reactions that make use of iodine can take place in two ways as described in the next section. These titrations make use of I_2/I^- redox reaction and the end point is detected by using starch as an indicator. The theory behind the iodometric estimation of cupric ions, Cu^{2+} is given along with the procedural details of the experiment.

Expected Learning Outcomes

After performing the experiment, you should be able to:

- define and differentiate between iodometry and iodimetry;
- state and explain the principle of iodometry;
- record the observations of the experiment;

- ❖ use the iodometric method in estimating Cu^{2+} ions; and
- ❖ calculate the strength of the Cu(II) ions in the given solution.

5.2 IODIMETRY AND IODOMETRY

Iodine is a mild oxidising agent and in the presence of a suitable reducing agent, it gets reduced to iodide ions, I^- according to the following equation:

$$I_2 + 2e^- \rightleftharpoons 2I^-,\ E^0 = 0.54\ V \quad \ldots (5.1)$$

On the other hand, a number 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.** However, 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.

Iodimetric titrations are used for estimating reducing agents while iodometric titrations are used for oxidising agents.

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.

Iodimetry: Titration with iodine

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.

Iodometry: Titration of iodine produced by a chemical reaction

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:

$$I_2 + Na_2S_2O_3 \rightleftharpoons 2NaI + Na_2S_4O_6 \quad \ldots (5.2)$$

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.

$$KI_2 + I_2 \rightleftharpoons K^+[I_3]^-$$

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 the 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.

5.2.1 Indicator in Titrations Involving Iodine

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. As 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 Sodium Thiosulphate

As explained 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 with the CO_2 dissolved in water. More so, even some microorganisms can decompose thiosulphate. Therefore, we do not use thiosulphate as a primary standard and its solution is standardised.

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:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \quad \ldots (5.3)$$

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,

$$6I^- \rightleftharpoons 3I_2 + 6e^- \quad \ldots (5.4)$$

The overall ionic equation for the titration can be obtained by adding Eq.5.3 and Eq. 5.4,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow Cr^{3+} + 3I_2 + 7H_2O \quad \ldots (5.5)$$

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,

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^- \quad \ldots (5.6)$$

$$I_2 + 2e^- \rightleftharpoons 2I^- \quad \ldots (5.1)$$

Since three moles of I_2 are liberated by one mole of $Cr_2O_7^{2-}$

$$3I_2 + 6e^- \rightleftharpoons 6I^- \quad \ldots (5.7)$$

The overall ionic equation for the titration of liberated I_2 with sodium thiosulphate can be obtained by adding Eq. 5.6 (multiplied by three) and Eq. 5.7,

$$[2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-] \times 3 \quad \ldots (5.6)$$
$$3I_2 + 6e^- \rightleftharpoons 6I^- \quad \ldots (5.7)$$
$$3I_2 + 6S_2O_3^{2-} \rightarrow 6I^- + 3S_4O_6^{2-} \quad \ldots (5.8)$$

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,

$$Cr_2O_3^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O \quad \ldots (5.5)$$
$$3I_2 + 6S_2O_3^{2-} \rightarrow 6I^- + 3S_4O_6^{2-} \quad \ldots (5.8)$$
$$Cr_2O_7^{2-} + 14H^+ + 6S_2O_3^{2-} \rightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O \quad \ldots (5.9)$$

We see from Eq. 5.9 that one mole of potassium dichromate is equivalent to 6 moles of sodium thiosulphate. Therefore, substituting the values in the molarity equation, the molarities are related by the following relationship.

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

or $$6M_1V_1 = M_2V_2$$

where M_1 and M_2 represent the molarities of potassium dichromate and sodium thiosulphate solutions and V_1 and V_2 are their volumes, respectively.

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.

5.3 ESTIMATION OF Cu(II) IONS IODOMETRICALLY USING SODIUM THIOSULPHATE

To determine the strength of Cu(II) ions in a given solution, it can be titrated against a standardised solution of sodium thiosulphate in the presence of an excess of KI using starch as an indicator. The type of titration involved is called iodometric titration. Let us learn the principle and the equations involved in the titration.

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 $S_2O_6^{2-}$, tetrathionate ion and reduction of Cu^{2+} to Cu^{+}. The reaction between Cu^{2+} and KI is given as,

$$2I^- \rightleftharpoons I_2 + 2e^- \quad \ldots (5.10)$$

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \quad \ldots (5.11)$$

Balancing the reaction between Cu^{2+} and potassium iodide by combining Eq. 5.10 and Eq. 5.11, we get,

$$2I^- \rightleftharpoons I_2 + 2e^- \quad \ldots (5.10)$$

$$Cu^{2+} + e^- \rightleftharpoons Cu^+] \times 2 \quad \ldots (5.11)$$

$$2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2 \quad \ldots (5.12)$$

We see that two moles of Cu^{2+} react with two moles of potassium iodide and liberates iodine. The liberated iodine reacts with sodium thiosulphate, in the following manner:

$$2S_2O_3^2 \rightleftharpoons S_4O_6^{2-} + 2e^- \quad \ldots (5.6)$$

$$I_2 + 2e^- \rightleftharpoons 2I^- \quad \ldots (5.7)$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \quad \ldots (5.8)$$

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.

$$2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2 \quad \ldots (5.12)$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \quad \ldots (5.8)$$

$$2Cu^{2+} + 2S_2O_3^{2-} \rightarrow 2Cu^+ + S_4O_6^{2-} \quad \ldots (5.13)$$

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 the molarity equation, the molarities are related by the following relationship:

$$\frac{M_3}{M_4}\frac{V_3}{V_4} = \frac{1}{1}$$

or $M_3V_3 = M_4V_4$

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:

$$2Cu^{2+} + \underset{\text{(excess)}}{KI} \longrightarrow 2CuI + 4K^{+} + I_2 \quad \ldots (5.14)$$

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,

$$Cu^{2+} + e^{-} \rightleftharpoons Cu^{+} \qquad E^0 = 0.17\,V \quad \ldots (5.15)$$

$$I_2 + 2e^{-} \rightleftharpoons 2I^{-} \qquad E^0 = 0.17\,V \quad \ldots (5.16)$$

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) sulphate with thiosulphate in presence of excess KI. [Hint: It involves two steps]

5.3.2 Requirements

Apparatus	No.	Chemicals
Burette (50 cm^3)	1	Potassium dichromate
Pipette (20 cm^3)	1	Dilute sulphuric acid
Conical flasks (250 cm^3)	1	Potassium iodide
Beaker (250 cm^3)	1	Glacial acetic add
Funnel (small)	1	Potassium ammonium thiocyanate
Volumetric flask (250 cm^3)	1	Distilled water
Measuring cylinder (10 cm^3)	1	Copper sulphate pentahydrate
Test Tube	1	Sodium thiosulphate
Wash bottle	1	Starch
Weighing bottle	1	Dil. ammonia solution
Volumetric flask (1000 cm^3)	1	
Burette stand	1	

Solutions Provided

Procedures for the preparation of these solutions are given for the sake of information. These solutions would be prepared by the counsellor.

Preparation of solution of Cu^{2+} ions

Weigh accurately 1.25 g of copper sulphate petahydrate and transfer it to a 250 cm^3 standard flask. Dissolve it in 20 cm^3 of water add 1-2 cm^3 of glacial acetic acid and make up to 250 cm^3 with water to prepare the *M* /50 standard solution.

The solution of copper sulphate undergoes hydrolysis. To prevent this, mineral acids like sulphuric acid is added to the solution but the reaction between KI and $CuSO_4$ to liberate iodine does not occur in the presence of any mineral acid. Hence the acid added to copper sulphate solution is neutralised by adding a slight excess of ammonia. The excess ammonia is then neutralised with acetic acid.

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 100 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

The iodometric determination of a solution of Cu(II) ion involves three steps as follows:

1. Preparation of standard solution of potassium dichromate
2. Standardisation of sodium thiosulphate solution by titrating against standard solution of potassium dichromate
3. Titration of the given Cu(II) ion solution against the standardised solution of sodium thiosulphate

The three steps are explained below.

1) Preparation of *M*/300 standard solution of potassium dichromate

Take approximate mass of a glass weighing bottle. Then weigh it accurately with about 0.245 g of potassium dichromate. 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 potassium dichromate. The difference between the two masses gives the actual amount of potassium dichromate transferred. Record these values in your observation note book. Finally, make the volume upto the mark by adding distilled water carefully.

2) 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 air. 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 the solution becomes a light pale yellow in colour. 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.

3) Titration of copper (II) solution against standardised sodium thiosulphate solution

Pipette out 20 cm^3 of the given solution of Cu(II) ions 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?

SAQ 4

Why is sodium hydrogen carbonate or sodium bicarbonate added in the standardisation of sodium thiosulphate using potassium dichromate as titrand?

5.3.4 Observations

Mass of weighing bottle = m_1= …….g

Mass of bottle + potassium dichromate = 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

$$= \frac{m \times 4}{\text{Molar mass}} \text{mol dm}^{-3}$$

$$= \frac{m \times 4}{294.19} \text{mol dm}^{-3}$$

= ……. mol dm^{-3}

Observation Table I: Potassium dichromate solution vs. sodium thiosulphate solution

Sl. No.	Volume of $K_2Cr_2O_7$ acid 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: Titration of given solution of Cu (II) ions vs. standardised sodium thiosulphate solution

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

Standardisation 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 (from Table I) = V_2 = ……. cm^3

Molarity of $Na_2S_2O_3$ solution = M_2 = ?

Using the molarity equation,

$$6M_1V_1 = M_2V_2$$

Molarity of $Na_2S_2O_3$ solution $= M_2 = \dfrac{6M_1V_1}{V_2}$

= …….. mol dm^{-3}

Estimation of the strength of given Copper (II) solution

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 $M_4\ V_4 = M_3\ V_3$

Molarity of copper (II) solution $= M_4 = \dfrac{M_3V_3}{V_4}$ = ... mol dm^{-3}

The strength of the given Cu (II) solution =

Molarity of the solution $\times$ atomic mass of copper $= M_4 \times 63.5 =$ .....g dm^{-3}

5.3.6 Results

The strength of Cu (II) ions in the given solution is found to be = …….g dm^{-3}

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

5.4 ANSWERS

Self-Assessment Questions

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. $2CuSO_4 + 4KI \rightarrow 2CuI + 2K_2SO_4 + I_2$

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

   $2CuSO_4 + 4KI + 2Na_2S_2O_3 \rightarrow 2CuI + 2K_2SO_4 + 2NaI + Na_2S_4O_6$

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.

EXPERIMENT 6

DETECTION OF EXTRA ELEMENTS (N, S, X) IN THE ORGANIC COMPOUNDS

Structure

6.1 INTRODUCTION

So far in this course we have introduced you to simple laboratory technique of volumetric analysis in which you have learnt how the different types of titrations are carried out. These quantitative analyses are useful in the determination of amount of constituents in mixtures. The compounds isolated from an organic reaction mixture or from some natural source may be unknown. Identification and characterization of the structures of unknown substances constitute vital part of organic chemistry. Introduction into this area is provided by a study of qualitative organic analysis, which is an essential part of the training of an organic chemist.

In this experiment, first we shall give you an overview of the stepwise procedures that may be followed to identify a pure unknown compound using classical methods. Then, we shall give you details of experimental procedure for detection of extra elements such as nitrogen, sulphur and halogens in the given organic samples.

In recent years, the development of chromatographic methods of separation and analysis by spectroscopic techniques have revolutionised the qualitative organic analysis. The chromatographic methods of separation will be discussed in consecutive experiments and spectroscopic methods will be discussed at higher level.

Expected Learning Outcomes

After performing the experiment, you should be able to:

- describe the steps involved in the identification of unknown compounds by classical qualitative organic analysis;
- carry out the physical examination of organic compounds;
- write chemical equations for various reactions taking place while carrying out various tests for elemental analysis; and
- perform experiments for detection of extra elements such as nitrogen, sulphur and halogens in the given organic samples.

6.2 CLASSICAL QUALITATIVE ORGANIC ANALYSIS FOR IDENTIFICATION OF A PURE COMPOUND

The classical qualitative organic analysis consists of a series of steps that help to establish the identity of the unknown compound. These steps are:

Step 1. Physical examination

Step 2. Elemental analysis to determine the presence of elements other than carbon, hydrogen and oxygen

Step 3. Solubility test in water, dilute bases and dilute acids

Step 4. Determination of physical constants such as melting point and boiling point

Step 5. Functional group analysis using classification tests

Step 6. Preparation of derivatives

Steps 1 to 4, are called preliminary tests. While analysing organic compounds, we can follow these four steps in any order but before performing the qualitative tests for functional groups. Our final step must always be the preparation of one or more solid derivatives. For performing final step, you need a good understanding of preparative laboratory techniques. These techniques will be discussed in Semester II Laboratory course.

Preliminary tests give us very important clues about the presence or absence of certain class of the compounds. In this experiment we shall consider only the basic preliminary steps 1: physical examination and 2: elemental analysis.

In an organic compound, elements carbon, hydrogen and oxygen are assumed to be present commonly. In addition to these elements, they may also contain nitrogen, sulphur and halogens (chlorine, bromine and iodine). The elements nitrogen, sulphur and halogens are called as extra elements.

The identification of extra elements in a given compound is a type of qualitative analysis since the experiment is dealing with the composition of an unknown compound. This experiment must be performed very carefully as further analysis of the functional groups present in organic compounds is according to the elements present in them. Experiments based on all the six steps used for classical organic qualitative analysis will be performed in Semester III Laboratory course. Let us discuss these basic preliminary steps 1and 2.

6.2.1 Physical Examination

In the physical examination, we consider the following points:

Check the sample purity: In this lab course we are providing unknown organic compounds in pure form so it is not necessary for you to check the sample purity. Otherwise, first step of qualitative organic analysis is the purity checked by boiling point or melting point determination or using chromatographic methods.

Note the physical state: The physical state of the compound whether it is solid or liquid should be indicated.

Note the colour: The colour is also informative. Common coloured compounds include nitro and nitroso compounds (yellow), *α*-diketones (yellow), quinines (yellow to red), azo compounds (yellow to red). Phenols and amines are often brown to dark- purple because of traces of air oxidation products.

Caution: Do not taste an unknown compound. To note the odour, cautiously smell the compound. Many organic compounds are intensely lachrymatory or worse.

Note the odour: The odour of many organic compounds is highly distinctive. Amines are recognisable by their fishy odour, esters are often pleasantly fragrant. Alcohols, ketones, aromatic hydrocarbons and aliphatic alkenes have characteristic odours. Thiols, isonitriles and low-molecular weight carboxylic acids possess unpleasant odours.

Make an ignition test: Take a small amount of given sample on a spatula and heat the spatula on a burner to see if the solid melts normally and then burns.

Observe the flammability and nature of the flame. A yellow, sooty flame is indicative of an aromatic or a highly unsaturated aliphatic compound, a yellow but nonsooty flame is characteristic of aliphatic compounds. Halogenated or highly oxygenated compounds often burn with difficulty or not at all (for example carbon tetrachloride is used as fire-extinguisher).

The characteristic odour of sulphur dioxide indicates the presence of sulphur in compound. Certain compounds like sugars char and leave a black residue on the spatula and emit a characteristic odour.

If a white, non-volatile residue is left after ignition, add a drop of water and treat the solution with litmus or pH paper. A sodium (or other metal) salt is indicated by the colour change to basic colour.

Activity: Carry out Physical Examination and Ignition Test of Some Organic Compounds

For this activity we are providing six organic compounds.

Requirements:	**Chemicals**	**Apparatus**
	Samples	Burner
		Spatula

Procedure

Take six organic samples from your counsellor and follow the procedure as mentioned above for physical state, colour, odour and ignition test for each sample. Do not throw your samples after performing these tests; you will need these samples for detection of extra elements.

Report your results in Table 1 given below:

Table 1: Physical examination of organic compounds

Sample No.	Physical state	Colour	Odour	Ignition test	Conclusion (Aromatic or Aliphatic)
1.					
2.					
3.					
4.					
5.					
6.					

Discuss your results with your counsellor.

SAQ 1

What kind of flame would you expect to see in an ignition test of the following compounds?

a) Oxalic acid

b) Benzoic acid

c) D-Glucose

d) 1-Naphthol

6.2.2 Elemental Analysis

The technique of elemental analysis involves the determination of elements which may be present in a compound. The halogens, sulphur, oxygen, and nitrogen are the elements other than carbon and hydrogen that are most

commonly found in organic molecules. There is no direct method for detection of oxygen. Its presence as part of a functional group becomes apparent later when you perform tests for functional groups in the Semester III Laboratory course. Presence of other hetero atoms may be detected using the **Lassaigne fusion** technique where the organic compound is heated with metallic sodium, or by **Middleton's fusion** technique using sodium carbonate and zinc in place of sodium.

In both methods analysis is based on the conversion of the hetero atoms present in the compound to water soluble inorganic salts such as cyanide, sulphide or halide.

Bonding in organic compounds is generally covalent, therefore, like inorganic compound, no direct method available for the detection of elements. In sodium fusion method covalent bonds of hetero atoms are broken on heating of organic compound with sodium metal. This result in the formation of inorganic ions involving these elements: X^- ions from halogens, S^{2-} ions from sulphide, CN^- ions from nitrogen. These ions can in turn be readily identified by inorganic qualitative methods.

$$C,N \xrightarrow[2)\ H_2O]{1)\ Na \text{ or } Zn/Na_2CO_3} Na^+CN^-$$

$$S \xrightarrow[2)\ H_2O]{1)\ Na \text{ or } Zn/Na_2CO_3} Na_2^+S^{2-} \text{ or } ZnS$$

$$X \xrightarrow[2)\ H_2O]{1)\ Na \text{ or } Zn/Na_2CO_3} Na^+X^-$$

X may be Cl, Br, I

Though, Middleton's method is less hazardous and also considered to be superior to Lassaigne fusion for the analysis of volatile compounds. But, for this method very pure zinc powder is required. In this course, we shall consider the Lassaigne fusion method first and then at the end of this experiment, detailed method of preparation of aqueous solution for the elemental tests using Middleton's method will also be given. You can follow any method depending upon the facilities available at your study centre.

6.3 EXPERIMENT: DETECTION OF NITROGEN, SULPHUR AND HALOGENS BY LASSAIGNE SODIUM FUSION METHOD

Owing to its potentially hazardous nature, the fusion operation should be carried out very carefully. Keep your face away from the mouth of the test tube at all times.

Avoid pointing the fusion tube in the direction of anybody else.

For this experiment, we will be using same six compounds which you have used for carrying out physical examination.

6.3.1 Introduction

The basis of the sodium fusion procedure is as follows. On fusion with sodium the elements present in organic compounds are converted to ionic forms involving nitrogen, sulphur and halogens if they were present in the organic compound. As mentioned above, nitrogen present in organic compounds gets converted to cyanide ions, sulphur present in organic compounds to sulphide ions and halogens present in organic compounds to halide ions. After the organic compound has been heated with sodium metal, the residue is hydrolysed with distilled water to destroy the excess sodium and dissolve the inorganic ions that are formed as a result of fusion reactions.

$$Na + C,N \xrightarrow[2)\ H_2O]{1)\ Na} Na^+CN^-$$
Sodium cyanide

$$Na + S \xrightarrow[2)\ H_2O]{1)\ Na} Na_2^+S^{2-}$$
Sodium sulphide

$$Na + X \xrightarrow[2)\ H_2O]{1)\ Na} Na^+X^-$$
Sodium halide

X = Cl, Br or I

The aqueous solutions of these ions are divided into five portions and each can be analysed by using following qualitative tests:

If, nitrogen and sulphur are present in sample, they will give precipitate with silver nitrate.

$NaCN + AgNO_3 \rightarrow AgCN\downarrow + NaNO_3$ (white ppt.)

$Na_2S + AgNO_3 \rightarrow Ag_2S + NaNO_3$ (black ppt.)

These precipitates may interfere with the halogen test. Thus, it becomes necessary to remove cyanide and sulphide ions from sodium fusion extract before performing test for halogens.

i) Detection of Nitrogen

First portion of the aqueous solution is carefully acidified, followed by addition of $FeSO_4$, and then $FeCl_3$. This converts the cyanide ions into ferric ferrocyanide, which precipitates as an intense blue solid called **'Prussian blue'**.

$$6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$
Sodiun ferrocyanide

$$Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$
Ferriferrocyanide (Prussain blue)

ii) Detection of Sulphur

In second portion of aqueous solution the sulphur can be detected by precipitation as black lead sulphide with lead acetate solution and acetic acid or by the appearance of violet or purple colour on addition of di-sodium pentacyanonitrosylferrate (II) (sodium nitroprusside) in the third portion.

$$Na_2S + Pb(CH_3COO)_2 \longrightarrow PbS\downarrow + 2CH_3COONa$$
Lead sulphide (Black)

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$
Sodium nitroprusside — Sodium thionitroprusside (Purple)

iii) Detection of Nitrogen and Sulphur when present together

When both nitrogen and sulphur are present together in an organic compound, sodium thiocyanate is formed during sodium fusion. Their presence can be detected by the appearance of blood red colour due to the formation of complex ion thiocyanotoiron(III) on addition of ferric chloride solution in the fourth portion of aqueous solution.

$$NaCNS + FeCl_3 \longrightarrow [Fe(CNS)]_2^+ + 2Na^+ + 3Cl^-$$
Sodium thiocyanate — Blood red colour

iv) Detection of Halogens

Fifth portion of aqueous solution is acidified with dilute nitric acid and boiled to remove any sulphide or cyanide ions that are expelled as hydrogen sulphide or hydrogen cyanide, respectively. Sulphide and cyanide must be removed because they interfere with the test for halogens. Divide this portion in two parts. In the first portion add silver nitrate solution. Presence of halogen in the compound is detected by the formation of a precipitate of silver halide:

$$NaX + AgNO_3 \longrightarrow AgX + NaNO_3$$

The colour of the precipitate provides a tentative indication of the halogen present:

AgCl (White precipitate)

AgBr (Light yellow precipitate)

AgI (Dark yellow precipitate)

After completing the first step, add ammonium hydroxide to dissolve the precipitate obtained on addition of silver nitrate. It is observed that the white precipitate of silver chloride is soluble, the light yellow precipitate of silver bromide is sparingly soluble and the dark yellow precipitate of silver iodide is insoluble.

$$AgX + 2NH_4OH \longrightarrow [Ag(NH_3)_2]X + 2H_2O$$

Positive identification of halide ions can be made by the following inorganic qualitative test. Add carbon tetrachloride or chloroform, and chlorine water to the second part of fifth portion of aqueous solution. Shake the solution and check the colour of chloroform or carbon tetrachloride layer (lower layer). Violet colour is due to iodide ions, orange or brown colour is due to bromide ions and no colour and positive test with $AgNO_3$ indicate the presence of chloride ions.

$$2NaBr \xrightarrow{Cl_2} 2NaCl + Br_2$$

$$2NaI \xrightarrow{Cl_2} 2NaCl + I_2$$

SAQ 2

Discuss the role of sodium metal in fusion reaction.

SAQ 3

Why is it necessary to remove cyanide and sulphide ions from the sodium fusion extract before testing for the presence of halide ions tests?

6.3.2 Requirements

Apparatus

Apparatus for filtration (Fig. 6.1)

Burner

China dish

Five fusion tubes

Five test tubes

Spatula

Test-tube stand

Tongs

Tripod stand

Wire gauze

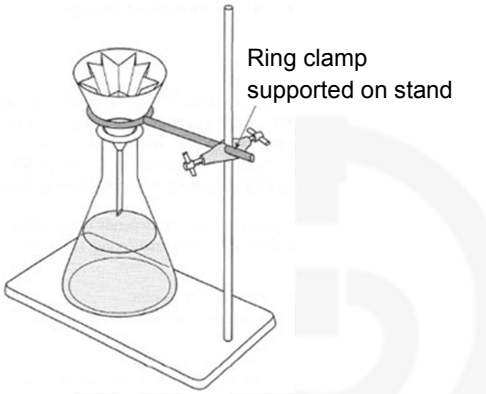


Fig. 6.1: Apparatus for filtration of fusion products

Chemicals

Acetic acid

Ammonium hydroxide

Carbon tetrachloride or Chloroform

Chlorine water

Dilute hydrochloric acid (5 %)

Dilute nitric acid (5 %)

Dilute sulphuric acid (5 %)

Iron(II) sulphate (Ferrous sulphate)

Iron(III) chloride, (Ferric chloride) (5%).

Lead acetate solution (0.15 M)

Samples of organic compounds

Silver nitrate solution (5%)

Sodium metal (4mm cube)/ Zinc dust + Sodium carbonate

Solution of disodium pentacyanonitrosylferrate (II) (0.1%) (Sodium nitroprusside)

6.3.3 Procedure

Add 15 cm^3 of distilled water into a clean china dish and place it near to your burner. Place about 20 mg of your sample in the bottom of a small fusion tube or in case of liquid take one or two drops of liquid in the fusion tube with the help of a pipette or dropper. Use tongs to hold the fusion tube. Put a piece of sodium roughly a 4 mm cube into the mouth of the test tube, without allowing it to come into contact with the substance at the bottom. Heat the sodium gently over a small flame until it melts and runs down into the sample. There may be a very vigorous reaction when the molten sodium touches the sample. Heat the tube gently for one minute; and then heat more strongly until the bottom of the tube glows red hot. Holding the wire gauze with tongs in your free hand, drop the red hot fusion tube into the water of china dish and cover it immediately with the wire gauze. If the fusion tube does not break, when it comes in contact with water, crush it with the help of a glass rod. Allow any excess sodium to react. You may repeat the process of sodium fusion using one or more ignition tubes to obtain concentrated test solution. Place the

Caution: Manipulate sodium with a knife and tongs or forceps. Never touch it with fingers. Wipe it free of kerosene with dry filter paper.

Red hot fusion tube will shatter on contact with water releasing any unreacted sodium, and the wire gauze will stop the loss of any material.

Do not throw any piece of sodium into the sink. It may cause fire.

The heating of aqueous solution with HNO_3 has the effect of removing any HCN or H_2S, if cyanide or sulphides are present which would interfere with halogen test. It may be omitted if nitrogen and sulphur have been shown to be absent.

china dish on the wire gauze on a tripod stand and boil the solution for two minutes (see Fig. 6.2). Filter the solution while hot, to remove the broken glass and charred material and divide this aqueous solution in five equal portions in five test tubes.

You may also perform Beilstein test for detection of halogens. Procedure is as follows:

Heat the tip of a copper wire in a burner flame until there is no further coloration of the flame. Let the wire cool slightly, then dip it into the fusion extract and again, heat it in the flame. A green flash is indicative of the presence of halogen. The Beilstein test is very sensitive, thus halogen-containing impurities may give misleading results. This test is unaffected by the presence of nitrogen.

$Cu + R–X \rightarrow H_2O + CO_2 + CuX$

Colour of flame is due to the formation of CuX (X = Cl, Br, I)

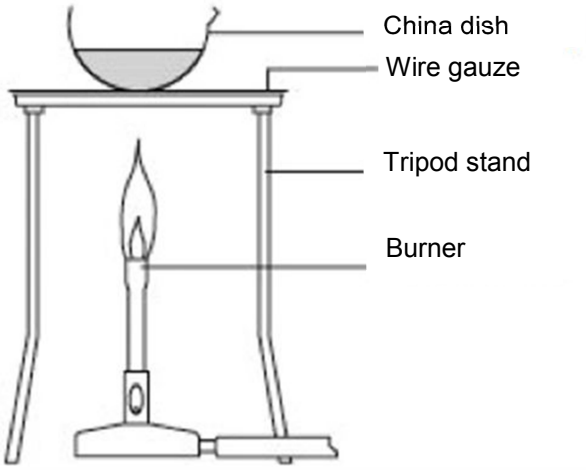


Fig. 6.2: Arrangement for boiling sodium fusion extract

1. Detection of Nitrogen

Add 200 mg of iron(II) sulphate to the first portion. Heat the solution to boiling and add 2 drops of ferric chloride solution. Add sufficient dilute sulphuric acid to dissolve any precipitate and make the solution acidic. The formation of a deep blue precipitate or colouration (Prussian blue) indicates the presence of nitrogen in the original organic compound. If the solution is green or blue-green, filter it; wash the filter paper with distilled water, and examine the residue for blue colouration.

2. Detection of Sulphur

i) Acidify the second portion of aqueous solution with acetic acid, and add a few drops of lead acetate solution. A black precipitate of lead sulphide, PbS indicates the presence of sulphur in the original organic compound.

ii) In the third portion of aqueous solution, add 2 cm^3 of disodium pentacyanonitrosylferrate (II) solution. The purple colouration which fades slowly on standing confirms that sulphur is present.

3. Detection of Nitrogen and Sulphur together

Acidify the fourth aqueous portion with dilute hydrochloric acid. Add a few drops of ferric chloride solution. Formation of blood red colour indicates the presence of both nitrogen and sulphur together in the given compound.

4. Detection of Halogens

To the fifth portion of aqueous solution, add sufficient nitric acid to render the solution acidic and boil the mixture until its volume has been halved. Divide this solution in two parts after cooling. In first part, add 1 cm^3 of silver nitrate solution. The observation of a white or yellowish thick precipitate indicates the presence of halogen in the original organic

compound. A faint turbidity should not be interpreted as a positive test. Tentative identification of the particular halogen may be made on the basis of colour: Silver chloride is white, silver bromide is pale yellow, and silver iodide is yellow. Now add 4-5 cm^3 ammonium hydroxide to the above precipitate and shake the contents. Observe the solubility of the precipitate. Complete solubility of white precipitate, indicates the presence of chlorine, a partial solubility of light yellow precipitate indicates the presence of bromine and insolubility of dark yellow precipitate indicates the presence of iodine in the organic compound.

To further confirm the presence of halogen, add 0.5 cm^3 of carbon tetrachloride or chloroform to the second part. Add chlorine water drop wise to the mixture with gentle shaking. The appearance of a brown colouration in the bottom layer indicates bromine, whereas a purple or violet colouration indicates iodine. By the process of elimination, a sample which gives a white precipitate with silver nitrate, but no colouration on treatment with chlorine water must contain chlorine.

Repeat above mentioned procedure for all given six organic compounds and report your results in Table 3.

6.3.4 Observations

Report your observations in detail for each sample in your practical note book in the format given below:

Table 6.2: Identification of extra elements in the given organic sample

Sample No.	Test	Observation	Inference
1.	Test for Nitrogen: ..... Test for Sulphur: ..... Test for Nitrogen and Sulphur present together: ..... Test for Halogens:		

6.3.5 Result

The given organic sample contains 1. ....., 2. ..... extra element(s).

Discuss your result with your counsellor.

Once you have completed experiments with these samples, try few more samples which may contain one or more than one extra element.

6.4 DETECTION OF NITROGEN, SULPHUR AND HALOGENS BY MIDDLETON'S METHOD

In this method an organic compound is heated with a mixture of sodium carbonate and zinc dust, nitrogen and halogens if present in the compound get converted into water soluble sodium cyanide and halides, respectively and sulphur gets converted into insoluble zinc sulphide. The water soluble cyanide and halogens so formed are detected as discussed earlier in Lassaigne's method, whereas insoluble zinc sulphide is treated with acid and hydrogen sulphide so evolved is detected by lead acetate.

Procedure

Add 15 cm^3 of distilled water into a clean china dish and place it near to your burner. Mix about 20 mg of the sample with a powdered mixture of zinc dust (10 mg) and sodium carbonate (15 mg) and transfer this mixture in a small fusion tube. In case of liquid take one or two drops of liquid in a fusion tube with the help of a pipette or dropper and add the powdered mixture of zinc dust and sodium carbonate. Use tongs to hold the fusion tube. Heat the fusion tube first gently over a small flame and then strongly till it becomes red hot.

Holding the wire gauze with tongs in your free hand, drop the red hot fusion tube into the water of china dish and cover it immediately with wire gauze. If the fusion tube does not break when it comes in contact with water, crush it with the help of a glass rod. Filter the solution whilst hot, preserve the residue divide the filtrate in three parts and perform the test for nitrogen and halogens as described in Lassainge's method. To the residue left in the china dish, add about 8 cm^3 of dilute hydrochloric acid, immediately cover the china dish with a filter paper moistened with lead acetate solution. Sulphur if present, in the form of zinc sulphide will react with HCl to form hydrogen sulphide and will turn lead acetate paper to brown or black due to formation of lead sulphide.

$$ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$$

$$H_2S + Pb(OAc)_2 \longrightarrow PbS + 2AcH$$

Black coloured ppt

6.5 LABORATORY NOTE BOOK PREPARATION

In the beginning of this course, we have discussed some important points which you should keep in mind while preparing a laboratory note book for Chemistry experiments. Here we will discuss a possible format for organic qualitative analysis experiments discussed above.

Each experiment should start on a fresh page, which should contain a title and experiment number at the top. A sample note book format for the identification of extra element(s) is given here.

Experiment No.....: Identification of extra element(s) in given organic sample (sample No....).

1. Physical Examination:

Sample No.	Physical state	Colour	Odour	Ignition test	Inference (Aromatic or aliphatic)
1.					

2. Elemental Analysis:

Sample No.	Test	Observation	Inference
1.	Test for Nitrogen: ..... Test for Sulphur: ..... Test for Nitrogen and Sulphur present together: ..... Test for Halogens:		

3. Result:

The given organic sample contains 1. ....., 2. ..... extra element(s).

6.6 ANSWERS

Self-Assessment Questions

1.

	Observation	Inference
a)	Non-sooty flame	Aliphatic Compound
b)	Sooty flame	Aromatic
c)	Charring with smell of sugar	Carbohydrate
d)	Sooty flame	Aromatic Compound

2. The organic compounds are basically of a chain of carbon atoms to which various other atoms are covalently attached. Sodium is a strong reducing agent that will cause the break of the carbon chain. It also will convert those other atoms that are covalently bonded to the carbon chain to inorganic ion. Note sodium itself is oxidized to Na^+ in this process.

3. When we carry out $AgNO_3$ test for halide ions, if cyanide and sulphide ion are also present in sodium fusion extract, they will also precipitate as AgCN and Ag_2S along with precipitate of silver halide. Therefore, it becomes necessary to remove CN^- & S^{2-} ions before performing $AgNO_3$ test for halide ions.

EXPERIMENT 7

SEPARATION AND IDENTIFICATION OF THE COMPONENTS OF A GIVEN MIXTURE OF AMINO ACIDS BY PAPER CHROMATOGRAPHY

Structure

7.1 INTRODUCTION

In chemistry, it is necessary to separate, isolate, purify and identify components of complex mixtures. Simple separation techniques such as distillation, crystallisation, extraction are quite useful when the components of mixture are chemically and physically different and are few in number. For example, the isolation of pure benzoic acid from its diethyl ether solution requires the use of distillation to remove the more volatile diethyl ether. The chemical structures, intermolecular forces and hence boiling points of these two substances differ considerably, allowing the use of such a technique of separation. However, where the components of a mixture resemble each other very closely in structure, simple separation techniques are of little value. For example, amino acids are closely related chemically and physically, none of the techniques mentioned above, can be used for the separation of such types of mixtures.

Similarly when, we carry out reactions in the laboratory, many a times the resulting product is not a single compound but a mixture having many components which are structurally related. Thus techniques are needed which could be used to separate such closely related substances. There are techniques, known as **chromatographic techniques** available for separation of such mixtures. In this experiment and in the next experiment, you will be studying about these techniques. You will also perform two experiments: Experiment 7 and Experiment 8 based on paper chromatography, which is one of the simplest chromatographic technique**.**

Expected Learning Outcomes

After performing the experiment, you should be able to:

- explain the meaning of the terms chromatography, stationary phase and mobile phase;
- explain the mechanisms of partition as applied to chromatography;
- calculate R_f values for different organic compounds;
- set up experimental arrangement for paper chromatography; and
- separate and identify amino acids from the mixture of two amino acids by paper chromatography.

7.2 THE ORIGINS OF CHROMATOGRAPHY

The word **chromatography** is Greek in origin (*chroma* - colour; *graph* - writing). The technique of chromatography was first applied to the separation of coloured pigments and dyestuffs, as evident from the pioneering work of Tswett who in 1906 separated the pigments from leaves into coloured bands by passing a solution of the pigments down a glass tube packed with powdered chalk. The separation of pigments that Tswett achieved was due to the process called **'adsorption'**. The most adsorbed pigment remains close to the top of the column and the least adsorbed pigment is 'washed through' to form the lowest band in the column.

The term *chromatography* is applied to the process which involves the distribution of a sample between a stationary phase and a mobile phase.

In 1941 Martin and Synge used liquid-impregnated columns of absorbent to obtain good separation of components in complex mixtures. The mechanism of separation was in this case a **partitioning** or **distribution phenomenon** involving each component in the mixture. We will consider the nature of these mechanisms of separation in more detail in the experiment part.

A. J. P. Martin and R. L. M. Synge were jointly awarded the Nobel Prize in 1952 for their work on partition chromatography.

Apart from column chromatography, many other chromatographic techniques were developed in last few decades. These can be listed as:

(1) Paper chromatography (PC)

(2) Thin-layer chromatography (TLC)

(3) Column chromatography (CC)

(4) Gas chromatography (GC)

(5) Gas-liquid chromatography (GLC)

(6) High resolution gas chromatography (HRGC)

(7) High performance liquid chromatography (HPLC).

The last four methods are useful in achieving a high degree of separation or resolution and often involve use of elaborate and expensive apparatus.

Chromatography is used to isolate, purify the components of complex mixtures in the laboratory both for analytical and preparative purposes. Chromatography is used in labs right from the simple techniques such as paper chromatography to the sophisticated ones such as Gas chromatography and HPLC which find applications in research labs and industries.

In this experiment, you will be using the simplest laboratory chromatographic method, paper chromatography "which is relatively cheap." Nevertheless, the basic principles remain the same and with skillful usage surprisingly good separations can be achieved. You will also do some experiments based on this chromatography during practical sessions. Let us now study the language of these techniques. But before that answer the following SAQ.

SAQ 1

Which of the following characteristics would you say must be present for a mixture to be satisfactorily separated by column chromatography? (Tick the correct choice).

a) Be coloured ☐

b) Be volatile ☐

c) Be related by similar chemical structure ☐

d) Show a differential adsorption to the column. ☐

7.3 TERMINOLOGY OF CHROMATOGRAPHY

Various terms are frequently used and they form the language of chromatographic techniques. These are explained below:

(i) Chromatography

The historical origins of the word chromatography have already been discussed earlier. All types of chromatography have certain basic features, although from the design of the apparatus, this may not be apparent. The basic methodology involved is as follows:

The mixture to be separated is added to a moving 'solvent' which may be liquid or gas. This moving stream, now containing components, is passed over or through a fixed medium, which is specially designed to separate the individual constituents in the original mixture.

However, there are many variations and hence in many cases, it is difficult to see the common link between the various chromatographic methods.

(ii) Mobile Phase and Stationary Phase

The moving component in the chromatographic technique is called the **mobile phase**, which is normally a liquid or a mixture of liquids, except in gas chromatography where a gas is employed. The fixed medium is called the **stationary phase**. Thus if the sample consisting of a mixture of components (usually referred to as solutes) is added to the mobile phase, then the components by a variety of physical processes will be carried along in the moving stream to varying degrees.

Table 7.1 classifies some of the chromatographic methods. However, the nature of the process whereby separation takes place is rarely confined to one physical mechanism, and although the table indicates the nature of the distribution process in each case, this is merely the most important factor.

Table 7.1: Classification of chromatographic methods

Nature of the Separation Process	Mobile Phase	Stationary Phase	Kind of Chromatography
Partition	Liquid	Liquid	Partition chromatography Paper chromatography Column chromatography
Partition	Gas	Liquid	Gas-liquid chromatography
Adsorption	Liquid	Solid	Adsorption chromatography Thin-layer chromatography Column chromatography Ion-exchange chromatography
Adsorption	Gas	Solid	Gas-solid chromatography

Now work through the following SAQ.

SAQ 2

For the examples given below, indicate what are (i) the mobile phase and (ii) the stationary phase?

a) Paper chromatography

(i)…… (ii)……

b) Thin layer chromatography

(i)…… (ii)……

c) Partition column chromatography

(i)…… (ii)……

d) Ion-exchange chromatography.

(i) …… (ii) ……....

Let us now understand the basic ideas involved in partition chromatography by performing the experiment given in the next Section.

7.4 EXPERIMENT: SEPARATION AND IDENTIFICATION OF AMINO ACIDS IN A MIXTURE

In this experiment you are going to separate and identify amino acids using paper chromatographic technique. This chromatographic technique is the simplest among all the chromatographic methods. It does not require much complicated apparatus and surprisingly good separation can be achieved. Let us now study the basic principle and mechanism of separation of this technique.

7.4.1 Principle of Paper Chromatography

Paper chromatography is based on partition principle. The underlying principle governing the separation of components in paper chromatography (liquid-liquid) chromatography can be demonstrated using a static partitioning model.

Suppose a solvent, such as water, containing two solutes is added to a separating funnel as shown in Fig. 7.1 (a).

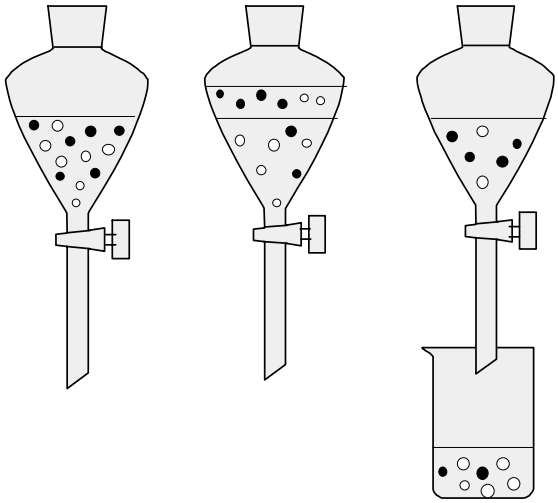


Fig. 7.1: Partial separation of solutes using two immiscible solvents

In Fig.7.1, the two solutes are represented by black and white circles. If a second solvent immiscible with the first is added and the two solvents are shaken together, then some of the solute molecules will transfer to the second solvent forming the upper layer.

As you can see in Fig. 7.1 (b), the black molecules are more soluble in the second solvent. If the stopper is removed and the first solvent is run off via the tap, then a partial separation will occur, with white molecules predominantly in the first solvent and black molecules predominantly in the second solvent. This is shown in Fig. 7.1 (c).

You can show this phenomenon readily in your own laboratory as follows:

(1) Dissolve a small crystal of iodine in 5 cm^3 of aqueous potassium iodide solution in a test-tube. Note the brown coloration that forms.

(2) Then carefully add 5 cm^3 of tetra chloromethane (carbon tetrachloride), using a dropping pipette and shake the test-tube gently. Notice how the tetra chloromethane layer, which was clear, is now purple.

(3) Cork the test-tube and shake vigorously, with care. The purple colour in the organic layer intensifies while the aqueous layer becomes paler.

The colour changes that you observed in this experiment reflect the fact that the iodine, which started off in the aqueous layer, has transferred mainly to the organic layer. No matter how much the mixture is shaken, the ratio of concentrations of iodine in the two layers will remain constant, irrespective of the actual volumes of both solvents, provided only that the temperature remains constant.

Although solid iodine is deep purple in colour, its colour in KI solution is brown while in the organic layer it reverts to purple colour again.

When equilibrium is reached, i.e. there are no more tendencies for the iodine to pass into the organic layer; we can define mathematically this partition or distribution process by the following expression:

$$\frac{\text{Concentration of solute in organic layer}}{\text{Concentration of solute in aqueous layer}} = K_D \qquad \ldots.(7.1)$$

Although it was originally believed that the paper chromatography is based on partition principle. Therefore it was originally named as paper partition chromatography. It is now generally recognised that the paper more commonly acts by a combination of partition, adsorption, and ion exchange mechanisms.

Where K_D is called the **partition** or **distribution coefficient**.

This value of K_D is independent of the amount of solute taken or a volume of solvents used but depends on temperature because solubility is temperature dependent.

The explanation just given relates to static systems, where a component, on the basis of solubility consideration, partitions itself between two immiscible solvents. But in partition chromatography, one of the immiscible solvents is *mobile*.

Let us now understand the mechanism of separation of components of solute in paper chromatography.

7.4.2 Mechanism of Separation

To demonstrate the water content of a filter paper, weigh a filter paper circle on an analytical or top-loading balance (accurate to ± 0.01 g). Dry the circle in an air oven set at 105 °C for one hour. Then cool it in a desiccator and reweigh it. You can then calculate the percentage of absorbed water.

In paper chromatography, the stationary phase is water held on paper in cellulose fibers and the mobile phase is some solvent which runs up or down the paper and the solutes are partitioned between it and the water. The solutes separate out according to their partition coefficients; the one which favours the mobile phase being carried along the paper more quickly. The components of solute are separated completely or partially in distinct colour zones if sample components are coloured, otherwise they are located by the application of different reagents.

To understand how the separation takes place, we need to look more closely at the structure of the filter paper. We know that filter paper consists of numerous cellulose fibers which attract a certain amount of water from the atmosphere. Each fiber can be considered to be made up of a number of cells and each cell consists of a fibrous part with its associated water. The

separation is achieved by partitioning the components of a mixture between the moisture in the cells and the moving solvent flowing over these cells. (Remember the static model which you have read earlier.) It is the relative solubility of each component in the stationary phase (water) and the mobile phase (solvent) which decides the rate at which the component is transferred to the moving phase. Those components which are more soluble in the mobile phase move further; and the components which are more soluble in water will tend to remain longer in the water adhering to the fibers.

A pictorial representation of the partitioning process is given in Fig. 7.2.

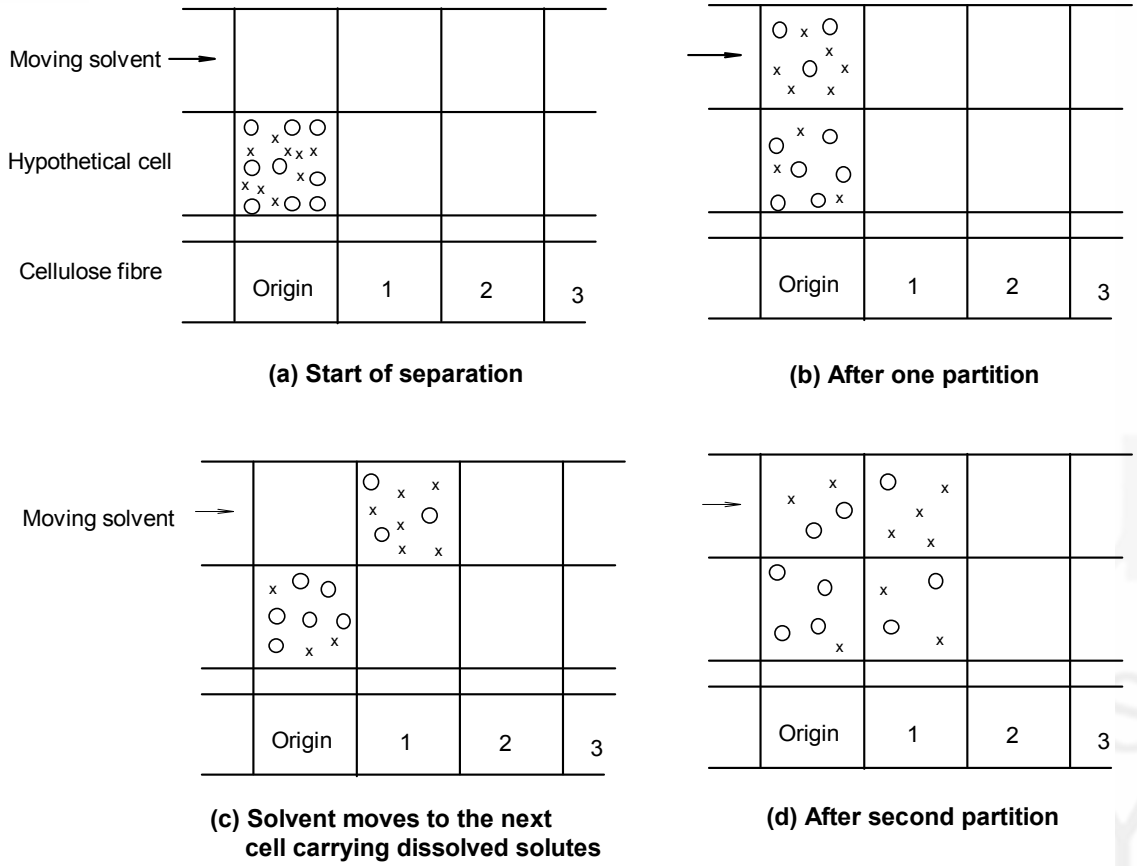


Fig. 7.2: A diagrammatic representation of the partitioning process in paper chromatography

In this figure we have shown how the separation of two components has taken place. Component A (represented by the circles) is *twice* as soluble in the stationary phase, i.e. its partition coefficient is 0.5. Component B (represented by the crosses) is *twice* as soluble in the mobile phase, i.e. its partition coefficient = 2. Fig. 7.2 (a) represents the start of the process, where equal amounts of A and B (equal numbers of crosses and circles) are dissolved in the water cell. In Fig. 7.2 (b), an equal volume of moving solvent is in contact with the first hypothetical water cell, and partitioning (i.e. dividing of the components between the two liquids according to their solubility) will take place so that twice the number of molecules of B will be found in the mobile phase. Remember that B is twice as soluble in the moving solvent. Pictorially, then, there are twice as many crosses as circles. The situation is reversed in the static water cell where twice as many molecules of A are to be found.

Chromatography is a *dynamic* partition process so that a mobile solvent moves on to a situation represented by Fig. 7.2 (c). A second partition will take place to give situation represented by Fig. 7.2 (d), where two adjustments will take place - one at the origin and one at cell 1. At the origin, components A and B will again partition into the mobile solvent in the ratio of 2:1 in favour of B. Thus there are now two crosses in the moving phase and only one in the water cell. A second readjustment will also occur between the mobile and stationary phases in cell 1. In this case, however, as A is more soluble in the water, there will be twice as many molecules of A in this phase (two circles as opposed to one in the mobile phase).

By an extension of this process, it is possible to see why B is carried along in the mobile phase to a greater extent than A. In practice, this process is repeated countless times, eventually giving a sharp separation of the two components in the form of two spots on a paper chromatogram (see Fig. 7.3). The rate at which a component has moved is then determined by its **Retardation factor**, (R_f) or **Retention factor**, which is defined as follows:

$$R_f = \frac{\text{Distance moved by the centre of the solute spot}}{\text{Distance moved by solvent front}}$$

Thus, R_f values for component A will be as shown in Fig. 7.3.

$$R_{f(A)} = \frac{\text{Distance moved by the centre of spot of component A}}{\text{Distance moved by solvent front}} = \frac{x_A}{y}$$

Similarly, retardation factor for component B,

$$R_{f(B)} = \frac{\text{Distance moved by the centre of spot of component B}}{\text{Distance moved by solvent front}} = \frac{x_B}{y}$$

For good separation, the components should have different R_f.

Where, x_A and x_B are linear distances of centre of the spots measured from the line of origin where mixture of solute is applied and y is the distance travelled by solvent front from the starting point as illustrated in Fig. 7.3. R_f values range from 0.00 to 1.00. Small R_f values indicate little tendency to move with the solvent and thus reflect low solubility of solute in mobile phase. Large R_f values conversely indicate a high solubility of solute in mobile phase.

So as long as the correct solvent and type of chromatography paper are used, a component can be identified from its Retardation factor.

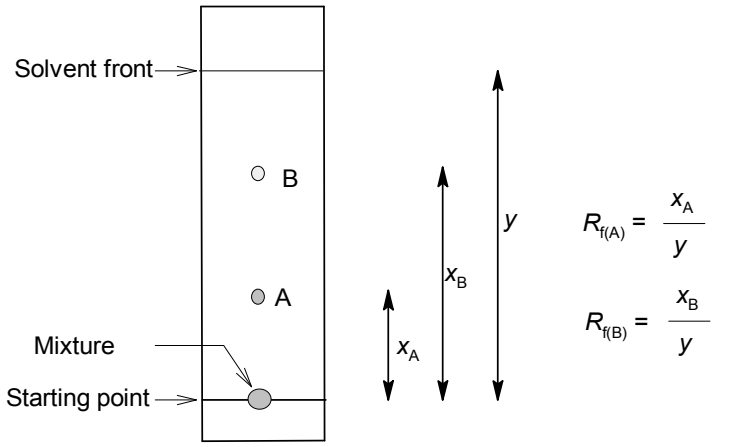
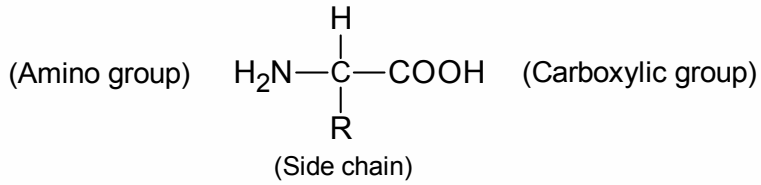


Fig. 7.3: Procedure for calculation of retardation factor (ratio), R_f

Solvent System (Mobile Phase) for Amino Acid Separation:

As mentioned above, the separation of the components mainly depends on the relative solubility of the components of solute (sample) in mobile phase. Therefore, the nature of solvent system plays important role in the development of paper chromatogram. Various solvent systems have been tried out for the separation of amino acids. While selecting a solvent system for the separation of amino acids, some basic understanding of the structure of amino acids is necessary.

As the name suggests, each amino acid contains an amino group, – NH_2, and a carboxylic acid group, – COOH. The molecular structure of a generic amino acid is provided below:



Amino acids with nonpolar R	Amino acids with polar R	Amino acids with polar charged R
R = -CH_3, Alanine	R = -CH_2OH, Serine	R = -CH_2COOH, Aspartic acid
R = -$CH(CH_3)CH_3$, Valine	R = -CH_2SH, Cysteine	R = -CH_2CH_2COOH, Glutamic acid
R = -$CH_2CH(CH_3)_2$, Leucine	R = -$CH_2(OH)CH_3$, Threonine	R = -$(CH_2)_4$ - NH_2 , Lysine
R = -CH_2Ph, Phenylalanine		R = -$(CH_2)_3$ - NH(NH) - NH_2, Arginine

There are 20 different amino acids that make up our proteins, and they closely resemble in structure except the structure of the side chain R. In glycine, the simplest amino acid, R is a hydrogen atom. Amino acids can be categorised into three main types, on the basis of nature of their side chains. These are amino acids with nonpolar, uncharged polar and charged polar side chains, respectively. The nonpolar groups have generally an aliphatic or an aromatic side chain. For examples, alanine, valine, phenylalanine, etc., have nonpolar hydrocarbon side chains, therefore, are less soluble in water. The uncharged polar types have side chains containing hydroxyl, amide or sulphydryl groups (thiols). These amino acids like serine, cysteine and have polar but neutral R groups thus tend to promote water solubility. The charged polar groups may have carboxylic group (aspartic acid, glutamic acid) or a basic group (lysine, arginine) in their side chain. Both acidic and basic R groups tend to promote water solubility. Therefore, because of the differences in interaction of polar and nonpolar side chains with water, amino acids will show different partition coefficients i.e. relative solubility with solvent system of mobile phase and water of stationary phase. Thus, one which favours the mobile phase being carried along the paper more quickly and one which favours the stationary phase remain near the base line.

There is no universal solvent system which is capable of separating all the usual amino acids. We can try different solvent systems such as acidic (phenol-water, 1-butanol-acetic acid-water), basic (pyridine-water, 1-propanol- aqueous ammonia) or neutral (1-butanol, methyl ethyl ketone) solvent systems, which can provide us the best separation.

The paper chromatogram can be developed in many ways such as ascending: here development of paper occurs due to the solvent movement in upward direction on the paper; descending: here the development of paper occurs due to solvent moves downwards on the paper; horizontal or radial mode: here the solvent travels from centre towards periphery of circular chromatographic paper; two dimensional: here the chromatogram development occurs in two directions at right angle to each other. In our present experiment we will be using ascending mode to develop our chromatogram.

For our present experiment, we will be following an easy ascending paper chromatography technique and 1-butanol-glacial acetic acid-water in the ratio 12:3:5 as solvent system. This experimental set up does not require special apparatus.

SAQ 3

In paper chromatography, the rate at which the components move in the mobile phase is decided by which of the following factors:

a) The number of components in the mixture that is spotted on the paper

b) The relative solubility of the components in the mobile and the stationary phases

c) The time for which the chromatogram is allowed to run

The basic principles discussed above now can be easily demonstrated using the simplest of apparatus and chemicals. You can try the following experiment at your Study Centre's Chemistry Lab. The exercise will take up very little time.

7.4.3 Requirements

Apparatus		**Chemicals**
Chromatographic tank	1	1-Butanol
Boiling tubes	4	Glacial acetic acid
Measuring cylinder (100 cm^3)	1	Any three amino acids from the following: [L-alanine, L-leucine, L-lysine L-aspartic acid, L-methionine]
Test tubes	5	
Spotting capillaries	5	
Separatory funnel	1	Ninhydrin
Whatman No. 1 filter paper sheet		
Spraying bottle	1	

Solutions provided

1. **Sample solutions:** Provide solution of any three amino acids as mentioned above. Make one unknown sample solution by mixing any two of these three amino acids.

Their solutions can be prepared by dissolving 15 mg of each amino acid separately in 1 cm^3 of distilled water. Warm if a particular amino acid is not soluble in cold.

2. **Detector:** Ninhydrin reagent (0.2%): Take 100 cm^3 of 1-butanol and 100 cm^3 of water in a separating funnel. Shake gently and allow it to form the layers. Remove the lower aqueous layer. Transfer the upper organic layer to a spraying bottle and to this add 0.2 g of ninhydrin, shake well and use as the detector for amino acids.

7.4.4 Procedure

Proceed according to the following steps:

1. Preparation of Developer (solvent system): Prepare the developer as per your requirement by mixing 1-butanol-glacial acetic acid-water in the ratio 12:3:5 by measuring the required volumes.

2. Place the developer in the chromatographic tank so that the height of the developer is less than 1 cm. Place the lid and allow the tank to be saturated with the solvent vapours.

3. Cut the chromatographic paper strip of the required size (usually 10 cm x 10-30 cm for four spot and breadth may be changed as per the number of spot(s). On the strip draw a line with pencil at about 1 cm from one end. This will be the bottom of the chromatogram. Mark off equally spaced points along this line. (They should be separated by about 2 cm). Your samples will be applied to these spots.

4. Apply the solutions of three known amino acids and solution of unknown mixture of the amino acids to the point of application separately on the marked strips using spotting capillaries or tooth picks. Use a fresh capillary or tooth pick for each solution. Remember the position of the known amino acids on the strip. You can label the paper at the top with the name of each of the known amino acid and label the last as unknown.

5. After spotting, dry the spots by allowing the solvent to evaporate. You can use a hot air dryer to dry the paper as illustrated in Fig. 7.4. Repeat spotting process again.

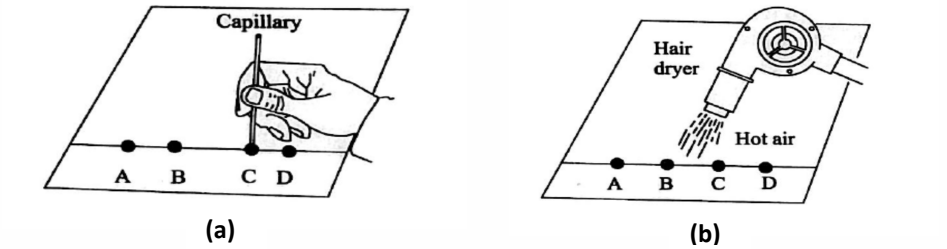


Fig. 7.4: Illustration of (a) spotting of solute sample using glass capillary tube and (b) drying process using hair dryer

6. Suspend the spotted and dried paper strip in the chromatographic tank with the help of a supporting glass road or hanger so that the lower end touching the developer. Care should be taken to see that this is done gently and the strip is vertical. The spots should always be above the developer level (see Fig. 7.5). Cover the chromatographic jar with its lid.

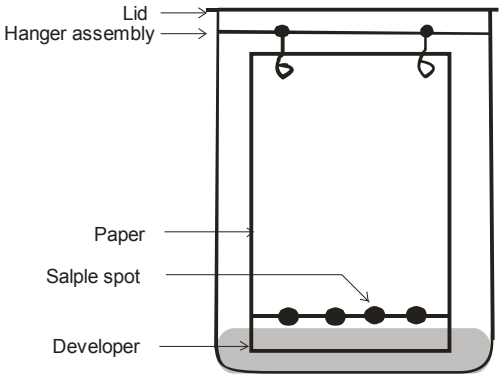


Fig. 7.5: Some typical experimental arrangement for developing paper chromatogram

7. Allow the developer to rise along the paper and wait till the developer (solvent front) reaches near the upper end of the paper.

8. Remove the paper strip from the tank and mark the solvent front with the help of a pencil.

9. Dry the strip until the acetic acid odour from the strip is no more present.

10. After the chromatogram has dried, spray the paper with the ninhyrin reagent solution using a spraying bottle.

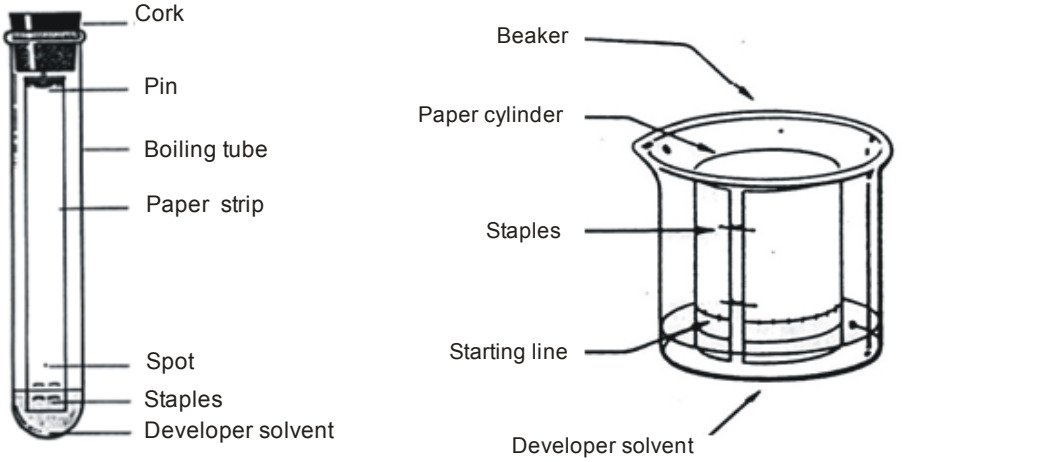
11. Heat the strip at 105 ^{o}C either in an oven or a hot plate or use hot air dryer until the coloured zones of amino acids are seen.

12. Encircle the coloured zones and mark the centre of each zone.

13. Measure the distance of each spot centre from the starting line and also the distance by which the solvent front has moved.

14. Calculate the R_f value for each spot on the strip. From the comparison of R_f values, you can determine which amino acids are present in your unknown sample. Report your results in the Observation Table I.

Alternatively you can run a paper chromatogram in 500 ml beaker by making a paper cylinder as shown in Fig. 7.6. Common boiling tubes can also be used to run paper chromatograms (see Fig. 7.6).



Boiling tube for developing

Running a chromatogram by making paper cylinder
Beaker can be covered by aluminium foil

Fig. 7.6: An alternate method for developing paper chromatogram

7.4.5 Observations and Calculations

Observe the colour of the spots of various amino acids on paper chromatogram. Measure the distance (*x*), to which the centre of spot for each amino acid has moved from the original point of application and the distance (*y*), to which the solvent front has moved from the original line on the paper.

Calculate the R_f values by the relation: R_f=x/y, for each known amino acid and for the unknown. Present the data in an Observation Table below.

Observation Table I

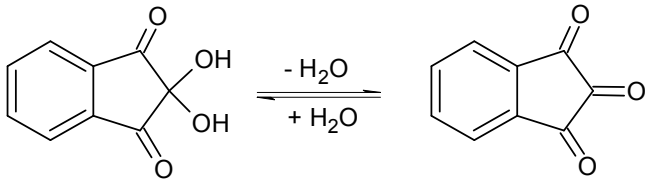
Amino acid	***x***	***y***	$R_f = \frac{x}{y}$
1. --------			
2. --------			
3.---------			
Given Mixture Unknown A Unknown B			
Unknown A's R_f resembles with ..... Unknown A's R_f resembles with			

7.4.6 Result and Discussion

The given mixture sample contains:

1. A.....
2. B.....

The mobile phase rises up along the paper by capillary action, rapidly at first, and then more slowly as the solvent front rises. The movement of an amino acid along the paper depends on its solubility in mobile phase, and a number of other factors. Therefore, the different amino acids move along the paper at different rates and may have different R_f values. The significant differences in R_f values of certain amino acids result into a clean separation. The most widely used reagent for detecting amino acids is ninhydrin. Ninhydrin is the 2-hydrate of indane-1,2,3 trione (or triketohydrindene hydrate) with the following formula.

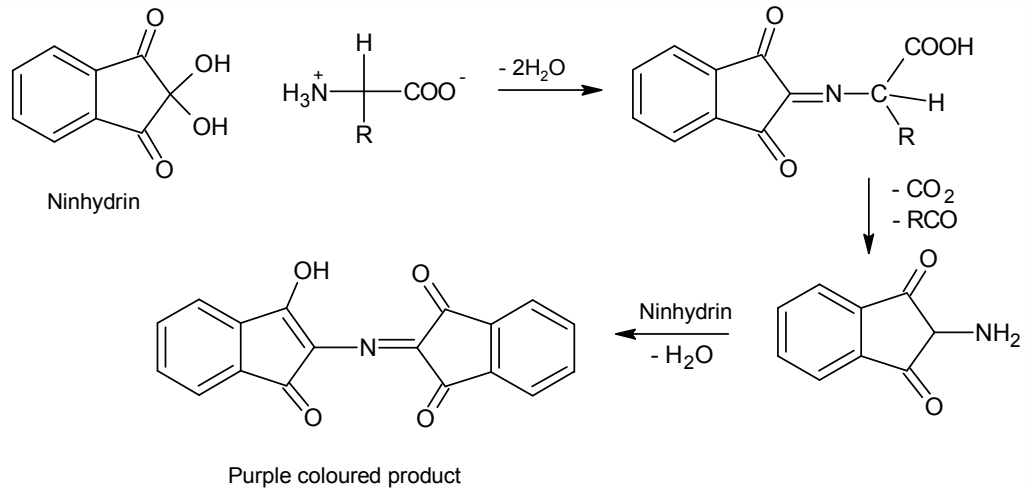


Hydrated form of Ninhydrin Unhydrated form of Ninhydrin

It reacts with amino acids to yield highly coloured products.

$$\text{Amino acid} + \text{Ninhydrin} \xrightarrow{\text{Heat}} \text{coloured product}$$

The different steps in colour formation between ninhyrine and amino acids are shown below:



The formation of visible colour with ninhydrin has limits of detection that may vary from 0.01-0.5 μg depending on the particular amino acid.

7.5 ANSWERS

Self-Assessment Questions

1. You should have answered (d) as this is the chief mechanism of separation on a column. It usually happens that there is a structural similarity between components separated in this way though this is not an essential characteristic.

2. a) (i) liquid – (ii) liquid b) (i) liquid – (ii) solid c) (i) liquid – (ii) liquid d) (i) liquid – (ii) solid

3. (b) is the correct answer. Paper chromatography separations are mainly decided by the differential solubility of the components between the two liquid phases.

EXPERIMENT 8

SEPARATION AND IDENTIFICATION OF THE SUGARS PRESENT IN THE GIVEN MIXTURE BY PAPER CHROMATOGRAPHY

Structure

8.1 INTRODUCTION

In the previous experiment you have separated amino acids by paper chromatography. In this experiment you will again use paper chromatography for the separation of sugars.

The term sugar applies to monosaccharides, and disaccharides, which are all soluble in water and thereby distinguishable from polysaccharides. Many natural sugars are sweet; however, the sweetness varies greatly with stereochemical configuration.

Paper chromatographic method has proved to be of great significance for both qualitative and quantitative separations of sugars. On a large scale, it has proved to be of immense value in the sugar industries, in the analysis of fruit juice and in a number of other fields.

Various developers may be used for particular paper chromatographic separations. The developers which are used for this experiment may be modified in order to achieve more satisfactory separations of certain sugar mixtures.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ explain the principle of paper chromatography; and
- ❖ separate and identify sugars by paper chromatography

8.2 PRINCIPLE

The basic principle of paper chromatography has already been discussed in earlier experiment. In case of sugars, distribution of solute (sugars) between the stationary and mobile phases, that is, the partition process is the major factor in the paper chromatographic separation of sugars. Their partition coefficients are substantially in favour of the aqueous phase. Therefore, with non-aqueous developers, sugars appear on the paper chromatogram with low R_f values, whereas with developers containing larger aqueous ratio, the R_f values of sugars are much higher. This is because a sugar molecule containing larger number of hydroxyl groups is readily soluble in water and makes the partition coefficient in favour of the aqueous phase. Further, the R_f values of sugars are affected by their structural formulae, their molecular mass, the number of – OH groups, and presence of other kinds of groups such as aldehydes or ketones etc. Commonly used mobile phase or developers for separation of sugars are 1-Butanol-acetone-water (20:70:10), 1-butanol-acetic acid -water (40:10:50), 1- Butanol-pyridine-water (60:40:30), etc.

In this experiment you will learn the paper chromatographic separation of simple sugars.

8.3 REQUIREMENTS

Apparatus		Chemicals
Chromatographic tank	1	Acetic acid, silver nitrate, ammonia solution, anisidine hydrochloride
Boiling tubes	4	
Test tubes	5	1-Butanol, sodium borate, phenol red, methanol, aniline, acetone, phthalic acid
Measuring cylinder (100 cm^3)	1	
Beaker (250 cm^3)	1	Sugars (any three): D-glucose, D-fructose, D-xylose, L-rhamnose, D-galactose, lactose, maltose, sucrose, D-mannose
Spotting capillaries	4	
Spraying-bottle	1	
Whatman No.1 filter paper sheets		

Solutions Provided:

1. **Unkown sugar sample solution:** It can be prepared by dissolving any two sugars in water from the list of three sugars given to students as known sugars.
2. **Detector:** Any one or two of the following detectors may be prepared considering the types of sugars given to students as samples.

Detector-1: Ammoniacal silver nitrate: Take 5 cm^3 of saturated aqueous solution of silver nitrate, add 50 cm^3 of acetone, finally add ammonia solution to make the solution clear and basic in nature.

Detector-2: Aniline hydrogen phthalate: Dissolve 1 cm^3 of aniline and 1.66 g of phthalic acid in 100 cm^3 of 1-butanol saturated with water. Both these detectors 1 and 2 give coloured or dark spots with reducing sugars.

Detector-3: (For non-reducing sugars): Prepare a solution by mixing 0.25M sodium borate + phenol red + methanol in (1:2:7) proportion.

Detector 4: Aniline-Diphenylamine-phosphate: This reagent is superior to other reagents for the location of sugars on the chromatogram. The reagent can be prepared by mixing the following solutions before use in the proportions stated below:–

(i) 4 percent solution of aniline in 95 percent alcohol (5 volumes);

(ii) 4 percent solution of diphenylamine in 95 percent alcohol (5 volumes);

(iii) syrupy phosphoric acid (1 volume).

The reagent has the advantage of being effective for all reducing and non-reducing sugars and oligosaccharides and is therefore, of general application to all sugars. It produces blue, green, yellow or brown coloured bands with sugars, the nature of the colour depending on the type of sugar.

8.4 PROCEDURE

For this experiment, you will be going to use same apparatus arrangement as discussed for the earlier experiment.

Proceed according to the following steps:

1. Preparation of Solutions:

   i) Developer (1-Butanol-acetone-water (20:70:10): using 100 cm^3 measuring cylinder take 70 cm^3 acetone, 20 cm^3 1-butanol and 10 cm^3 of water in a dry 250 cm^3 beaker.

   ii) Sample solutions: Prepare the aqueous solution of any three of the following by dissolving 0.2-0.5 g of each sugar in 5 cm^3 of water in a small test tube. The sugars are: D-glucose, D-fructose, D-xylose, L-rhamnose, D-galactose, lactose, maltose, sucrose, D-mannose (D-glucose, D-fructose, D-xylose, L-rhamnose, D-galactose, D-mannose, lactose, maltose are reducing sugars as they have aldehyde group in open chain form).

2. Place the developer in the chromatographic tank so that the height of the developer is less than 1 cm. Cover the tank with its lid and allow the tank to be saturated with the solvent vapours.

3. Cut the chromatographic paper strip of the required size. On the strip draw a line with pencil at about 1 cm from one end. This will be the bottom

of the chromatogram. Mark off equally spaced points along this line separated from each other by about 2 cm. Your samples will be applied to these points.

4. Apply the samples of three known sugar solutions and unknown sample of mixture of sugar solutions to the points of application separately on the marked strips using spotting capillaries or tooth picks. Use a fresh capillary or tooth pick for each solution.

5. After spotting, dry the spots by allowing the solvent to evaporate. You can use hot air dryer to dry the paper. Repeat spotting process again. Remember the position of the known sugars on the strip. You can label the paper at the top with the name of each of the known sugars and label the last unknown mixture.

6. Suspend the spotted and dried paper strip in the chromatographic tank with the help of a supporting glass road or hanger so that the lower end touches the developer. Care should be taken to see that this is done gently and the strip is vertical. The spots should always be above the developer level (see Fig. 7.5). Cover the chromatographic tank with its lid.

7. Allow the developer to rise along the paper and wait till the developer (solvent front) reaches near the upper end of the paper.

8. Remove the paper strip from the tank and mark the solvent front with the help of a pencil.

9. Dry the strip until the odour from the strip is no more present.

10. After the chromatogram has dried, spray the paper with the provided Detector reagent solution using a spraying bottle.

11. Heat the strip at 105 ^{o}C either in an oven or a hot plate or use hot air dryer until the coloured zones of sugars are seen.

12. Encircle the coloured zones and mark the centre of each zone.

13. Measure the distance of each spot centre from the starting line and also the distance by which the solvent front has moved.

14. Calculate the R_f value for each spot and also for the spots the mixture contained. From the comparison of R_f values you can determine which sugars are present in your unknown sample. Report your result in the Observation Table.

8.5 OBSERVATIONS AND CALCULATIONS

Observe the colour of the spots of various sugars on paper chromatogram. Measure the distance (x) to which the centre of spot of each sugar has moved from the original point of application, and the distance (y) to which the solvent front has moved from the original point on the paper.

Calculate the R_f values by the relation: R_f = x/y, for each known amino acid and for the unknown. Present the data in an Observation Table below.

Observation Table

Sugars	***x***	***y***	$R_f = \frac{x}{y}$
1. --------			
2. --------			
3.---------			
Given Mixture Unknown A Unknown B			
Unknown A's R_f resembles with ..... Unknown A's R_f resembles with			

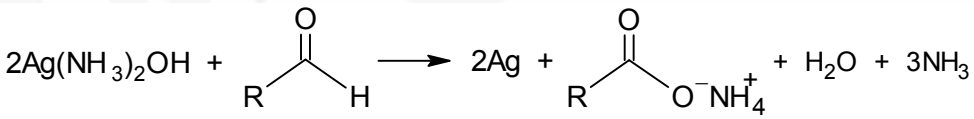
8.6 RESULT AND DISCUSSION

Sugars present in the unknown sample are:

1. A……..

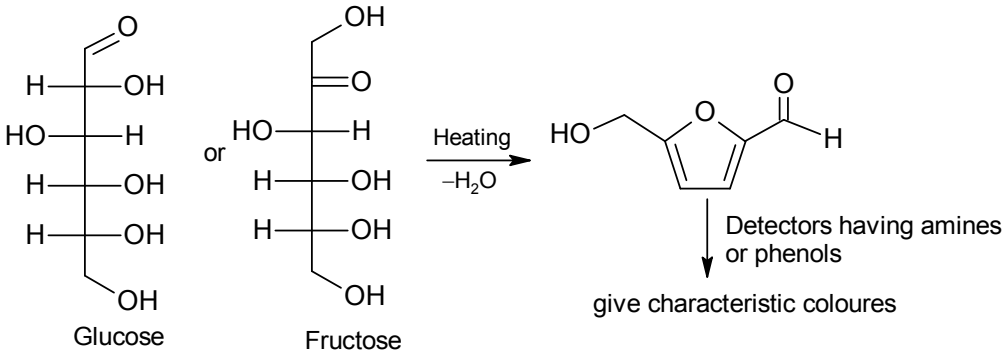
2. B……..

The colour of the sugar zones on the chromatogram depends on the detector used. For example, detector-1 (ammoniacal silver nitrate) on reduction, it results into metallic silver. Therefore, the reducing sugars give rise to brown-black spots after heating to 100 °C.



Aldose sugars

The colour development with detectors 2, 3 and 4 depends on the following mechanism. Heating of sugar with an acid produces furfural with pentose sugar and 5 hydroxymethylfurfural with hexose sugars which can be condensed with an aromatic amine or phenol to give characteristic colored spots.



Glucose Fructose

FURTHER READING

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