UNIT 1 BASIC LABORATORY SKILLS

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1.1 INTRODUCTION

In this introductory unit, we shall describe some of the experimental techniques. You are going to use these techniques during this laboratory course. Therefore, you must understand the principles behind these techniques. In some cases, the required apparatus for an experimental technique will also be discussed.

We shall start with a discussion on laboratory safety and first aid. We shall explain the main features of titrimetric analysis. We shall then state the method of finding the mass of a substance using an analytical balance; this discussion will help you in understanding the method of preparation of standard solution. The use of thermometers will be illustrated with reference to the determination of melting point of a substance. Finally the method of filtration will be explained.

Objectives

After studying this unit, you should be able to:

- state the measures to be taken under laboratory safety and first aid,
- explain the types of titrations and the principle of titrimetric analysis,
- discuss the method of using an analytical balance for weighing a substance,
- state the different ways of expressing the concentration,
- explain the method of preparation of a standard solution
- carry out titrimetric calculation using the given data,

- state the method of determination of melting point of a substance, and
- explain the technique of filtration.

1.2 LABORATORY SAFETY AND FIRST AID

Laboratory is a place for learning the experimental skills. You are strongly advised to be careful at all times. It is recommended not to perform unauthorised experiments. This will ensure your safety as well as the safety of your fellow-students. Even a small accident involving minor injury must be reported to the counsellor. The following instructions should be observed during the laboratory work.

i) You must wear a laboratory coat or apron over your clothes while working in the chemistry laboratory. This will save you from injury and protect your clothes from damage.

ii) Handle the hot glass carefully; it cools very slowly and may be very hot without appearing so.

iii) Protect your eyes from any spurting of acid or a corrosive chemical. In case of such spurting into the eyes, immediately wash with lot of water and go to a doctor.

iv) You must not reach across lighted burners as it may result in an accident.

v) Wash your apparatus thoroughly with a washing powder.

vi) While heating substances, do not point the tube towards your neighbour or to yourself. A suddenly formed bubble may eject the contents violently and dangerously.

vii) When diluting sulphuric acid, pour the acid slowly and carefully into the water with constant stirring. Never add water to the acid as it may result in the liberation of a lot of heat.

viii) Read the label on the bottle carefully before using the required chemical. Never pour back the unused reagent into the bottle.

ix) Never touch or taste a chemical or solution as most of chemicals are either corrosive or poisonous.

x) Always bring your container to the reagent shelf and do not take the bottles to your desk.

xi) Do not insert the pipette or dropper into the reagent bottles; this helps in avoiding any possible contamination.

xii) Graduated cylinders and bottles are not to be heated because these break very easily and their volume also changes.

xiii) At the end of the experiment, clean and dry the glass apparatus and wipe off the top of the working table. Ensure that the gas and water taps are closed before you leave the laboratory.

Laboratory First-Aid

If a corrosive substance falls on your skin, immediately wash the spot with large quantities of water, followed by remedial action indicated below:

Acid spill : Treat with sodium bicarbonate or ammonium carbonate (2M) solution; then apply vaseline or a soothing cream.

Base spill : Treat with acetic acid (1 M) followed by vaseline or a soothing cream.

'M' is a unit for concentration. You will understand this unit in Sec. 1.5 of this unit.

Bromine : Treat with 2 M ammonia; keep the affected part dipped in dilute sodium bisulphite solution till bromine is washed off. Finally apply vaseline.

Phenol : Wash with ethanol and then take hospital treatment.

The most common accidents in the chemistry laboratory involve cuts, burns or fire. The first-aid to be given in each case is below :

Cuts : 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; it should be followed by proper dressing of the wound.

Burns : Wash the burnt part with cold water for sometime and then apply Burnol to it.

Fire : A small fire in a beaker, caused by the vapours of an imflammable 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 put off by wrapping a thick blanket around the body.

1.3 TITRIMETRIC ANALYSIS

During this laboratory course, you will be often doing **titrimetric analysis**. Titrimetric analysis generally consists in determining the volume of a solution of accurately known concentration which is required to react completely with a known volume of the solution of a substance being estimated. The solution of accurately known concentration is called the **standard solution**. The standard solution contains a definite amount of the solute per litre (dm^3) of the solution. The term, volumetric analysis, is also used in the place of the term, titrimetric analysis.

Titration is the process of adding a standard solution to a test solution (or vice versa) until the reaction is just complete. The point at which the completion of reaction occurs is called the **equivalence point** or the **end point**. Let us explain these two terms. The stage at which the reacting solutions are used up in their stoichiometric proportions is called the **equivalence point**. The detection of equivalence point is often done using instrumental measurements at various stages of titration. Conductometer and mV/pH meter are two such instruments used for the determination of equivalence point. In experiments 2 and 3 of CHE-03 (L) course, their usage in titrimetric analysis has been illustrated.

Let us now explain the term, the end point. Sometimes it is possible to use a substance to indicate the completion of titration. Such a substance is called an indicator and the equivalence point determined using an indicator is called the **end point**. An indicator indicates the completion of reaction by a change in physical property such as colour. The basic requirement for an indicator is that its colour should be quite different before and after the end point. Ideally, end point should be close to the equivalence point. But the colour change occurs only after the equivalence point; hence the end point differs at least slightly from the equivalence point. A well known example of indicator is phenolphthalein used in acid-base titration. It is pink in basic solution and colourless in acidic solution. In

experiments 1, 4, 9, 10 and 11 of CHE–03 (L) course, the use of indicators for titrimetric analysis has been explained.

For carrying out the titrimetric analysis of any given substance, a reaction must satisfy following conditions:

a) The substance to be estimated must react completely with another of known strength in stoichiometric proportions.

b) There must be a simple and instantaneous reaction.

c) An indicator may be used for identifying the completion of titration by the change in colour of the solution. In the absence of indicators, instrumental method should be available to conduct a titration.

Next let us discuss the types of titrations.

1.3.1 Types of Titrations

There are four main types of titrations as given below.

a) Neutralisation titration or acid-base titration

Neutralisation titration involves the titration of a base with an acid. The reaction essentially involves the combination of hydroxyl ions with the hydrogen ions to form water. A typical example is the titration of sodium hydroxide against hydrochloric acid.

b) Precipitation titration

Precipitation titration results in the formation of a precipitate. An example for this type is the titration of silver nitrate against sodium chloride.

c) Oxidation–reduction titration

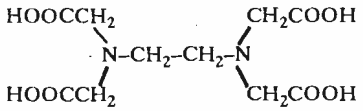
Oxidation–reduction titration involves the change in the oxidation number or transfer of electrons among the reacting substances. The principal oxidising agents are potassium permanganate, potassium dichromate, iodine and potassium iodate. The reducing agents are ferrous and stannous compounds , oxalic acid and sodium thiosulphate.

A typical example of this type is the titration of potassium permanganate against ferrous ammonium sulphate.

d) Complexometric titration

In complexometric titration, a complexing reagent forms complex ions with metal ions like Ca^{2+} and Mg^{2+}. Sodium salt of EDTA(ethylenediamine tetraacetic acid) is often used as a complexing reagent in titrations.

The complexing reagent is also called a ligand. A complex ion is a metal ion with one or more ligands bonded to it.



EDTA

Before trying to know how titrations are carried out, let us know some of the apparatus used during titrations.

1.3.2 Apparatus for Titrimetric Analysis

The apparatus for titrimetric analysis is of three principal kinds:

(i) Volumetric flasks (ii) pipettes and (iii) burettes.

Let us discuss each of them.

i) Volumetric Flasks

Volumetric flasks are used for the preparation of standard solutions and for diluting the sample to known volumes. The volumetric flasks have a flat bottom, pear shaped body and long narrow neck. These have a ring engraved around their neck. When filled up to this ring, the volumetric flask contains the volume of the liquid marked on it. The volumetric flasks are of varying capacities such as 100 cm^3, 200 cm^3, 250 cm^3, etc. As an example, 100 cm^3 flask is illustrated in Fig. 1.1.

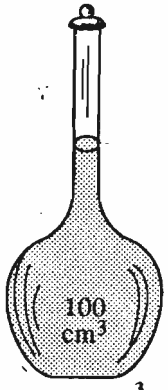


Fig. 1.1 : 100 cm^3 volumetric flask.

In Sec. 1.6, we shall see the use of volumetric flasks in preparing a standard solution.

ii) Pipettes

Pipettes are used to transfer known volume of a liquid from one container to another. A pipette usually consists of a narrow tube with a bulb in the middle. The ring mark engraved on the stem indicates the length to which the liquid level must be drawn to get exactly the volume of the liquid marked on the bulb. Some pipettes, known as graduated pipettes, are calibrated so that any volume upto its maximum capacity can be transferred. The pipettes of volume 1 cm^3, 2 cm^3, 5 cm^3, 10 cm^3, 20 cm^3 and 25 cm^3 are used commonly. As an example, 20 cm^3 pipette is indicated in Fig. 1.2 (a).

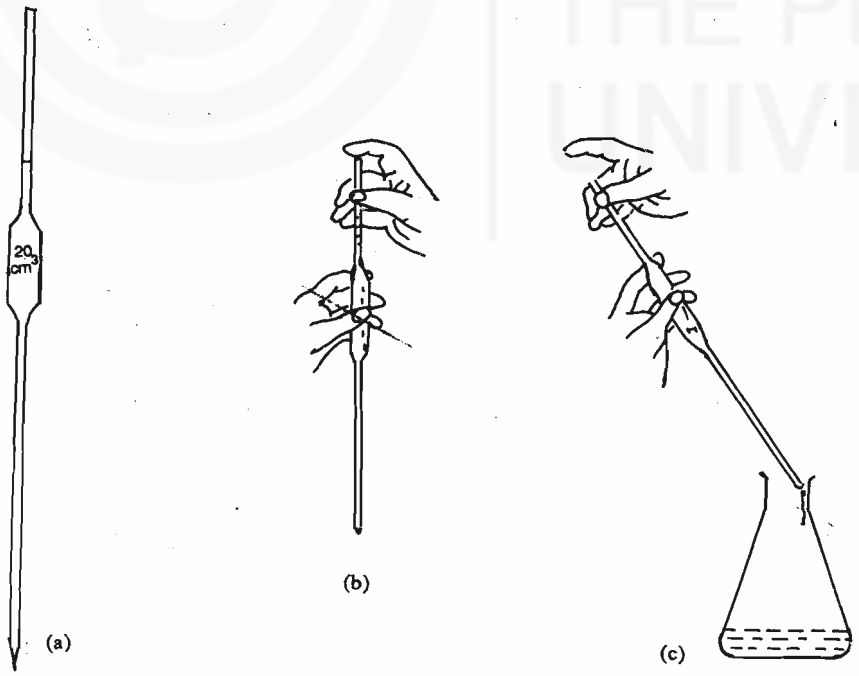


Fig. 1.2 : a) pipette; b) handling a pipette
c) draining out the pipetted solution.

Before using a pipette for transferring a liquid for estimation, it has to be thoroughly washed with a good quality detergent, followed by plenty of water and

finally with distilled water. It is then to be rinsed with a solution which is to be pipetted. For rinsing, the solution is taken in a clean dry beaker. The pipette is dipped into the solution and the solution is sucked into the pipette to fill it about half its volume. The upper tip of the pipette (the suction end) is closed by the finger tip. The pipette is then taken out ad held horizontal between the two hands and rolled gently. This ensures the wetting of the walls of the pipette. Make sure that the solution in the pipette does not reach the suction end. The solution is then drained into the sink and the process is repeated. This completes the rinsing process. Now we can use the pipette for transferring the solution for estimation. The solution is drawn through the pipette past the ring mark. The suction end is closed by the tip of the index finger (Fig. 1.2 (b)). By rolling the finger-tip slightly, excess liquid is allowed to drain out until the meniscus descends to the ring mark. Now the liquid in the pipette is allowed to drain out into the receiving vessel (Fig. 1.2 (c)). By touching the walls of the receiving vessel with the tip of the pipette, the last drop is also transferred. **Do not blow out the last drop.**

iii) Burettes

Burette is a common device for measuring precisely the volume of a liquid used during titration. There are two well-known types of burettes. The first type consists of a calibrated tube with a narrow end to which a glass tubing is attached by means of a rubber tubing. To the rubber tubing, a spring-clip is attached. When you press the clip, the liquid flows out of the burette. In another type of burette, a stopcock is used instead of spring-clip. The burette is graduated, the zero being at the top. Mostly we use 50 cm^3 burette. For some titrations, we use 5 cm^3 burette. A 50 cm^3 burette is shown in Fig. 1.3 (a).

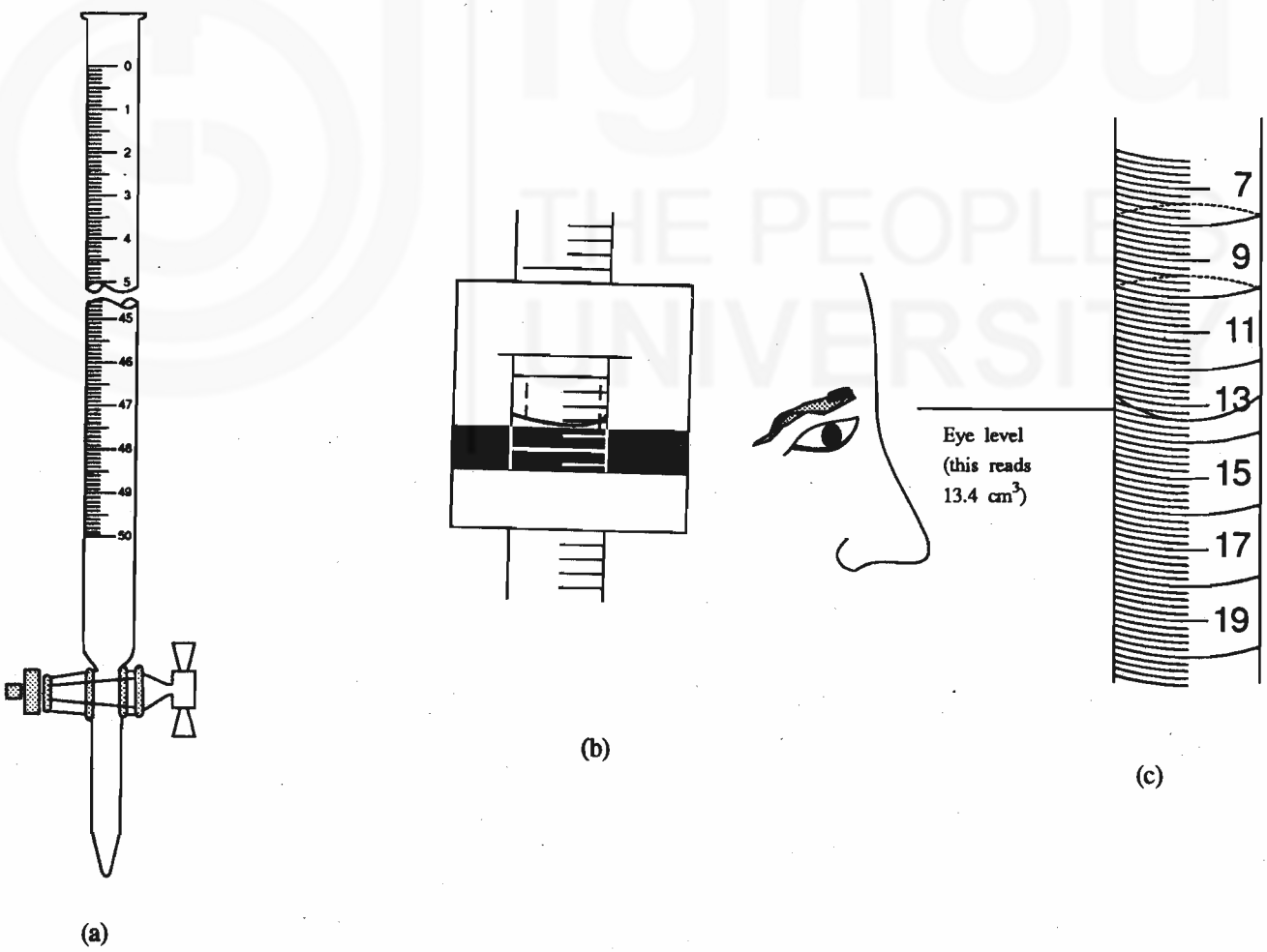


Fig. 1.3 : a) Burette (with a stopcock) b) using a parallax card c) eye level for burette reading.

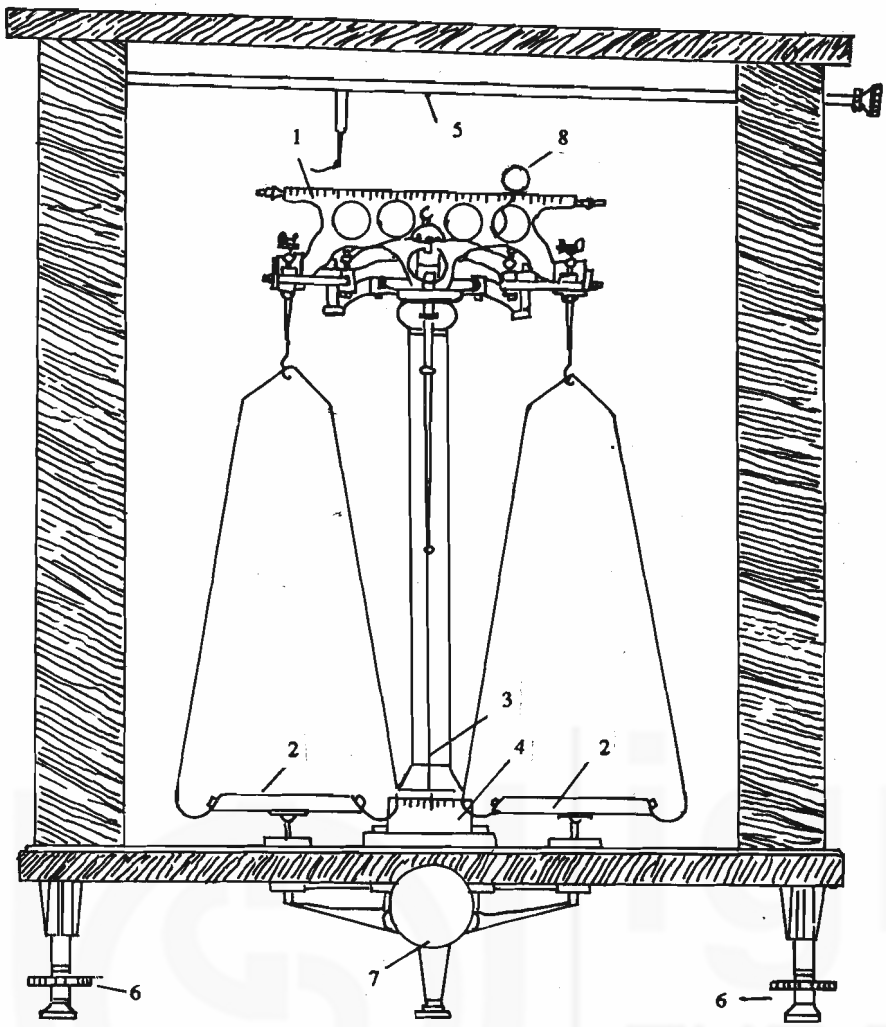


Fig. 1.5 : Analytical balance;

(1) beam (2) pans (3) pointer (4) scale (5) rider-carrier (6) levelling screws (7) arrest-knob (8) rider.

graduated, with the zero of the scale at the center of the beam, with major divisions reading 1 mg and the subdivisions reading 0.2 mg. Both ends of the beam are thus graduated. So an analytical balance can weigh only up to an accuracy of 0.2 mg (or 0.0002 g). The balance is fixed inside a glass case. A rider-carrier is attached to the case which is parallel to the balance beam and is slightly above it. An arrest-knob for the beam-control is on the outside of the balance case. The balance case is supported on levelling screws. You will be provided with a set of weight box and fractional weights (Figs. 1.6 (a) and (b)) for use on analytical balance.

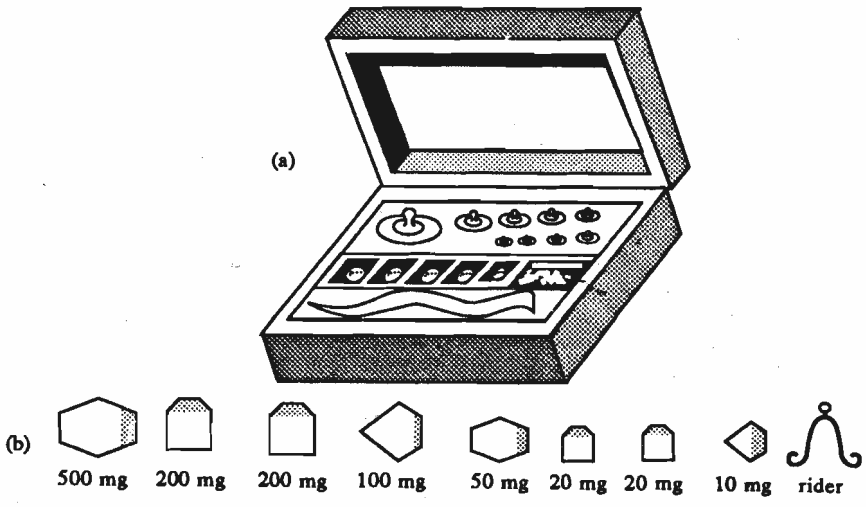


Fig. 1.6 : a) Weight box and b) fractional weights.

Using an Analytical Balance for Weighing

Before using a balance for weighing, we have to examine whether the balance functions properly. For this, first the side doors of the balance are to be closed. The arrest-knob is to be slowly and carefully turned counter-clockwise. When the arrest-knob is turned fully to the left, the pointer starts swinging around the centre of the scale. The first two swings are ignored. Then, starting with the third swing, the extreme positions of the swing are noted for at least two more swings. The readings of the swings to the left and to the right must be equal or can differ by one unit only during each swing. If the readings to the left and right are much different, the balance must be adjusted by means of the screws, for which you may request your counsellor.

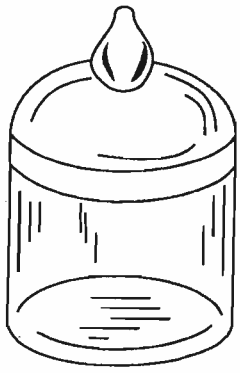


Fig. 1.7 : Weighing bottle.

After adjusting the balance (if necessary), we come to actual weighing. For this purpose, we use a glass or a plastic weighing bottle, Fig. 1.7. 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 and the door is closed. 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 with the help of forceps and, the right side door is closed.

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

The arrest knob is once again turned to the left and the movement of the pointer is seen. If it moves more to the left, then the weights transferred are in excess of the mass of the bottle. In that case, some weights have to be removed . On the other hand, if the pointer moves more 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 using 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 15g weight would be lighter and 16 g weight would be heavier. After this, the fractional weights marked in mg, have to be added in decreasing order till the two sides are balanced. Do not use fractional weights less than 10 mg; you should use a rider in such cases. A rider (Fig. 1.6 (b)) 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 with the help of the rider carrier. By varying the position of the rider on the beam, the two pans are balanced.

A rider is used for mass adjustments below 10 mg (0.01 g).

Mass of the object = (Weights added in grams)
+ (fractional weights added × 0.001) g
+ (main division of the rider position × 0.001) g
+ (subdivision of the rider position × 0.0002)g

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

Then the mass of the object

= 15 g + (240 × 0.001) g + (2 × 0.001) g + (3 × .0002) g
= 15.2426 g

Before filling the burette with a liquid, it has to be washed, first with a detergent, followed by plenty of water and distilled water. It is then rinsed with the liquid which is to be taken in it. For rinsing it, fill the burette to half its volume with the liquid, rotate it repeatedly keeping it horizontal between the two hands; then drain out the liquid. The burette is then vertically mounted on the stand and is filled with the liquid through a funnel. After taking out the funnel, the meniscus is adjusted to any definite graduation mark in the burette by drawing out the necessary volume of the liquid through the stopcock (or spring clip). It is not necessary for the meniscus to be at zero mark, since the volume delivered from a burette can be obtained simply by noting the difference between the initial and final readings.

To avoid error in burette reading, you may make use of a parallax card. Parallax card is a small piece of cardboard covered with white paper in which the lower half is blackened with ink. While reading a burette, adjust the dividing line at the same level as the meniscus as shown in Fig. 1.3 (b).

In order to avoid the parallax, view the position of the burette such that the front and rear levels of the liquid coincide, Fig. 1.3 (c). For accurate titration results, the volume of liquid used for titration should neither be too large nor too small. Titre value is obtained by noting the difference between the intial burette reading and final burette reading (after titration).

1.3.3 Carrying out a Titration

In general, during titration, a standard solution taken in the burette, is added dropwise to a test solution in the conical flask (Fig. 1.4).

A solution for which the concentration is known accurately is called a standard solution.

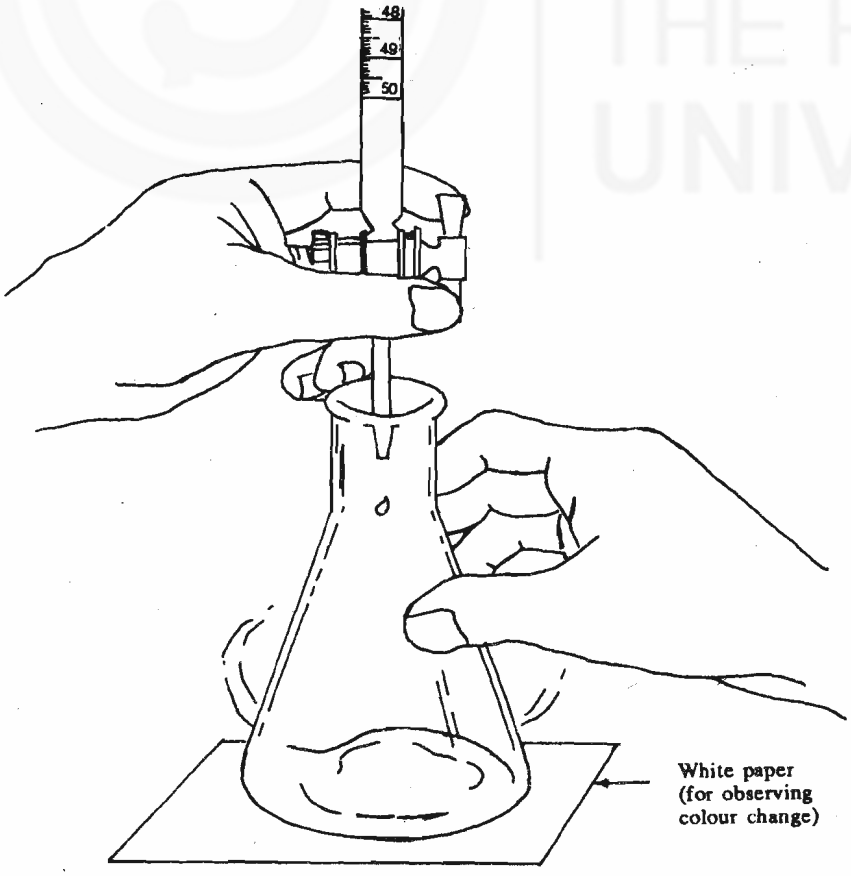


Fig. 1.4 : Delivery of a liquid from a burette.

The purpose of the titration is to find the concentration of the test solution. The equivalence point (or the end point) is determined. The volume of the standard solution delivered through the burette for attaining the equivalence point is known as the titre value. From the titre value, the concentration of the standard solution and the volume of the test solution, it is possible to calculate the concentration of the test solution. The calculation part will be discussed in Sec. 1.7. In the next section, we shall discuss weighing of a substance. This will help us in understanding Sec. 1.6 in which the preparation of standard solution is going to be discussed.

SAQ 1

Define the term, titrimetric analysis.

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SAQ 2

You are given a solution of sodium hydroxide of known concentration and you are asked to find out the concentration of given hydrochloric acid solution. Indicate a method based on each of the following :

i) determination of end point

ii) determination of equivalence point

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In the next unit, we shall discuss SI units for various physical quantities.

1.4 WEIGHING A SUBSTANCE

Mass is the quantity of matter of which the object is composed. Mass of an object is same, irrespective of the location where it is weighed.

Throughout this laboratory course, we use an analytical balance to find the mass of an object.

Weight of an object is the **force** exerted on it by gravitational attraction. The gravitational force and the weight differ at different locations on the earth. A spring balance is used to find the weight of an object.

The internationally accepted unit (SI unit) of mass is kilogram. One gram is one-thousandth part of one kilogram whereas one milligram is one-thousandth part of one gram. In this laboratory course, you would be measuring mass from a few milligrams to grams. You would be using analytical balance for weighing.

An analytical balance (Fig. 1.5) can be used for finding masses to a precision limit of 0.2 mg. As we proceed with the study of this laboratory course, you will notice that many experiments involve at least one measurement of mass. Hence the accuracy of your experiment will depend largely on your skill of using the analytical balance. The analytical balance actually compares the unknown mass of a sample with a standardised mass.

In an analytical balance, (Fig. 1.5), two pans are suspended from the ends of the balance beam. A pointer is attached to the center of the balance beam and it projects down to a scale at the base. The upper edge of the balance beam is

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

Mass of the substance (m g)
= (Mass of the bottle with substance (x g))
– (mass of the bottle after transferring the substance (y g))
i.e., $m = (x–y)$ g

You will see the way of entering the data for weighing towards the end of Sec. 1.6.

You are advised to observe following precautions for getting accurate results during weighing :

a) Ensure that your balance is in good condition. In case there is any malfunctioning, it may be reported to the counsellor.

b) Clean the pans. Never release the beam arrest-knob abruptly as this may damage the balance and you may not get reliable results.

c) Arrest the beam before adding or removing either the sample or the weights.

d) Never place the hot objects for weighing on the balance. An object must be cooled to attain the room temperature before weighing.

e) Always shut the doors of the balance before raising the pans using the arrest-knob.

f) Handle the sample with a piece of paper. The weights must be picked with forceps only.

g) Avoid jerks to the balance.

Having learnt in general about some apparatus to be used in the experiments of this lab course, let us now understand the various terms and concepts used in many of the experiments. Before proceeding to the next section, try the following SAQ's.

SAQ 3

What is the precision limit of an analytical balance ?

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SAQ 4

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

g	mg	position of rider
10		
5	200	6.1
2	100	
1	50	

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1.5 EXPRESSION OF CONCENTRATION

The term 'concentration' refers to the relative amounts of a solute and a solvent in a solution. **Solute** is the dissolved substance in a solution. **Solvent** is the substance in which the solute is dissolved. **Solution** is the homogeneous mixture of a solute and a solvent. Before we discuss the different ways of expressing the concentration of a solution, let us explain a few terms used in quantifying a substance.

The number of ^{12}C atoms in 0.012 kg (i.e., 12 g) of ^{12}C is equal to 6.022×10^{23}

Mole, denoted as mol, is the amount of a substance that contains as many elementary entities as in 0.012 kg of ^{12}C 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 Avagadro number, N_A, which equals 6.022×10^{23}.

Relative molecular mass is unitless, since it represents a ratio.

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 the mass of pure ^{12}C isotope (12.000 a.m.u.). We find the relative molecular mass by multiplying the atomic mass of each element in the molecule by its subscript in the formula and then adding the total for each element to get the grand total, e.g., one molecule of CO_2 has relative molecular mass of 44, which is calculated as :

$$[(12 \times 1) + (16 \times 2)] = (12 + 32) = 44$$

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

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.

The relative molecular mass of oxalic acid dihydrate $[(COOH)_2 \cdot 2H_2O]$ crystals is equal to 126. Hence, the molar mass of oxalic acid dihydrate crystals = 126 g mol^{-1}.

It is better to use the phrase 'amount of a substance' rather than 'number of moles of a substance'.

Amount of a substance is given by the ratio of the mass of the substance to its molar mass.

$$\text{Amount of a substance} = \frac{\text{Mass}}{\text{Molar mass}} \quad \ldots (1.1)$$

Thus the amount of substance having mass equal to molar mass is called mole. Let us now see various methods of expressing the concentration of a solution.

Molarity

For titrimetric purposes, we express concentration in terms of molarity denoted by symbol M. Molarity is defined as the amount present in one dm^3 of the solution. It can be expressed as follows:

$$\text{Molarity} = \frac{\text{Amount of solute}}{\text{Volume of solution in dm}^3} \quad \ldots (1.2)$$

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

The molarity 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}.

Using Eq. 1.1,

$$\text{amount of a solute} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{m\ \text{g}}{M_\text{m}\ \text{g mol}^{-1}}$$

$$= \frac{m}{M_\text{m}}\ \text{mol} \qquad \ldots (1.3)$$

Volume of the solution = $V\ \text{cm}^3$

Since $1000\ \text{cm}^3 = 1\ \text{dm}^3$,

$$\text{Volume of the solution} = V\ \text{cm}^3 \times \frac{1\ \text{dm}^3}{1000\ \text{cm}^3}$$

$$= \frac{V}{1000}\ \text{dm}^3 \qquad \ldots (1.4)$$

Using Eqs. 1.1 to 1.4,

$$\text{molarity of solution} = \frac{\text{Amount of solute}}{\text{Volume of solution in dm}^3}$$

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

$$\text{i.e., molarity} = \frac{1000\,m}{M_\text{m}\,V}\ \text{mol dm}^{-3} \qquad \ldots (1.5)$$

By substituting the volume of a solution in cm^3 unit in the above expression, molarity of a solution can be calculated.

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

$$\text{Normality} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in dm}^3\text{)}} = \frac{\text{Mass}}{\text{Equivalent mass} \times \text{volume of solution(in dm}^3\text{)}}$$

We are not discussing the methods of arriving at the equivalent masses of substances, since we are not going to use normality in our calculations.

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 independent of the type of chemical reaction. Normality, on the other hand, can change as the equivalent mass of a substance depends on the chemical reaction involved in the titration. For example, $KMnO_4$ can have equivalent mass of 158.04 g, 52.6 g or 31.6 g 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 in all the titrimetric experiments. However, percentage, formality and molality, are some other ways of expressing concentration. These 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 solution of volume $100\ \text{cm}^3$, then we get a 10% mass by volume, i.e., 10% m/V solution of NaCl in water.

(b) If instead of preparing 100 cm^3 of solution, we add enough water (to 10 g of NaCl) 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 enough 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.

We shall use percentage units for denoting the concentration of solutions in Units 5, 12 and 13 of this course.

Formality

For certain ionic compounds, e.g., NaCl, which are completely dissociated in solution, it is less accurate to talk in terms of (molecules or) molar mass. Here, it is more appropriate to talk of formality than of normality or molarity. Formality is defined as the number of gram formula masses dissolved per dm^3 of the solution.

$$\text{Formality of a solution (F)} = \frac{\text{Mass of the substance in gram unit}}{\text{Gram formula mass}} \times \frac{1}{\text{Volume of the solution in dm}^3\text{ units}} \quad \ldots (1.6)$$

The gram formula mass of a substance is obtained by multiplying the atomic mass of each element by its subscript in the formula and then adding the total for each element to get the grand total. Thus, one gram formula mass of sodium chloride $= [(1 \times 23) + (1 \times 35.45)]$ g = 58.45 g

Molality

The molality of 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 :

$$\text{Molality} = \frac{m_1 \times 1000}{m_2 \times M_m} \quad \ldots (1.7)$$

where,

m_1 = mass of the solute (in g)
m_2 = mass of the solvent (in g)
M_m = Molar mass of the solute (in g mol^{-1})

The molality scale is useful for experiments in which depression of freezing point, elevation of boiling point, and relative lowering of vapour pressure, are measured. For example, we shall see its use in Unit 8.

SAQ 5

Calculate the molarity of a sodium hydroxide solution, if 500 cm^3 of the solution contains 2 g of solute.

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1.6 PREPARATION OF STANDARD SOLUTION

You may recall that a standard solution is one for which the concentration is known accurately. A standard solution may be prepared by dissolving an accurately weighed, pure stable solid (solute) in an appropriate liquid solvent. Preparation of a standard solution is generally the first step in any quantitative experiment; hence it is important to know how to prepare a standard solution.

Primary and Secondary Standards

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

1) It must be easily available and easy to preserve.

2) It should not be **hygroscopic** nor should it be otherwise affected by air.

3) It should be readily soluble in the given solvent.

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

Some of the available primary standards for titrations are given below along with their relative molecular mass (M_r) values:

Potassium hydrogen phthalate (KHP), $C_8H_5O_4K$ (an acidic substance) $M_r = 204.2$

Anhydrous sodium carbonate, Na_2CO_3 (a basic substance) $M_r = 106$

Potassium dichromate, $K_2Cr_2O_7$ (an oxidising agent) $M_r = 294.2$

Arsenic (III) oxide, As_2O_3 (a reducing agent) $M_r = 197.6$

Potassium iodate, KIO_3 (an oxidising agent) $M_r = 214.0$

Sodium oxalate, $Na_2C_2O_4$ (a reducing agent) $M_r = 134.0$

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 in not possible. Examples are alkalies and various inorganic acids. These substance cannot be obtained in pure form. Therefore, concentration of these substances is to 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.** Now let us discuss the method of preparation of a standard solution.

Alkalies (sodium hydroxide and potassium hydroxide) are hygroscopic. Further, these absorb carbon dioxide from air and, some part of the alkalies get converted into carbonates. Hence, alkalies cannot be used as primary standards.

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. 1.5 as follows:

$$\text{Mass of the solute } (m) = \frac{\text{Molarity} \cdot M_m \cdot V \cdot}{1000} g \qquad \ldots (1.8)$$

The solute is weighed in an analytical balance as explained before (Sec. 1.4), transferred into a volumetric flask with the help of a funnel and dissolved in a small quantity of the solvent. The solution is then made up to the mark by carefully adding the solvent. This can be done using a wash bottle or with a pipette. It is then shaken thoroughly to get a homogeneous solution.

In preparing a standard solution of concentration, say, around 0.1 M, the mass of the substance weighed need not be exactly equal to the mass required for 0.1 M. It can be slightly less or more, but the weighing must be accurate. From the mass of the solute actually taken, molarity of the solution can be calculated using Eq. 1.5.

In the example given below, we show how to enter the data for

- weighing potassium hydrogen phthalate (for preparing a standard solution) and,
- calculation of molarity of the solution.

Preparation of 250 cm^3 of a standard solution of potassium hydrogen phthalate

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

Mass of the weighing bottle + potassium hydrogen phthalate = m_2 = ... g

Mass of the bottle after transferring the salt = m_3 = ... g

Mass of potassium hydrogen phthalate = $m_2 - m_3 = m$ = ... g

Molar mass (M_m) of potassium hydrogen phthalate = 204.2 g mol^{-1}

Volume of potassium hydrogen phthalate solution prepared = 250 cm^3

Molarity of potassium hydrogen phthalate (M_1) is calculated using Eq. 1.5 as,

$$M_1 = \frac{m \times 1000}{M_m \times 250} = \frac{m \times 4}{204.2} = \ldots\ldots \text{ mol dm}^{-3}$$

SAQ 6

You are asked to standardise the solutions of following substances. Suggest a primary standard for each.

(i) hydrochloric acid

(ii) potassium permanganate (an oxidising agent)

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1.7 TITRIMETRIC CALCULATIONS

You may be interested to know as to how titrimetric calculation is done. For this purpose, let us consider the general case of a reaction between two substances, A and B, yielding C and D, as per the stoichiometric equation:

$$pA + qB \longrightarrow rC + sD \qquad \ldots (1.9)$$

where p, q, r and s are the stoichiometric coefficients. As per Eq. 1.9, p moles of A are required for q moles of B for complete reaction. At any instant, the amount of A and B reacted are related as follows:

$$\frac{\text{Amount of A reacted}}{\text{Amount of B reacted}} = \frac{p}{q} \qquad \ldots (1.10)$$

Suppose that during titration, V_A cm^3 of A of molarity M_A has reacted with V_B cm^3 of B of molarity M_B.

p and *q* are known, once stoichiometric equation is written.

Amount of A reacted = Molarity of A × volume of A in dm^3
(using Eq.1.2)

$$= M_A \cdot V_A/1000 \qquad \ldots (1.11)$$

[since V_A is given in cm^3 units]

Similarly, amount of B reacted

$$= \text{Molarity of B} \times \text{volume of B in dm}^3$$

$$= M_B \cdot V_B/1000 \qquad \ldots (1.12)$$

Using Eqs. 1.10 to 1.12,

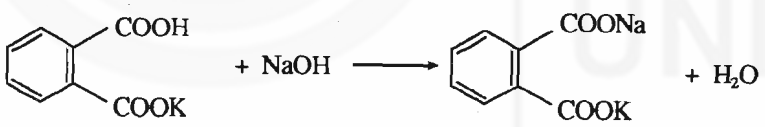
We get, $\dfrac{M_A V_A/1000}{M_B V_B/1000} = \dfrac{p}{q}$

or $$\frac{M_A V_A}{M_B V_B} = \frac{p}{q} \qquad \ldots (1.13)$$

Assume that a standard solution of A (M_A known) is available. The volume of A (V_A) required to react with a known volume of B (V_B) is found out by titration. Since *p* and *q* are known from the stoichiometric equation, the molarity of B (M_B) can be determined using Eq. 1.13. See the following examples.

(i) The reaction between sodium hydroxide and potassium hydrogen phthalate

Sodium hydroxide and potassium hydrogen phthalate (KHP) react according to the equation:



By comparison with Eq. 1.9,
p = Coefficient of KHP = 1
q = Coefficient of NaOH = 1

Let the molarities of potassium hydrogen phthalate and sodium hydroxide solutions be represented as M_1 and M_2. Let the volumes of these two solutions used during neutralisation be V_1 and V_2, respectively.

Using Eq. 1.13,

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

or $$M_1 V_1 = M_2 V_2 \qquad \ldots (1.14)$$

The tabulation of titration data and calculation method for the standardisation of sodium hydroxide solution using standard potassium hydrogen phthalate are given below:

Indicator : Phenolphthalein

Colour change : Colourless to pink

Potassium hydrogen phthalate vs. sodium hydroxide solution

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

Determination of molarity of sodium hydroxide solution

Molarity of potassium hydrogen phthalate = M_1 = ... mol dm^{-3}

Volume of potassium hydrogen phthalate solution = V_1 = 20 cm^3

Volume of NaOH solution used (from the above table) = V_2 = ... cm^3

Molarity of NaOH solution = M_2 = ?

Using Eq. 1.14,

$M_1 V_1 = M_2 V_2$

Molarity of NaOH solution $= M_2 = \dfrac{M_1 V_1}{V_2}$

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

Since M_1, V_1 and V_2 are known, M_2 can be calculated.

ii) The reaction between oxalic acid and potassium permanganate in presence of dilute sulphuric acid

The stoichiometric equation for this reaction is given below :

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

Here again, p = Coefficient of $H_2C_2O_4$ = 5 and

q = Coefficient of $KMnO_4$ = 2

Using Eq. 1.13, $\dfrac{M_{H_2C_2O_4} V_{H_2C_2O_4}}{M_{KMnO_4} V_{KMnO_4}} = \dfrac{5}{2}$

or $2\,M_{H_2C_2O_4} V_{H_2C_2O_4} = 5\,M_{KMnO_4} V_{KMnO_4}$ ... (1.15)

For this case, we do not intend giving the tabulation of titration data. But we illustrate the use of Eq. 1.15 in the calculation of molarity of oxalic acid. Assume that 25 cm^3 of oxalic acid of unknown concentration requires 20 cm^3 of 0.02 M potassium permanganate for complete reaction.

Using Eq. 1.15, $M_{H_2C_2O_4} = \dfrac{5}{2} \dfrac{M_{KMnO_4} V_{KMnO_4}}{V_{H_2C_2O_4}}$

$$= \frac{5 \times 0.02\,M \times 20\,\text{cm}^3}{2 \times 25\,\text{cm}^3}$$

$$M_{H_2C_2O_4} = 0.04\ \text{M}$$

Thus the molarity of oxalic acid is 0.04 M.

Based on the study of Secs. 1.3-1.7, we can sum up the steps involved in the titrimetric estimation of a test solution using primary and secondary standards. To illustrate the steps, we consider the estimation of given ferrous sulphate solution. Assume that oxalic acid is used as a primary standard while potassium permanganate solution is used as a secondary standard.

Step	Illustration
1. Weigh the necessary amount of the primary standard.	1. Weigh the necessary amount of oxalic acid crystals.
2. Prepare the solution of primary standard from the amount weighed in step (i).	2. Dissolve the oxalic acid crystals in water and make up to known volume to prepare a standard solution.
3. Titrate the secondary standard against the primary standard using proper medium. From the titre value, calculate the concentration of secondary standard (using equation similar to Eq. 1.13).	3. Titrate potassium permanganate solution against standard oxalic acid solution in presence of dilute sulphuric acid. Calculate the concentration of potassium permanganate solution (using Eq. 1.15)
4. Titrate the secondary standard against the test solution using proper medium. Calculate the concentration of test solution (using equation similar to Eq. 1.13).	4. Titrate potassium permanganate solution against ferrous sulphate solution in presence of dilute sulphuric acid. Calculate the concentration of ferrous sulphate solution using the following equation. $$\frac{M_{FeSO_4} V_{FeSO_4}}{M_{KMnO_4} V_{KMnO_4}} = \frac{10}{2} = 5$$ (Write the balanced equation for $FeSO_4$–$KMnO_4$ reaction and verify this equation).

Based on the study of this section, answer the following SAQ.

SAQ 7

Write an equation similar to Eq. 1.14 for the reaction between sodium carbonate and hydrochloric acid.

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1.8 HEATING METHODS

In this lab course, you will use the following heating devices:

i) burner

ii) water bath

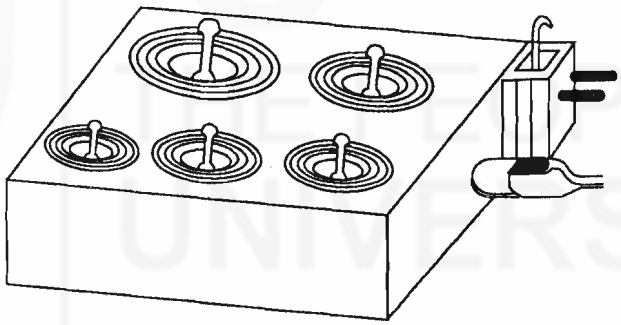
iii) oil bath

Since many of the substances get decomposed at high temperatures or are inflammable, care should be exercised in using the heating devices.

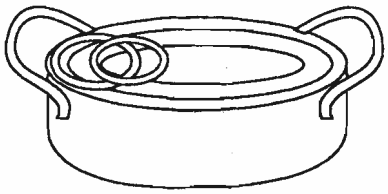
Direct heating on a burner flame should be avoided as far as possible. Heating on a burner should be done using a wire gauze. While using a burner, all inflammable and volatile materials should be removed away from the burner.

A water bath, an oil bath or a sand bath should be used to provide uniform heating. For temperatures upto 100°C, a water bath is generally employed. The simplest form of a water bath consists of a beaker containing water. Water is boiled in a beaker and, the vessel to be heated is kept on the rim of this beaker. If a test tube or a boiling tube is to be heated, it can be kept immersed in it as such or by clamping it using a stand. You may be using an electrically heated water bath or a copper water bath (which can be heated on a burner). These two water baths are shown in Figs. 1.8(a) and (b).

Each of these water baths is covered with rings, which can be adjusted according to the size of the vessel to be heated.



(a)



(b)

Fig. 1.8 a) : Electrically heated water bath b) copper water bath.

An oil bath or a sand bath is used when heating is carried out in the range 100–200°C. An oil bath can be made by filling a copper bowl with a liquid like paraffin oil. A sand bath is a shallow iron plate filled with sand. Both these baths are heated by means of a burner.

SAQ 8

It is proposed to study the miscibility of 10 cm^3 mixtures of phenol and water at different volume by volume percentage compositions in the temperature range 35°C and 75°C. Suggest a simple heating arrangement for this experiment.

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1.9 USE OF THERMOMETERS

Temperature measures the degree of hotness of a body. Temperature scales such as celsius scale are, in general, empirical and arbitrary. The thermodynamic scale or the kelvin scale, is based on the second law of thermodynamics. It is independent of the properties of any particular substance. It is defined in terms of the efficiency of a thermodynamically reversible heat engine. The temperature in the kelvin scale (T K) and that in the celsius scale (t°C) are related as follows :

In Unit 8 (Block 2) of Physical chemistry course, thermodynamic scale of temperature has been explained.

$$T\ \text{K} = t°\text{C} + 273.15$$

The kelvin scale of temperature suffers from lack of convenient instruments for measurement. In this course, we shall use thermometers calibrated in celsius unit. Typical examples are mercury thermometers. We shall be using 0-360°C and 0-110°C thermometers. The former is sensitive to 1°C, whereas the latter is sensitive to 0.1°C. We shall be using thermometers for various purposes. Some of them are given below :

i) For determining the heat capacity and the enthalpy of neutralisation (Unit 7)

ii) For determining the melting point (for estimating the molar mass of a nonvolatile solute using Rast method) (Unit 8)

iii) For obtaining the phase diagram of a given system (Units 12 and 13)

iv) For studying the rate of a reaction (Units 15 and 16)

To illustrate one of the above mentioned uses of thermometers, we shall discuss the method of finding out the melting point of a substance.

Determination of Melting Point

The melting point of a solid is that temperature at which the solid changes into liquid at one atmosphere pressure. A pure solid has a sharp melting point. For a pure solid, the difference between the temperature at which the collapse of the crystal is first observed and the temperature at which the sample becomes completely a liquid, does not exceed by 0.5°-1.0°. But an impure solid melts over a range of temperatures, depending on the amount of the impurity. Let us now discuss the experimental details for determining the melting point of a substance.

The freezing point of a substance is that temperature at which a liquid changes into a solid at one atmosphere pressure. The freezing point of a substance in the liquid state is the same as its melting point in the solid state. This principle is made use of in Unit 8 of this course.

Melting point can also be determined by keeping the liquid bath in

i) a long-necked flask, known as Kjeldahl flask, or

ii) a 100 cm^3 beaker.

Melting points are usually determined in capillary tubes open to the air. A capillary tube is a thin glass tube about 1-2 mm in diameter. For melting point determination, a capillary tube of about 8-9 cm long is taken and sealed at one end by holding it horizontally into the edge of a small burner flame for a few seconds while rotating it. The molten glass would seal the capillary. Formation of large glass beads should be avoided. Let us now see how the capillary tube is filled.

About 25 mg of the dry substance is placed on a clean porcelain plate and finely powdered with a metal or glass spatula forming it into a small heap. The open end of the capillary tube is pushed into the powder, when a small amount of the powder gets into the capillary tube. The solid is shaken down the tube by tapping the closed end of the tube gently on the work-table. The process is repeated until the length of the tightly packed material is about 3-5 mm. The outside of the tube is then wiped clean.

The capillary tube can be heated in a liquid bath or on an electrically heated metal block. You may be using Thiele's melting point apparatus (Fig. 1.9), which is a tube with a closed bent side–arm. On heating the bent side–arm, the heated liquid circulates and rises the temperature of the sample. The tube is filled with the liquid to just above the bent side-arm. No stirring is required. The bath liquid generally used is liquid paraffin, which can be safely heated upto 220°C; above this temperature it starts fuming and gets discoloured. Silicone oils, though more stable, are expensive.

The attachment of the capillary tube to the thermometer through moistening is due to the phenomenon of surface tension. You will study the phenomenon of surface tension in Unit 4 of this course.

If the arrangement used in your laboratory for noting the melting point is different from the one explained here, you can get the details of using the same from your counsellor.

Into the melting point apparatus, the thermometer is fitted through a cork. A section of the cork is cut away, so that the thermometer scale is visible and the heated air could escape. The filled capillary tube is moistened with the bath liquid which helps in attaching the capillary tube to the thermometer. The filled capillary tube is attached to the lower end of the thermometer in such a way that the substance is at the level of the middle of the mercury bulb. The thermometer, with the capillary tube attached, is then inserted into the bath. Care is taken that the open end of the capillary tube is well above the level of the liquid.

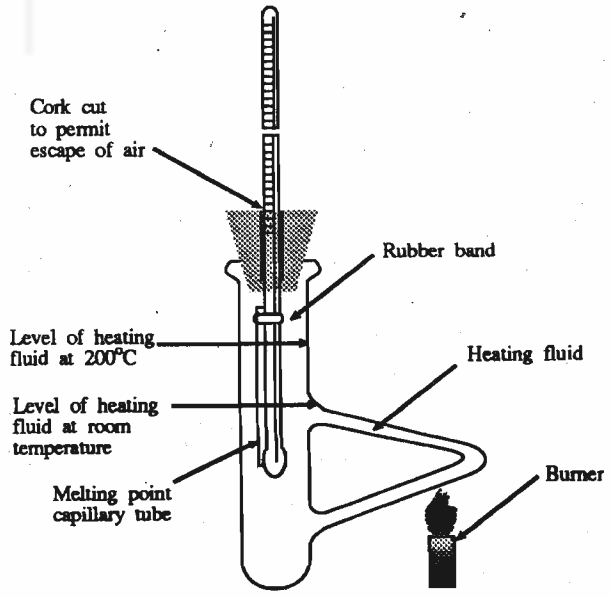

Fig. 1.9 : Thiele's melting point apparatus.

The melting poing apparatus is heated with a small flame comparatively rapidly till the temperature is about 15° below the melting point of the substance. Later it is heated slowly such that the rise of temperature is about 2° per minute. The temperature at which the substance starts to melt and the temperature at which it has completely liquified are noted. These two temperatures give the melting range. As said above, for a pure compound, the melting range should not exceed 0.5° – 1°. In case of an unknown compound, an approximate melting point may be taken first.

The following precautions must be observed while determining the melting point:

1. The capillary used must be of uniform bore.
2. The packing of the substance should be compact and uniform.
3. A sand bath must be placed below the melting point apparatus, in case the bath liquid is concentrated sulphuric acid.
4. A section of the cork must be cut away.
5. The heating of the flask must be slow.
6. The substance should be dry.

In the next section, we shall discuss filtration.

1.10 FILTRATION

Filtration is employed for separating a precipitate from a solution. For this, we make use of a funnel, a circular sheet of filter paper, a stand, a beaker, a glass rod and a wash bottle. A wash bottle is designed to deliver a fine stream of distilled water in a controlled way. A typical wash bottle is shown in Fig. 1.10.

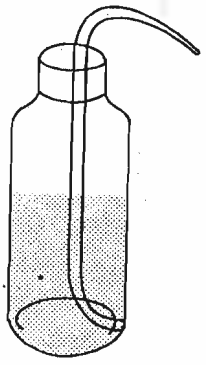

Fig. 1.10 : Wash bottle.

The first step in the filtration of a precipitate is to fold the filter paper properly into halves along any diameter as shown in Fig. 1.11(a). The side holding three quarters is opened to obtain a cone of the filter paper (Fig 1.11(b).

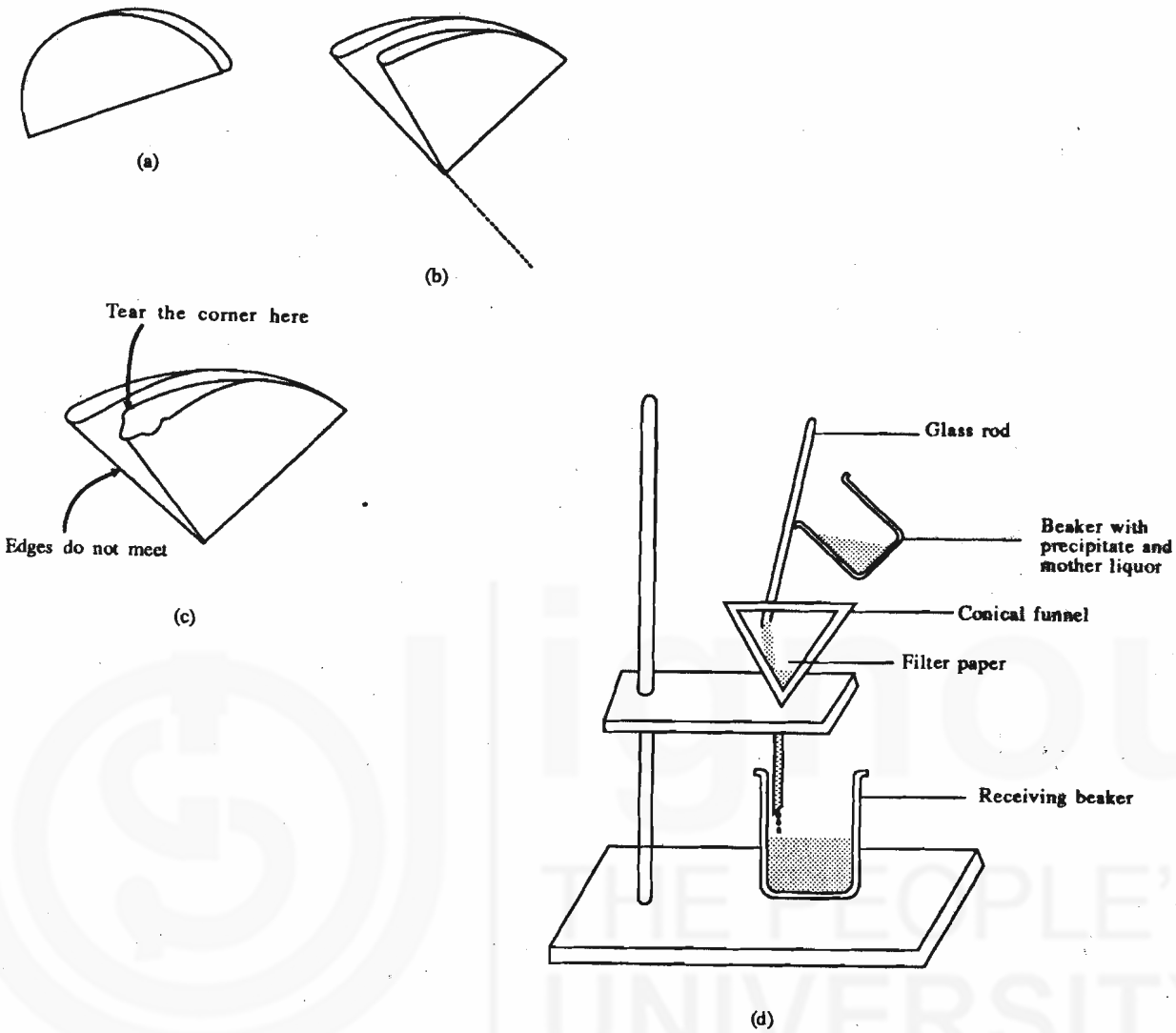

Fig. 1.11 : a) and b) Folding the filter paper c) tearing the corner d) filtration set-up

In order to get efficient filtration, tear off the upper tip of the filter paper cone (Fig.1.11(c)) so that the cone fits into the funnel. Also a long stem funnel should be used. The filter paper cone is fixed in the mouth of the funnel using a little water. Now the funnel is placed on a stand with its stem touching the side of the receiving vessel kept for collecting the filtrate. The mixture to be filtered is poured into the filter paper gently along a glass rod, the lower tip of which rests on three quarters of the filter paper cone (Fig.1.11(d)). The solid particles in the mixture will be collected on the filter paper, while the filtrate will be collected in the receiving vessel. At the beginning of filtration, the solid particles should be allowed to settle down and the liquid should be decanted into the funnel, leaving most of the precipitate in the vessel. The precipitate should be washed with the wash-liquid, the solid again allowed to settle down and the liquid transferred to the funnel. This process is repeated to free the precipitate of other ions. Finally the precipitate is completely transferred to the funnel using more of wash-liquid. Usually wash-liquid is water or a liquid in which the precipitate is insoluble. Wherever quantitative estimation is done, proper filter paper is to be used as per the advice of the counsellor.

1.11 SUMMARY

In this unit, we discussed the safety measures to be adopted while working in a chemistry laboratory. We explained some of the techniques which are useful in performing the experiments of this course. We also discussed the relevant calculations and the apparatus for these experiments.

1.12 ANSWERS

Self Assessment Questions

1) Titrimetric analysis consists in determining the volume of a standard solution which is required to react completely with a known volume of the solution of a substance being estimated.

2) i) Titration using phenolphthalein as an indicator

   ii) Titration using conductometer or mV/pH meter.

3) An analytical balance can be used for weighing masses to a precision limit of 0.2 mg.

4) 18.3562 g

5) As per Eq. 1.5, molarity $= \frac{1000m}{M_m V}$

$$= \frac{1000 \times 2}{40 \times 500} \text{ M}$$

$$= 0.1 \text{ M}$$

6) i) Sodium carbonate

   ii) sodium oxalate

7) CO_3^{2-} (from Na_2CO_3) + $2H^+$ (from HCl) $\longrightarrow$ H_2CO_3

Let M_1 and M_2 stand for the molarities of sodium carbonate and hydrochloric acid, respectively while V_1 and V_2 refer to the equivalent volumes of sodium carbonate and hydrochloric acid, respectively. In comparison to Eq. 1.13.

$$\frac{M_1 V_1}{M_2 V_2} = \frac{1}{2}$$

or $$2 M_1 V_1 = M_2 V_2$$

8) Mixtures of different compositions of phenol and water are to be taken in different test tubes and heated in water bath to study the miscibility temperature in each case.

UNIT 2 HANDLING OF DATA

Structure

2.1 Introduction

2.2 SI Units
- Basic Units
- Derived Units
- SI Prefixes
- Grammatical Rules for Representing SI Units

2.3 Some Useful Mathematical Operations
- Scientific Notation
- Using the Table of Logarithms
- Finding the Numbers from their Logarithms

2.4 Significant Figures
- Calculation of Significant Figures in a Number
- Addition and Subtraction Maintaining Significant Figures
- Multiplication and Division Maintaining Significant Figures
- Taking Logarithms and Antilogarithms Maintaining Significant Figures

2.5 Laboratory Note Book

2.6 Tabulation of Data and Plotting of Graphs

2.7 Summary

2.8 Answers

2.1 INTRODUCTION

In Unit 1, we studied some of the laboratory techniques which are to be used in this course. As part of this, we discussed the methods of expression of concentration and, titrimetric calculation. These two are, in fact, part of data handling techniques. Handling of data consists of processing the experimental data and expressing the values of the physical parameters with proper magnitude and units. Processing of data includes stepwise calculation to obtain the value of a parameter and representation of results using tables or graphs.

In this unit, we shall discuss the basic and derived SI units. We shall explain the principles to be followed in expressing a number in scientific notation. We shall define the term, significant figure. We shall explain how to maintain significant figures while doing calculations of various types such as addition, subtraction, multiplication, division, taking logarithms and antilogarithms etc. We shall finally discuss how to record the observations, tabulate the data and plot the graphs.

Objectives

After studying this unit, you should be able to

- state the SI units of basic and derived physical quantities,
- arrive at the SI units of a physical quantity,