UNIT 1 LABORATORY TECHNIQUES AND PROCEDURES

Structure

1.1 INTRODUCTION

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

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

Objectives

After reading this unit, you will be able to:

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

1.2 APPARATUS COMMONLY USED

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

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

1.2.1 How to Use a Pipette

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

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

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

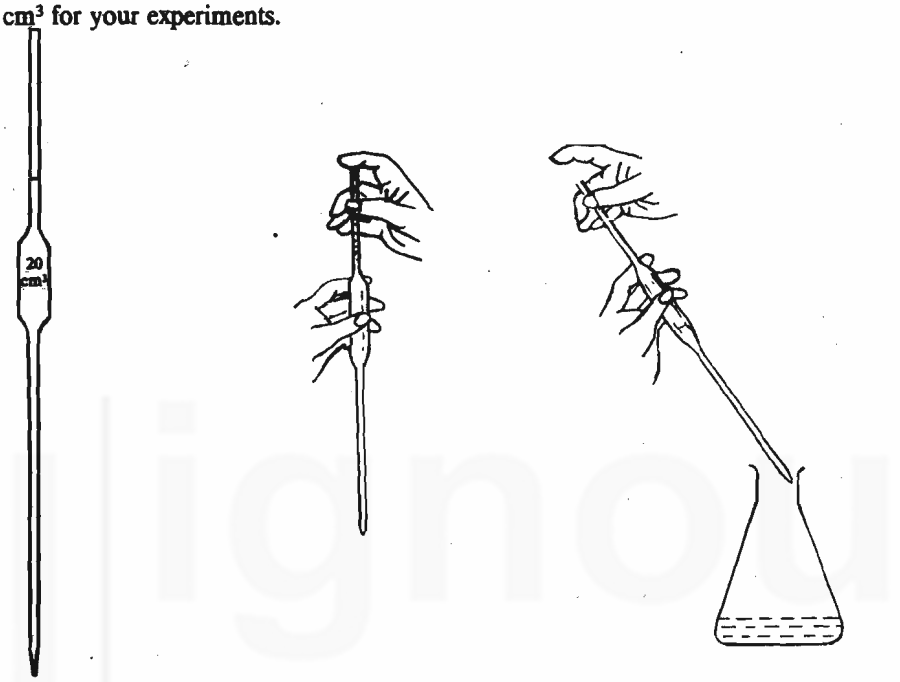

Fig. 1.1 : (a) Pipette. (b) Handling of a pipette. (c) Correct way to drain out the solution.

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

Concave meniscus
Convex meniscus

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

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

Fig. 1.2 : Graduated Pipette.

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

SAQ 1
Why should you not blow the last drop out of the pipette?

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1.2.2 How to Use a Burette

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

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

Fig. 1.3 : Burette.

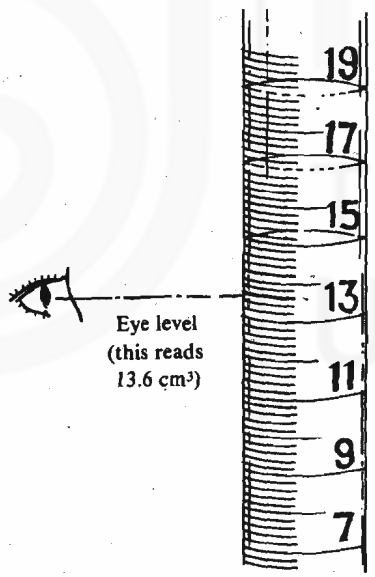

Fig. 1.4 : Eye level for burette reading.

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

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

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

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

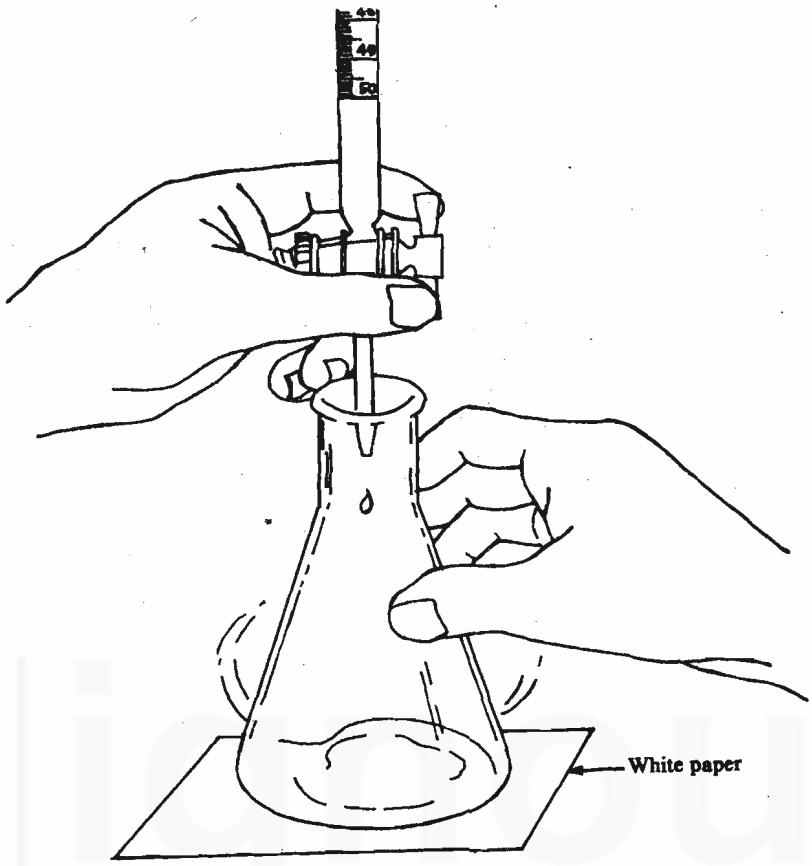

Fig 1.6 : Delivery of liquid from a burette.

1.2.3 How to Use a Volumetric Flask

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

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

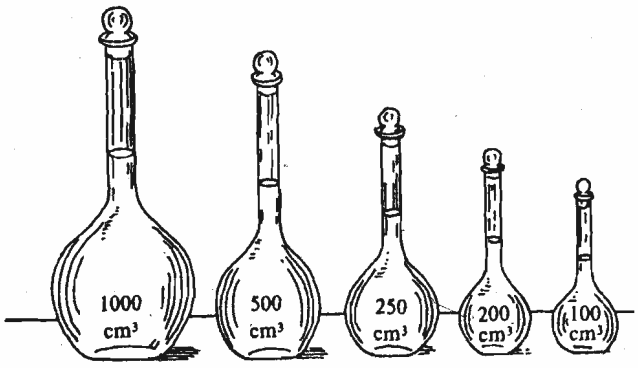

Fig. 1.7 : Volumetric flasks

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

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

1.2.4 How to Use an Analytical Balance

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

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

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

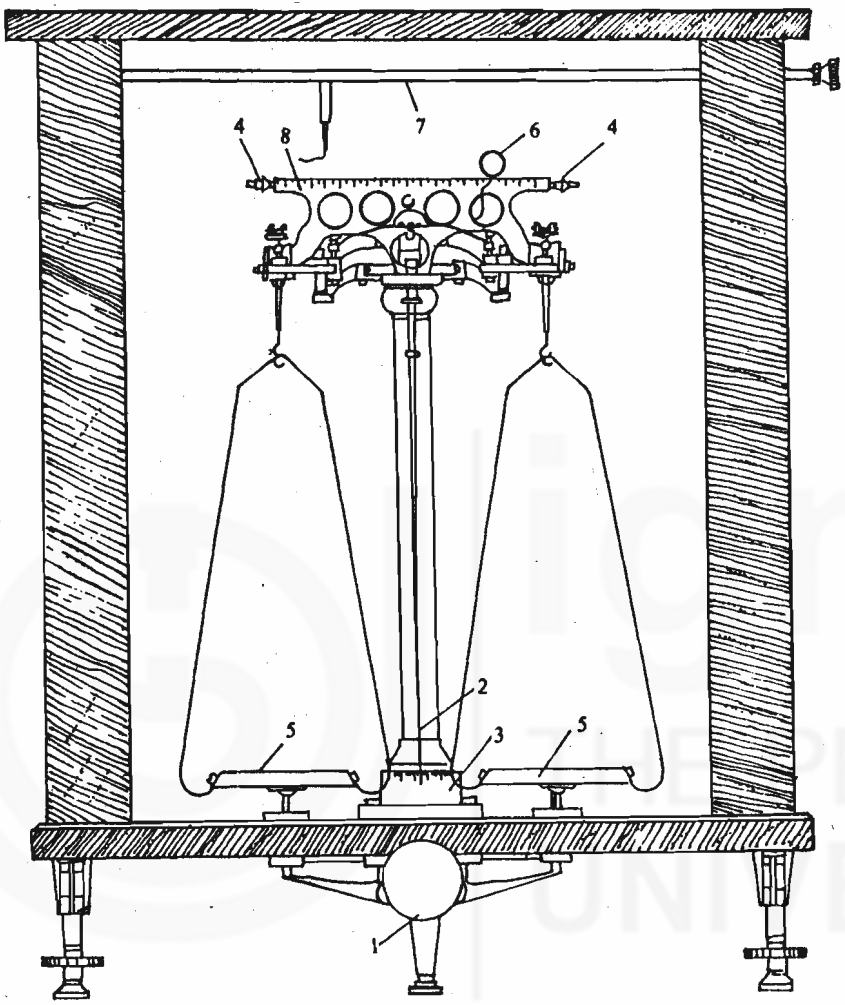

Fig. 1.8 : Analytical balance

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

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

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

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

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

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

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

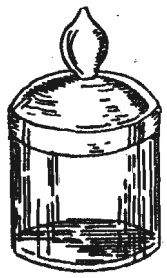

Fig. 1.9 : Weighing bottle

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

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

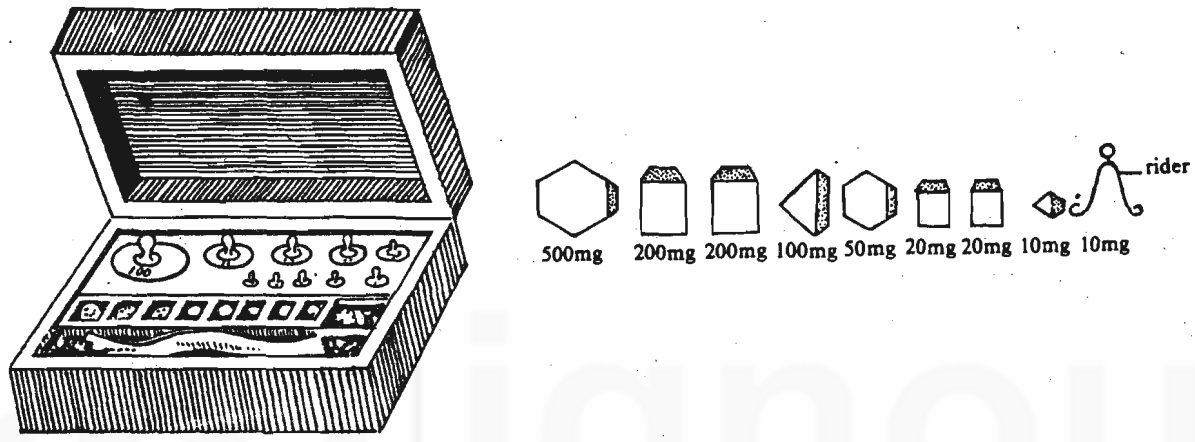

Fig. 1.10 : Weight box and weights

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

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

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

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

Mass of the object = (Weights added in grams)
+ (Fractional weights added $\times$ 0.001) g
+ (Main division of the rider position $\times$ 0.001) g
+ (Subdivision of the rider position $\times$ 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 $\times$ 20 mg. Let the rider position be 2 or the main divisions and 3 on the subdivisions.

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

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

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

$m = m_1 - m_2$ g

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

SAQ 2

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

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

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1.3 EXPRESSION OF CONCENTRATION

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

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

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

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

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

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

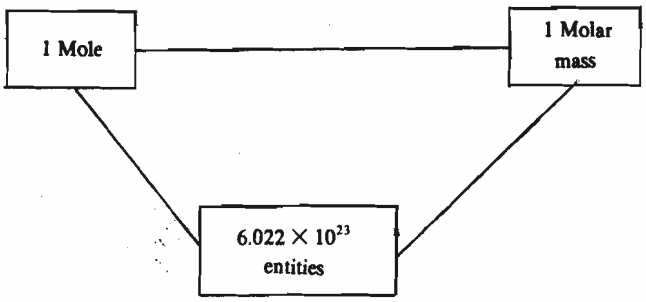
Relative molecular mass being relative is unitless.

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

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

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

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



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

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

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

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

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

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

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

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

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

Hence by definition,

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

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

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

1 ml = 1.000028 cm^3

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

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

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

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

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

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

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

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

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

Mathematically percentage is given as :

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

ppm = mg dm^{-3}
= μ g cm^{-3}
= 10^{-3} g dm^{-3}

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

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

SAQ 3

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

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SAQ 4

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

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1.4 STANDARD SOLUTION

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

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

Primary and Secondary Standards

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

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 :

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

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

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

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

Preparation of a Standard Solution

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

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

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

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

SAQ 5

On what criteria do

(a) sodium hydroxide and

(b) benzoic acid

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

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1.5 TITRATION

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

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

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

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

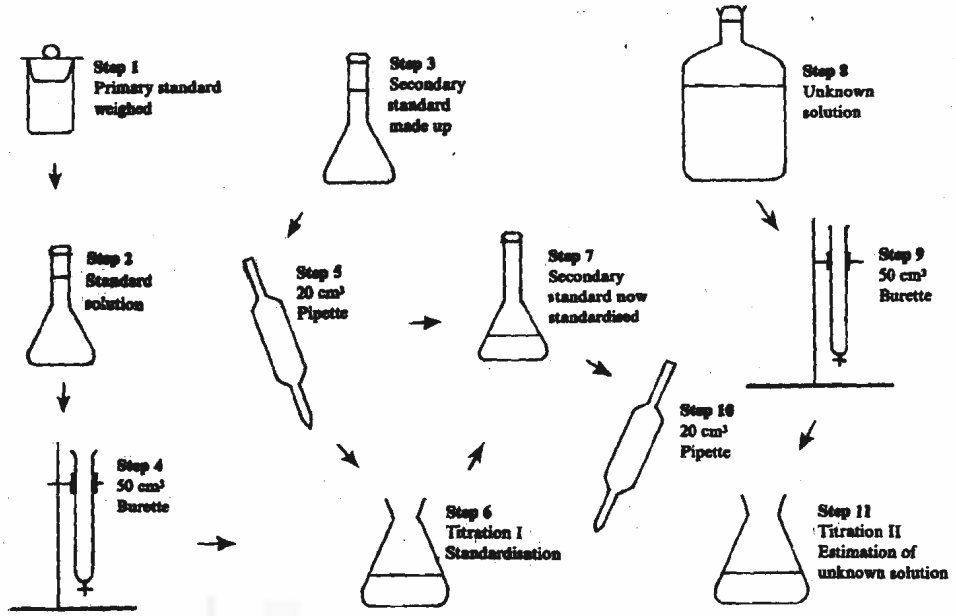

Fig. 1.11 : Steps in a titrimetric estimation

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.

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.

1.5.1 Types of Indicators

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

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

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

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

1.5.2 Types of Titrations

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

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

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

$NaOH + HCl \rightarrow NaCl + H_2O$

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

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

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

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

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

$KCl + AgNO_3 \rightarrow AgCl + KNO_3$

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

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

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

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

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

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

Objectives

After performing this experiment you should be able to :

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

1.6.1 Principle

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

$NaOH + HCl \rightarrow NaCl + H_2O$

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

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

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

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

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

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

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

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

Substituting Eq. 1.4 and 1.5 in Eq. 1.3:

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

or $M_1 V_1 = M_2 V_2$ ...(1.7)

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

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

$pA + qB \longrightarrow rC + sD$

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

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

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

1.6.2 Requirements

Apparatus

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

Solutions provided

Sodium hydroxide solution ($\simeq$ 0.1 *M*)
Hydrochloric acid solution (0.1 *M*)
Methyl orange indicator solution

1.6.3 Procedure

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

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

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

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

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

1.6.4 Observations

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

Observation Table I

HCl Vs. NaOH

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

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

1.6.5 Calculations

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

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

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

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

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

$$= 0.096\ M$$

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

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

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

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

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

= 3.84 g

1.6.6 Result

For the given sample experiment,

i) The molarity of the NaOH solution is 0.096 mol dm^{-3}

ii) Strength of NaOH = 3.84 g dm^{-3}

1.7 INSTRUMENTAL DETERMINATION OF EQUIVALENCE POINT

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

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

1. Conductometric Titrations

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

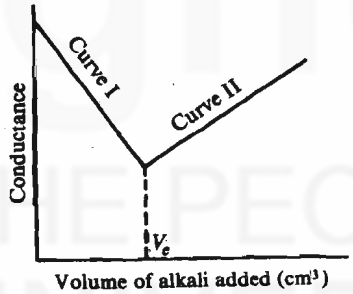

Fig. 1.12 : Conductance curve : Titration of NaOH against HCl

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

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

2. Potentiometric Titrations

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

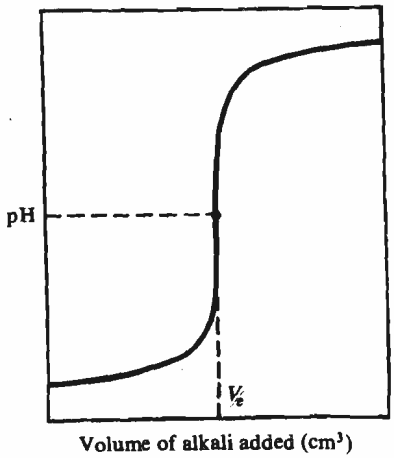

Fig. 1.13 : pH metric titration of HCl vs. NaOH

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

Colorimetry

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

Use of Instruments

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

SAQ 6

Tick ✓ on the correct statement/s.

Instrumental methods are preferred over indicator methods because

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

ii) Instruments are not very expensive.

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

iv) Instrumental methods do not require indicators.

1.8 COMMON LAB REAGENTS

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

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

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

1.9 SAFETY MEASURES IN THE LABORATORY

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

The Do's:

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

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

The Don'ts :

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

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

Table 1.1 : List of hazardous chemicals and their effects

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

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

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

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

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

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

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 a non-corrosive poison.

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

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

Table 1.2 : Remedies for a few chemical reagents

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

1.10 ANSWERS TO SAQs

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

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

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

   Where $M_m = 40$ g mol^{-1}
   $m = 4.000$ g
   $V = 500$ cm^3
   Therefore,

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

   $= 0.200$ mol dm^{-3}
   Thus, molar concentration $= 0.200\ M$

4. Again consider Eq. 1.1,

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

   Where $M_m = 169.87$ g mol^{-1}
   $V = 1$ dm^3 $= 1000$ cm^3
   $M = 0.1\ M$

   On substituting these values in the above equation, we have

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

   $= 16.987$ g

   Thus, mass of $AgNO_3$ required for 0.1*M* solution $= 16.987$ g.

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

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

6. i) ✓
   ii) ×
   iii) ×
   iv) ✓

UNIT 2 ACID-BASE TITRATIONS-I

Structure

2.1 INTRODUCTION

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

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

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

Objectives

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

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

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

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

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

2.2 THEORY OF ACIDS AND BASES

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

2.2.1 Definition of Acids and Bases

There are three common definitions of acids and bases.

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

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

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

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

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

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

Conjugate pair

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \quad \ldots (2.1)$$

Acetic acid Water Hydronium ion Acetate ion

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

Before proceeding further, answer the following SAQs.

SAQ 1

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

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

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

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

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

2.2.2 Ionisation of Water and the pH Concept

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

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

Many other solvents like NH_3 also undergo autoionisation.

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

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

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

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

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

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

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

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

Table 2.1 : Temperature dependence of K_w

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

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

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

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

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

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

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

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

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

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

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

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

The pH Concept

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

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

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

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

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

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

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

$pK_a = -\log_{10}K_a$

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

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

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

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

Multiplying by -1 gives

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

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

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

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

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

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

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

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

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

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

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

2.2.3 Dissociation of Weak Acids and Weak Bases

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

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

The equilibrium expression for this reaction is

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

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

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

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

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

$CH_3COOH \rightleftarrows H^+ + CH_3COO$

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

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

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

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

Similarly for the base B, we have

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

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

Now, $K_b = K\,[H_2O]$

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

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

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

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

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

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

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

SAQ 2

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

(i) Is this sample acidic or basic?

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

.....

.....

.....

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

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

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

.....

.....

.....

2.3 THEORY OF ACID-BASE TITRATIONS

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

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

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

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

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

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

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

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

pH = 7.0 + 2.37 − 0.65 = 8.72

Weak acid and strong base

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

Weak base and strong acid

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

Weak acid and weak base

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

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

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

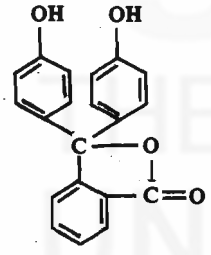
There are many methods available to detect equivalence point, experimentally, during titration. The most common method is the use of acid-base indicators. Indicators are organic dyes which change colour at or near the equivalence point to indicate the end of the reaction. In fact, the point at which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

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

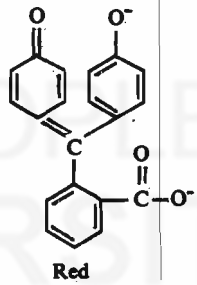
Other methods to detect equivalence point are pHmetry or potentiometry and conductometry. These methods will be discussed in detail along with Experiments 2 and 3. Now we will discuss the theory of acid-base indicator.

2.3.1 Acid-Base Indicators

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

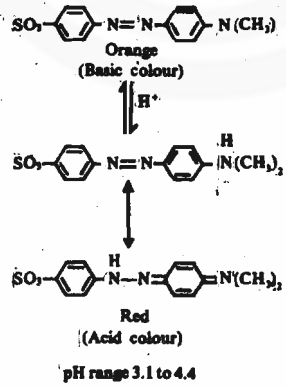


Colourless
(I)



Red
(II)

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



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

In general we have two possible indicator reactions :

$$\underset{\text{Acid colour (weak acid)}}{HIn} \rightleftharpoons \underset{\text{Basic colour}}{H^+ + In^-} \quad (2.15)$$

$$\underset{\text{Basic colour (weak base)}}{In + H_2O} \rightleftharpoons \underset{\text{Acid colour}}{InH^+ + OH^-} \quad (2.16)$$

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

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

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

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

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

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

and for the basic colour

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

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

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

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

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

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

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

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

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

2.3.2 Acid-Base Titration Curves

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

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

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

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

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

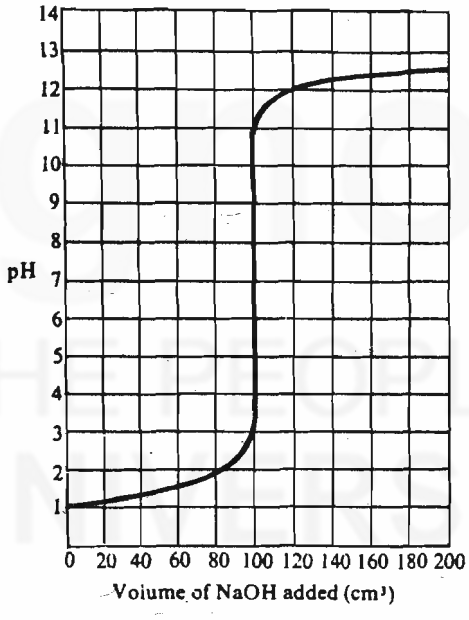


Fig. 2.1 : Strong acid-strong base titration curve

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

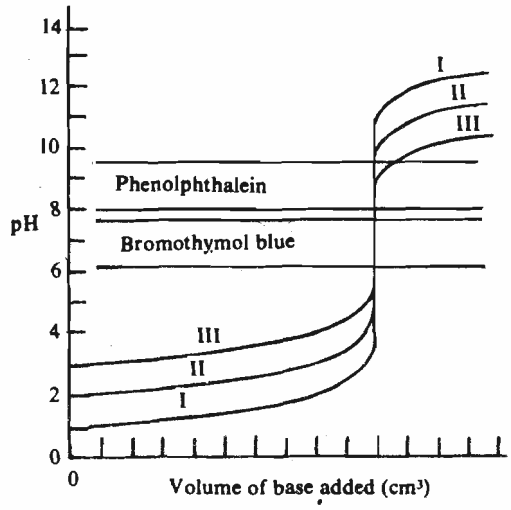


Fig. 2.2 : Titration curves for strong acid against strong base at three different concentrations

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

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

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

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

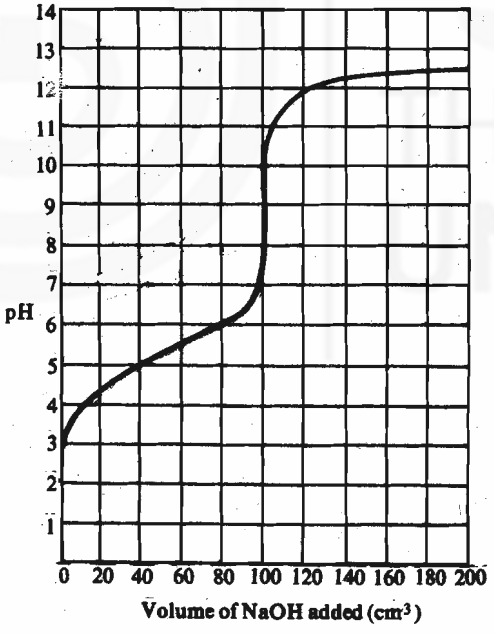


Fig. 2.3 : Titration curve for a weak acid with a strong base

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

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

The slowly rising flattered region before the equivalence point is called the buffer region.

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

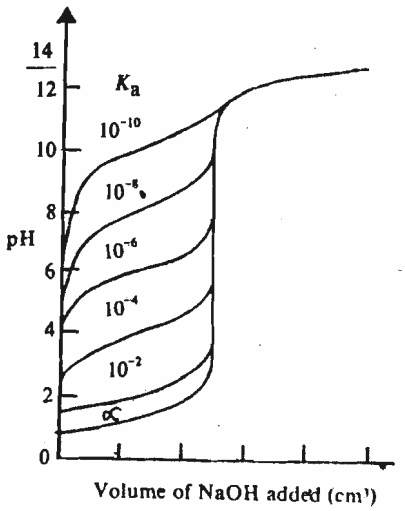


Fig. 2.4 : The effect of K_a on the titration curves for weak acid with a strong base

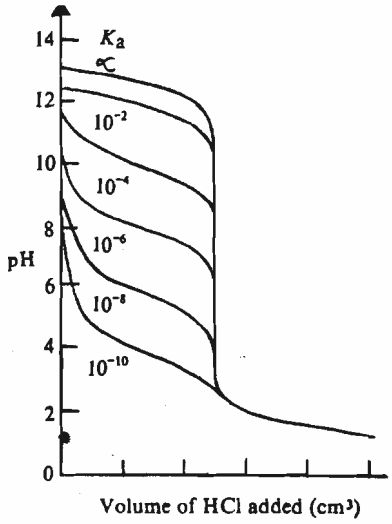


Fig. 2.5 : The effect of K_b on the titration curves for weak bases with a strong acid

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

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

SAQ 3

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

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

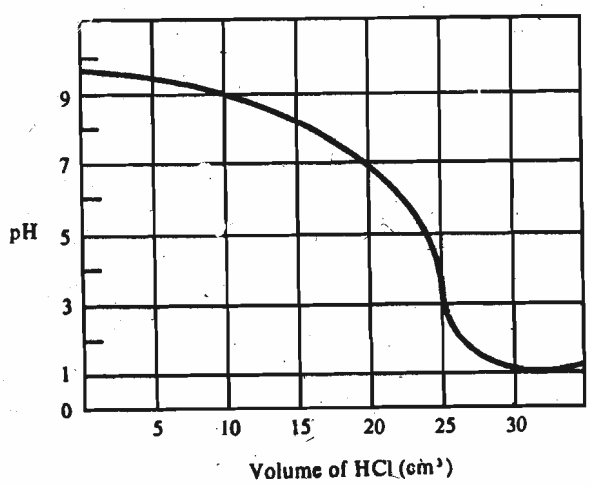


Fig. 2.6 : Acid-base titration curve; pH against volume of HCl

SAQ 4

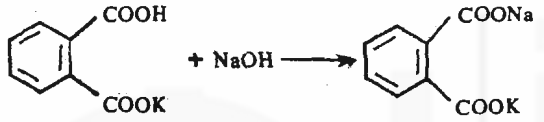
Indicate the buffer region in the titration curve given in Fig 2.3.

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

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

2.4.1 Principle

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



... (2.19)

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

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

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

In this titration phenolphthalein is used as indicator.

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

The stoichiometry of the titration is given by,

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O \qquad \ldots (2.21)$$

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

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

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

2.4.2 Requirements

Apparatus

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

Chemicals

Vinegar
Potassium hydrogen phthalate

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

Solutions provided

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

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

2.4.3 Procedure

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

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

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

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

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

2.4.4 Observations

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

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

Observation Table I
Potassium hydrogen phthalate vs. sodium hydroxide solution

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

Observation Table II
Vinegar solution vs. sodium hydroxide solution

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

2.4.5 Calculations

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

$M_1V_1 = M_2V_2$

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

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

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

$M_4V_4 = M_3V_3$

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

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

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

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

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

2.4.6 Result

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

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

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

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

titration. We may summarise them as :

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

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

iii) The indicator volume should be minimal.

iv) The colour should be clear and sharp.

v) The sample should be colourless.

vi) The sample must not be too dilute.

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

2.5.1 Principle

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

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

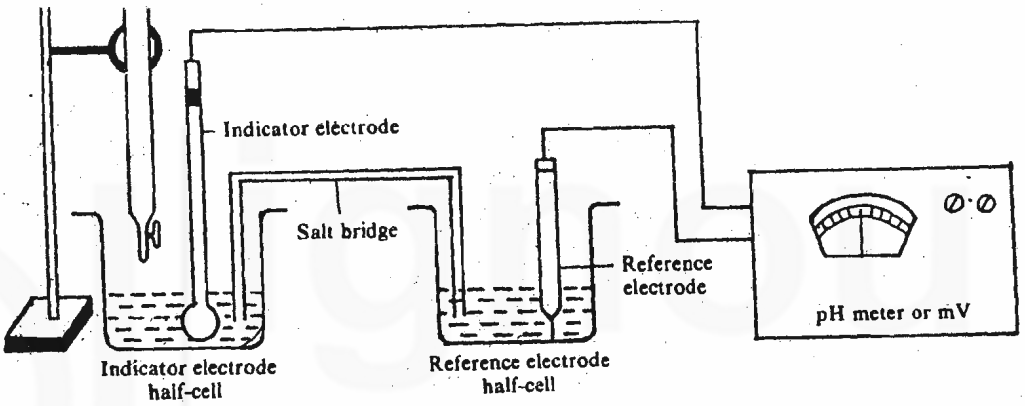


Fig. 2.7 : Apparatus for potentiometric titration.

Electric potential (E) is measured in volts (V). The smaller unit of potential is millivolt (mV).

$1mV = 10^{-3}V$

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

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

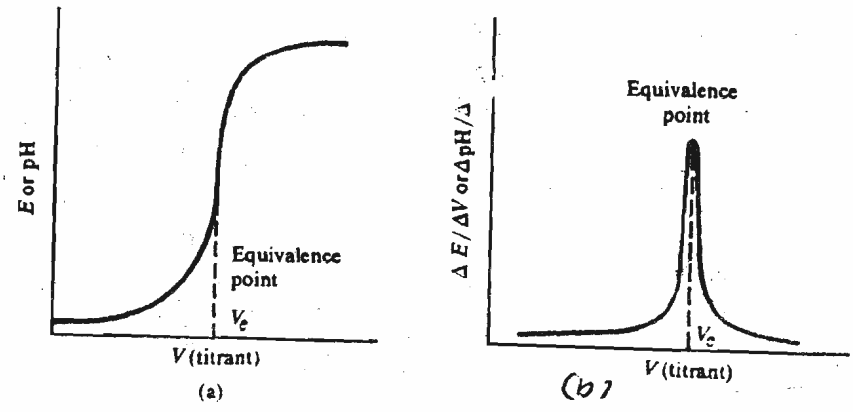


Fig. 2.8 : Methods of equivalence point determination (a) Normal plot (b) first derivative

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

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

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

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

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

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

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

At 298 K, Nernst equation has the form,

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

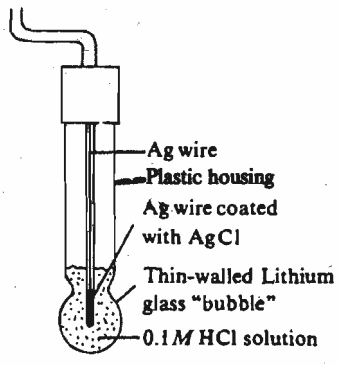
In the above equation, E is the electrode potential at a given concentration, E° is the standard electrode potential, i.e., at $1M$ concentration for a solution or 1 atm. for a gas, n is the number of moles of electrons transferred in the reaction and A, B, C and D are the species whose concentration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

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

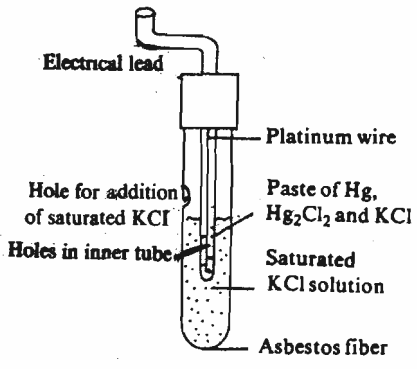
There are several electrode systems available for potentiometric pH determination. We are listing some of them in Table 2.6.

Table 2.6 : Electrode systems for hydrogen ion or pH measurement

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



Glass electrode



Calomel electrode

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

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

For the glass electrode, the Nernst equation has the following form :

$E = k + 0.0591$ pH, or

$E = k - 0.0591 \log [H^+]$

where k is the asymmetry junction potential, approximately a constant factor for an individual glass electrode.

For the quinhydrone electrode, Nernst equation has the following form :

$E = 0.700 + 0.0591 \log [H^+]$

or $E = 0.700 - 0.0591$ pH

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

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

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

Before that, try to answer the following SAQ.

SAQ 5

Give two advantages of potentiometric method of titration.

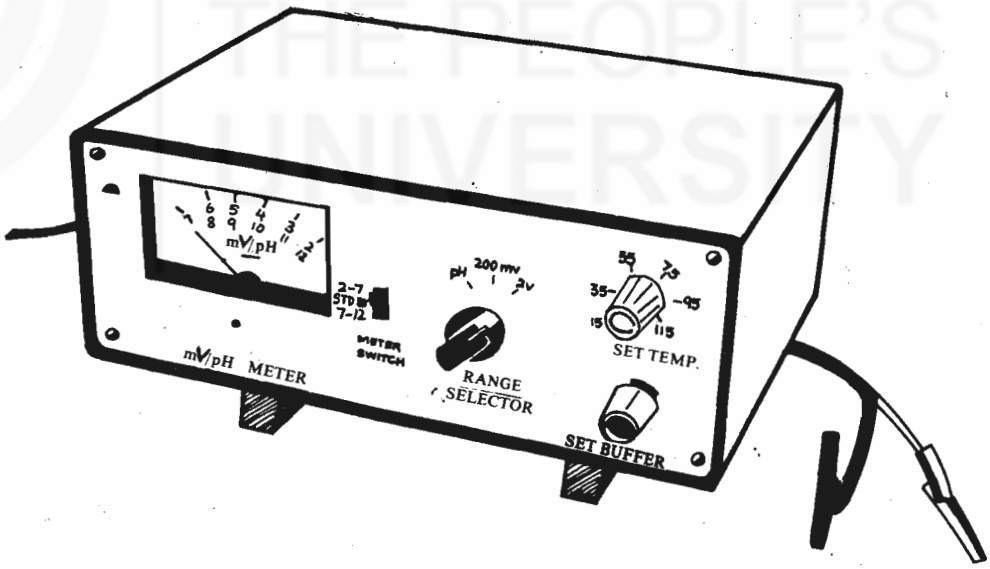
.....

.....

.....

2.5.2 pH Meter

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



Description of Controls

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

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

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

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

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

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

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

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

2.5.3 Calibration of pH Meter for pH Measurement

Requirements

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

Solutions provided

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

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

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

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

Procedure for Calibration of pH Meter

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

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

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

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

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

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

2.5.4 Requirements

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

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

Solution provided

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

2.5.5 Procedure

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

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

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

2.5.6 Observations

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

Observation Table I

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

2.5.7 Calculations

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

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

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

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

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

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

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

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

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

2.5.8 Result

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

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

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

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

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

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

2.6.1 Principle

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

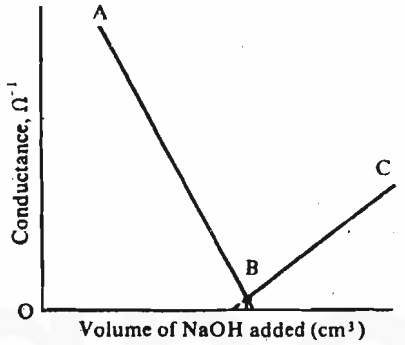


Fig. 2.10 : Conductometric titration curve for strong acid (HCl)—strong base (NaOH) titration

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

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

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$
(unionised)

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

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

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O$$
(poorly ionised) (ionised)

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

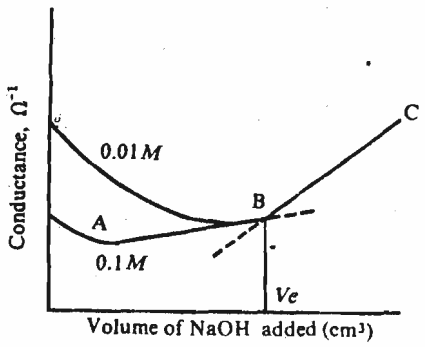


Fig. 2.11 : Titration of acetic acid against sodium hydroxide

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

SAQ 6

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

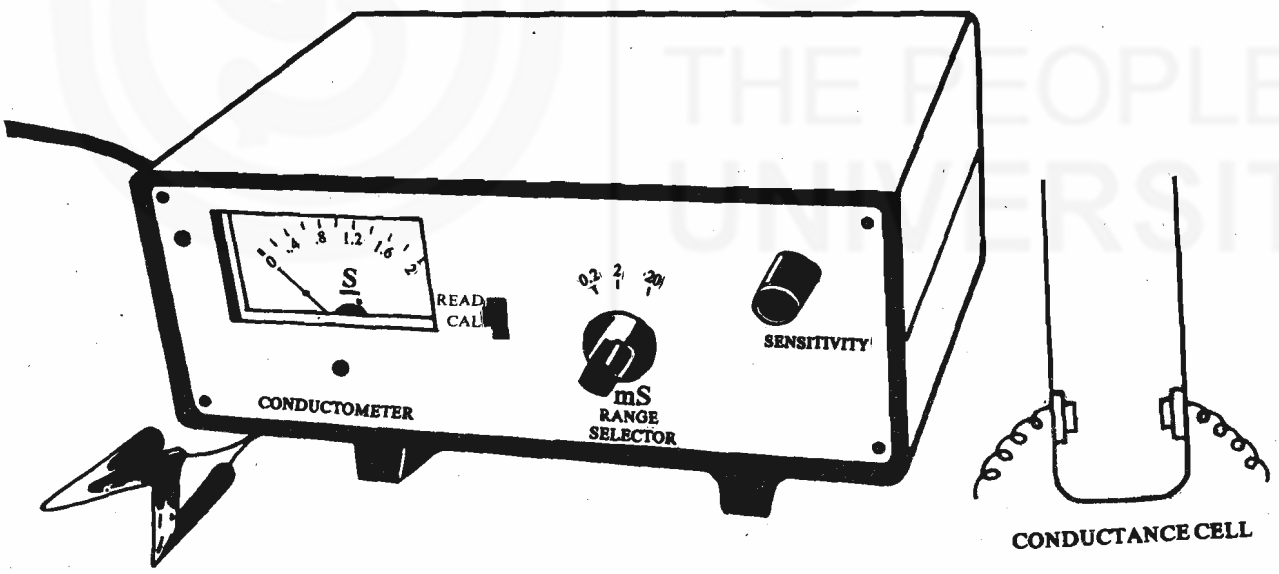
(a) Slope of curve AB depicts the increase of conductance due to the ionisation of sodium acetate formed.

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

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

2.6.2 Conductometer

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



Description of Controls

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

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

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

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

2.6.3 Calibration of Conductometer

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

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

2.6.4 Requirements

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

Chemical
Vinegar

Solution provided

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

2.6.5 Procedure

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

2.6.6 Observations

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

Observation Table I

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

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

2.6.7 Calculations

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

$$M_2 V_2 = M_1 V_1$$

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

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

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

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

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

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

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

2.6.8 Result

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

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

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

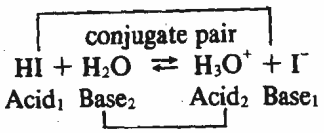
	Experiment 1	Experiment 2	Experiment 3
Correct value of strength in g dm^{-3}			
Calculated strength in g dm^{-3}			

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

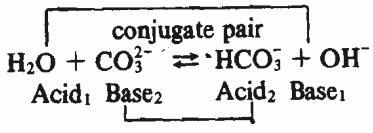
Based on what you have learnt, you can design experiments for analysis of some commercial products such as : estimation of citric acid in lemon juice, tartaric acid in wine, phosphoric acid in soft drinks, acetylsalicylic acid in aspirin, etc.

2.7 ANSWERS TO SAQs

1. a)



b)



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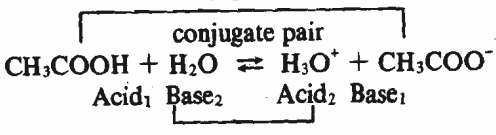
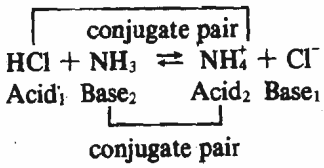


d)



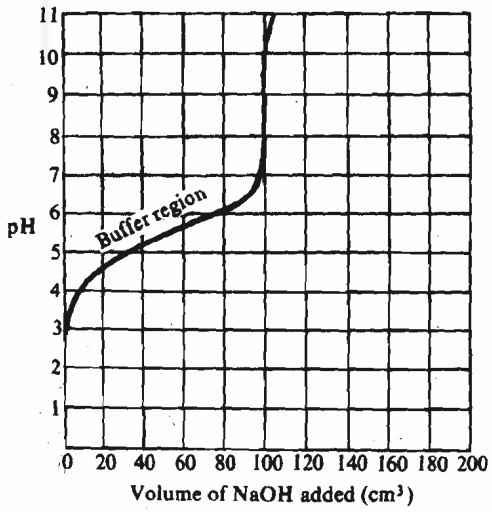
2. a) (i) Acidic (ii) $(H^+) = 1 \times 10^{-4}$ mol dm^{-3}, $(OH^-) = 1 \times 10^{-10}$ mol dm^{-3}

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

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

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

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



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

UNIT 3 ACID-BASE TITRATIONS-II

Structure

3.1 INTRODUCTION

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

Objectives

After performing this experiment you should be able to :

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

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

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

3.2.1 Principle

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

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

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad \ldots (3.1)$$

(carbonate ion) (bicarbonate ion)

The bicarbonate ion is further hydrolysed to carbonic acid :

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

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

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

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

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

Combining both the above equations we can write,

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

From Eq. 3.5, we can see that $p = 1$ and $q = 2$, substituting these values in Eq. 1.8, we get

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

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

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

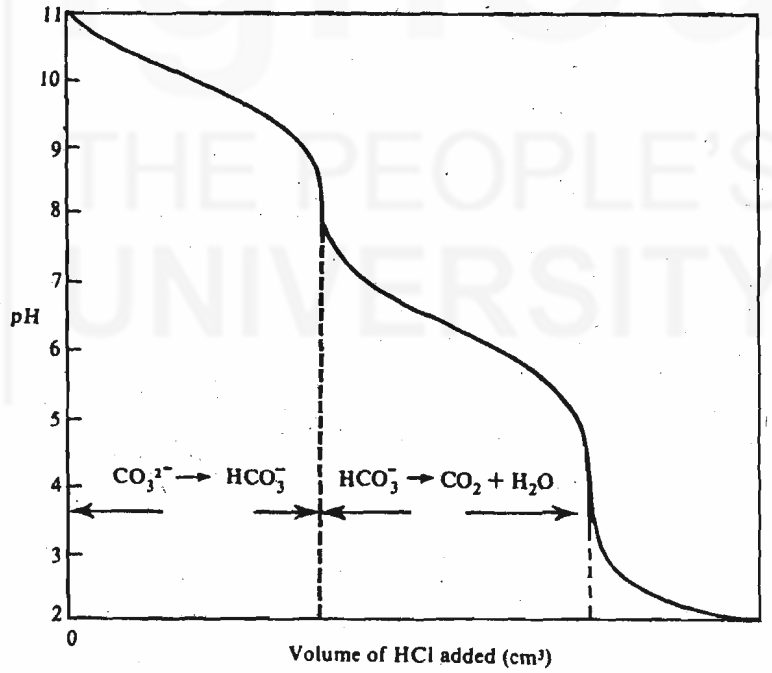


Fig. 3.1 : Titration curve for sodium carbonate titrated with hydrochloric acid.

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

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

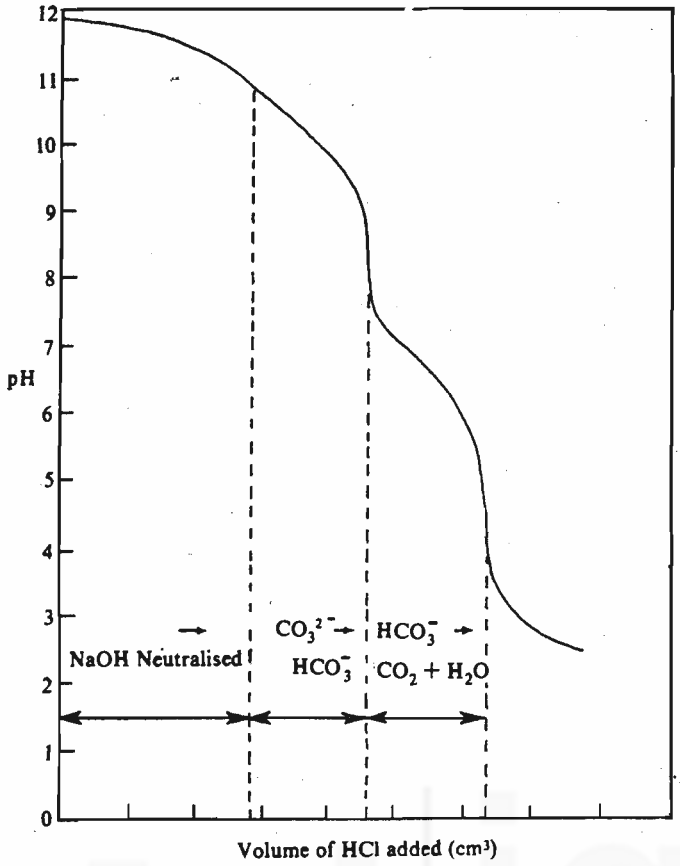


Fig. 3.2 : Titration curve for a mixture of sodium carbonate and sodium hydroxide titrated against acid.

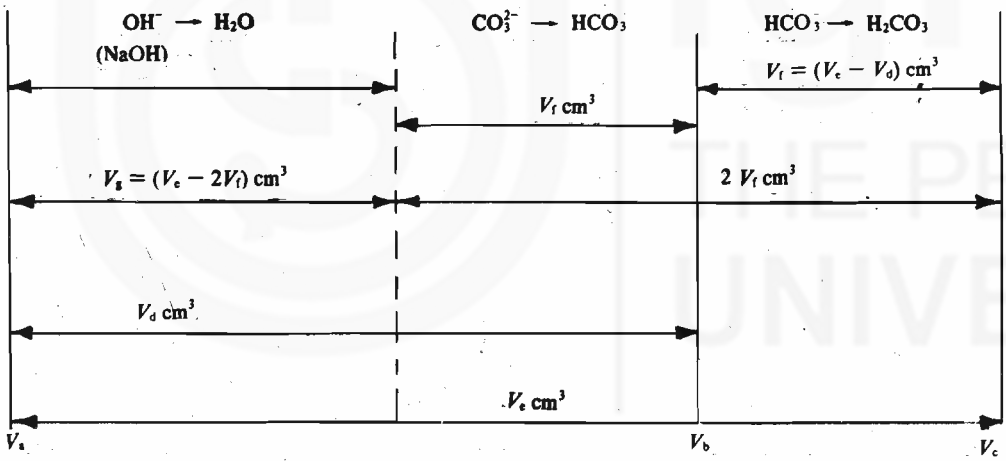


Fig. 3.3 : Titration of a mixture of sodium carbonate and sodium hydroxide with hydrochloric acid.

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

The corresponding chemical reactions may be summarised as :

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

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

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

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

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

Before proceeding further, answer the following SAQs.

SAQ 1

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

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

.....

.....

SAQ 2

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

a) CH_3COOH – NaOH

b) $NaHCO_3$ – HCl

c) K_2CO_3 – HCl

.....

.....

SAQ 3

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

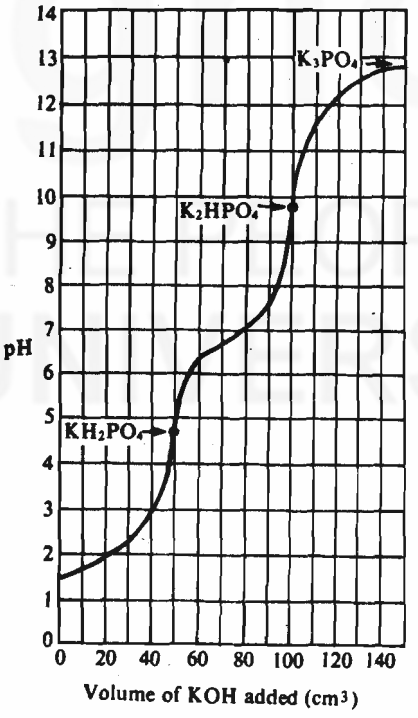


Fig. 3.4 : Titration of 50 cm² of 0.1 *M* H_3PO_4 with 0.1 *M* KOH

3.2.2 Requirements

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

Apparatus

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

Chemicals

Sodium carbonate

Mixture of sodium carbonate and sodium hydroxide.

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

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

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

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

3.2.3 Procedure

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

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

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

3.2.4 Observations

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

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

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

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

Observation Table I
Sodium carbonate solutions vs. hydrochloric acid solution

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

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

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

3.2.5 Calculations

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

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

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

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

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

Using Eq. 3.6,

$$2M_4V_4 = M_3 V_3$$

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

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

Strength of sodium carbonate present in the given solution = $M_4 \times$ Molar mass

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

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

$M_6\ V_6 = M_5\ V_5$

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

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

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

3.2.6 Results

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

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

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

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

$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

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

3.3 ANSWERS TO SAQs

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

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

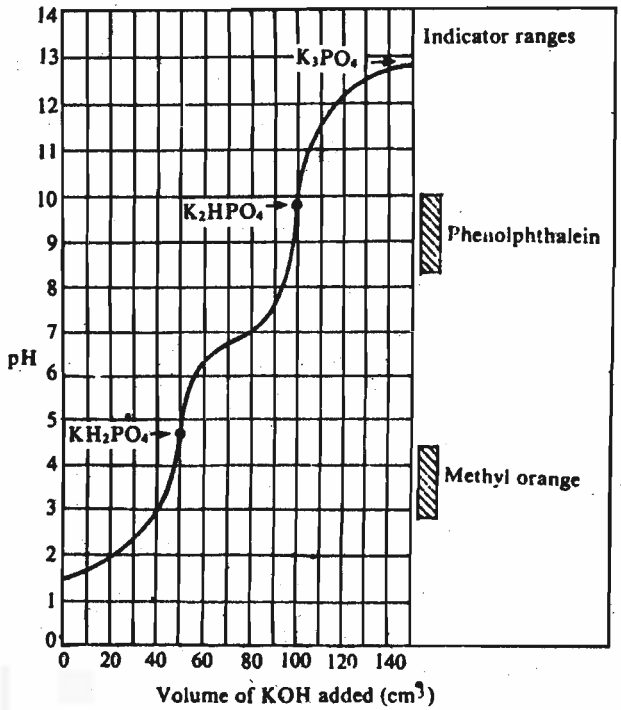


Fig. 3.5 : Titration 50 cm³ of 0.1 *M* H_3PO_4 with 0.1 *M* KOH