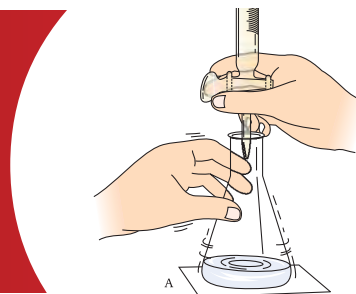# Titrimetric Analysis

Y ou are already aware that a substance is analysed to establish its qualitative and quantitative chemical composition. Thus, chemical analysis can be categorised as qualitative analysis and quantitative analysis. In this unit you will learn about determination of the amount of substance in solution. Depending upon the method adopted for determining the amount of chemical substances in solution, there are two methods of analysis namely, titrimetric analysis and gravimetric analysis. In titrimetric analysis measurement of only volumes is involved while in gravimetric analysis measurement of volumes as well as mass is involved.

Titrimetric analysis involves determination of the volume of a solution of accurately known concentration, which is required to react quantitatively with the measured volume of the solution of a substance, concentration of which is to be determined. The solution of accurately known concentration is called **standard solution**. The mass of the substance dissolved in the solution of unknown concentration is calculated from the volume of the standard solution used, the chemical equation and the relative molecular masses of the reacting compounds. The reagent of known concentration is called **titrant** and the substance being titrated is termed as **titrand**.

To carry out titrimetric analysis, standard solution is usually added from the long graduated tube called burette. The process of adding the standard solution to the solution of unknown concentration until the reaction is just complete is called **titration**. The point at which reaction is completed is called **equivalence point** or the **theoretical or stoichiometric end point**. It is not possible all the time to take standard solution in the burette. You will come to know about it later in this unit in the titration of sodium hydroxide with oxalic acid.

6.1 Detection of End Point

The end point is detected either by some physical change produced in the reaction mixture itself or by the addition of an auxiliary reagent, known as **indicator**; alternatively some other physical measurement may be used. At the completion of the reaction, the indicator shows a visible change e.g. (colour change or turbidity) in the solution being titrated. In an ideal titration, the visible end point coincides with the stoichiometric or theoretical end point; but in practice usually some small difference occurs. This represents **titration error**.

Indicator and the experimental conditions selected should be such that the difference between the visible end point and the theoretical end point is minimum.

6.2 REQUIREMENT FOR A REACTION IN THE TITRIMETRIC ANALYSIS

(i) The substance of which amount is to be determined by titrimetric analysis must react completely and rapidly with the other reagent in stoichiometric proportion.

(ii) The reaction should be fast and there must be alteration in physical or chemical property of the solution at the equivalence point, which can be detected by an indicator, or by measuring the potential difference or current etc.

6.3 ACIDIMETRY AND ALKALIMETRY

Titrimetric analysis can be carried out for various types of reactions. In this unit you will learn only about neutralisation reactions. These involve titrations of acids and bases. Standard solutions of acids (acidimetry) and bases (alkalimetry) are used in these titrations. In quantitative estimation through titrimetric analysis, concentration of solution is expressed in terms of molarity. It is number of moles of solute dissolved in 1 litre of solution.

$$\text{Molarity, } M = \frac{\text{number of moles of solute}}{\text{volume of solution in litres}}$$

Standard Solution

A solution of exactly known concentration is called standard solution. Any substance, which is stable at room temperature and does not react with solvent in which it is dissolved, can be directly weighed to prepare its standard solution. Description and preparation of these solutions is given below:

Primary and secondary standards

A **primary standard** is a compound of sufficient purity in which total amount of impurities does not exceed 0.01-0.02%. The standard solution can be prepared by direct weighing of a sample of primary standard followed by its dissolution in water (or solvent) to obtain a definite volume of solution. The substance to be used as a primary standard should also satisfy the following requirements:

1. It must be easily available in pure and dry form.
2. It should not undergo change in air i.e. it should not be hygroscopic, oxidised by air or affected by gases such as carbon dioxide present in the atmosphere or lose water of crystallization, so that it can be stored safely.
3. It should be easy to detect the impurities present in it.
4. It should have high **relative molecular mass** so that weighing errors are neglible.
5. Its reaction with another substance should be instantaneous and stoichiometric.
6. The substance should be readily soluble in water.

It is difficult to obtain an ideal primary standard. Therefore, substances having characteristics nearer to the primary standards are usually employed.

Unstable hydrated salts, as a rule, should not to be used as primary standards. However, sodium carbonate, sodium tetraborate, potassium hydrogenphthalate, oxalic acid, ferrous ammonium sulphate etc. can be used as primary standards because of their sufficient stabilities.

A solution of secondary standard is the one which may be used for standardization after finding out its exact concentration by titration against a standard solution of primary standard.

A secondary standard cannot be used for preparing standard solution by direct weighing. Sodium hydroxide and potassium permanganate are examples of secondary standards.

Before starting titrimetric analysis, you should be familiar with some techniques such as, weighing by using chemical balance, preparing standard solution, measuring volume by using burette and pipette.

6.4 INDICATORS IN ACID BASE TITRATION

Acid base indicators are sensitive to pH change. For most acid base titrations, it is possible to select indicators which exhibit colour change at pH close to the equivalence point. We will discuss here about only two indicators – phenolphthalein and methyl orange.

Phenolpthalein

Phenolpthalein is a weak acid, therefore it does not dissociate in the acidic medium and remains in the unionised form, which is colourless.

$$HPh \rightleftharpoons H^+ + Ph^-$$

Unionised	Ionised
Colourless	Pink

Ionised and unionised forms of phenolphthalein are given below :

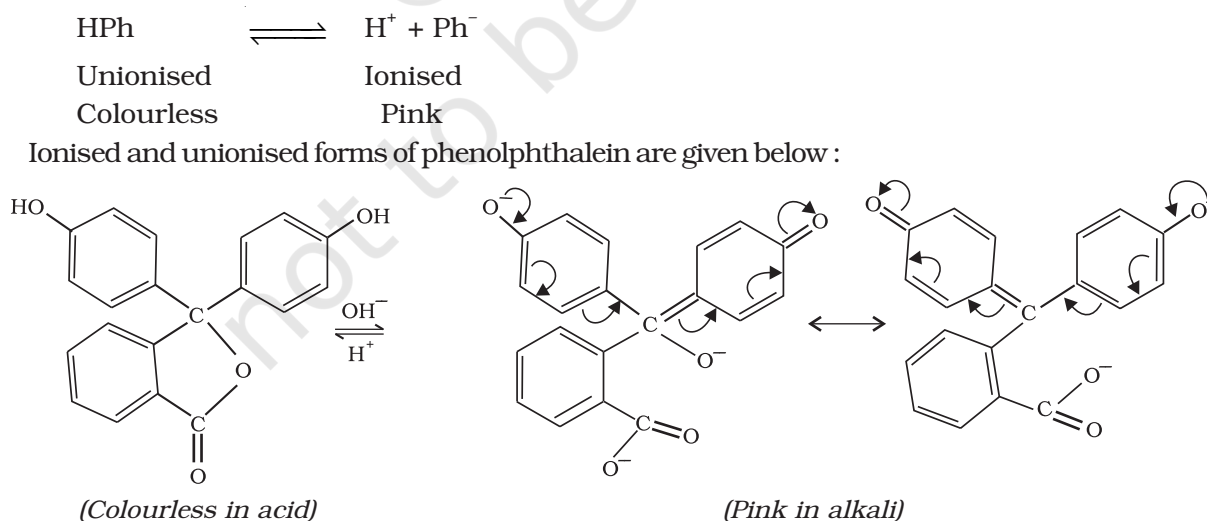(Colourless in acid)   (Pink in alkali)

Fig. 6.1 : Phenolphthalein in acidic and basic medium

In the acidic medium, equilibrium lies to the left. In the alkaline medium, the ionisation of phenolphthalein increases considerably due to the constant removal of H^+ ions released from HPh by the OH^- ions from the alkali. So the concentration of Ph^- ion increases in the solution, which imparts pink colour to the solution.

$$HPh \rightleftharpoons H^+ + Ph^-$$
$$NaOH \longrightarrow Na^+ + OH^-$$
$$H^+ + OH^- \longrightarrow H_2O$$
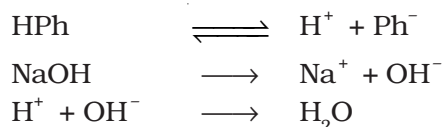
For a weak acid vs strong alkali titration, phenolphthalein is the most suitable indicator. This is so because the last drop of added alkali brings the pH of the solution in the range in which phenolphthalein shows sharp colour change.

Methyl orange

Methyl orange is a weak base and is yellow in colour in the unionised form. Sodium salt of methyl orange is represented as follows:
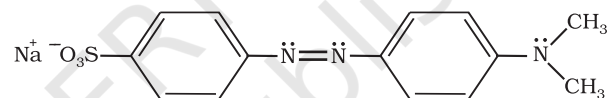
The anion formed from the indicator is an active species, which on accepting a proton (i.e acting as Bronsted Lowry base) changes from the benzenoid form to the quinonoid form. The quinonoid form is deeper in colour and thus is responsible for the colour change at the end point. This is illustrated in the following manner:
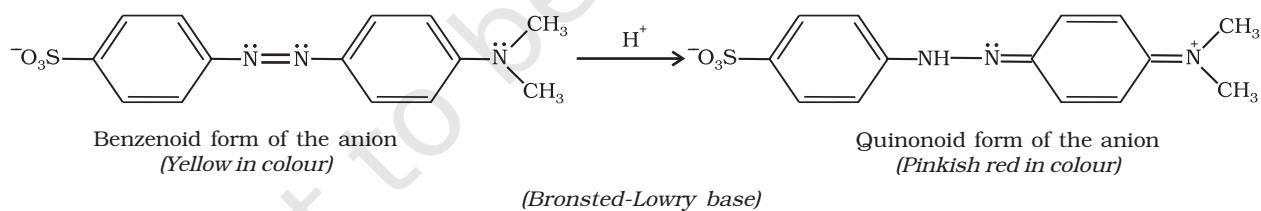

Benzenoid form of the anion
(Yellow in colour)

Quinonoid form of the anion
(Pinkish red in colour)

(Bronsted-Lowry base)

Fig. 6.2 : *Structures of Methyl orange*

Choice of Indicator

In the titration of strong acid and a weak base, methyl orange is chosen as indicator. When titration between strong base and weak acid is to be performed then phenolphthalein is a good indicator. In this case alkali is dropped from the burette and acid is taken in the tiration flask. Colour of the solution taken in the titration flask

changes from colourless to pink. This change of colour is easily perceptible to the human eye. If we take alkali in the titration flask, the colour change will be from pink to colourless and accuracy in noting the colour change may be less. In the titration of strong acid versus strong base anyone of the above indicators can be used. For the titration of weak acid vs weak base no indicator is available.
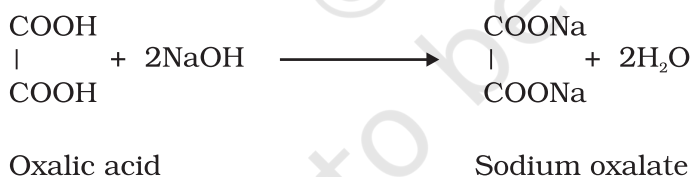
EXPERIMENT 6.1

Aim

Determination of the concentration (strength) of a given sodium hydroxide solution by titrating it against a standard solution of oxalic acid.

Theory

In the titration of a strong acid with a strong base, the amount of acid and base becomes chemically equivalent at the end point and the chemical reaction is called neutralization reaction. Near the end point there is a sudden change in the pH of the solution. If after end point even a small amount of base/acid is added the solution would become slightly alkaline or acidic respectively. In the titration between oxalic acid (weak acid) and sodium hydroxide (strong base), following reaction takes place:

$$\begin{array}{ccc} \text{COOH} & & \text{COONa} \\ | \qquad + 2\text{NaOH} \longrightarrow & | \qquad + 2\text{H}_2\text{O} \\ \text{COOH} & & \text{COONa} \end{array}$$

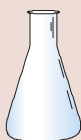Oxalic acid   Sodium oxalate

In this titration phenolphthalein (HPh) is used as an indicator. The concentration of unknown solution is calculated in g/L. Molarity of the solution can be calculated by using the formula

$$a_1 M_1 V_1 = a_2 M_2 V_2 \qquad \qquad ...(4)$$

where a_1, M_1, V_1 are respectively basicity, molarity and volume of acid used and a_2, M_2 and V_2 are acidity, molarity and volume respectively of base used in the titration.

Material Required

• Burette (50 mL)	:	One	
• Pipette (10 mL)	:	One	
• Conical flask (100 mL)	:	One	• Oxalic acid : As per need
• Burette stand	:	One	• Sodium hydroxide solution : As per need
• Funnel	:	One	• Phenolphthalein indicator : As per need
• White glazed tile	:	One	
• Measuring flask (100 mL)	:	One	

Oxalic acid

Sodium Hydroxide

Procedure

(A) Preparation of 0.1M Standard Solution of Oxalic Acid

Follow the procedure as described in Experiment No. 2.1.

(B) Titration of Sodium Hydroxide and Oxalic Acid Solution

(i) Clean the burette thoroughly, wash it with distilled water and finally rinse it with sodium hydroxide solution. (Always rinse the burette (Fig. 2.17) with the solution, which is to be taken in it). Clamp the burette vertically in a burette stand.

(ii) Fill sodium hydroxide solution into the burette through a funnel above the zero mark.

(iii) **Remove the air gap, if any, from the nozzle** of the burette by running the solution forcefully from the burette nozzle.

(iv) **Remove the funnel before noting initial reading of the burette**. Also while noting the reading, see that no drop of the liquid is hanging at the nozzle of the burette.

(v) Note the initial reading by keeping the eye exactly at the same level as the meniscus of the solution.

(vi) Pipette out 10 mL of oxalic acid solution in a washed and dried conical flask. Always wash the pipette with water and rinse (Fig. 2.21) with the liquid to be measured before pipetting out the liquid.

(vii) Add 1-2 drops of phenolphthalein indicator to the conical flask. Place the flask over the glazed tile as shown in Fig. 6.3 Titrate the acid with sodium hydroxide solution till a very faint permanent pink colour is obtained. Add sodium hydroxide solution in small amounts initially and then dropwise.
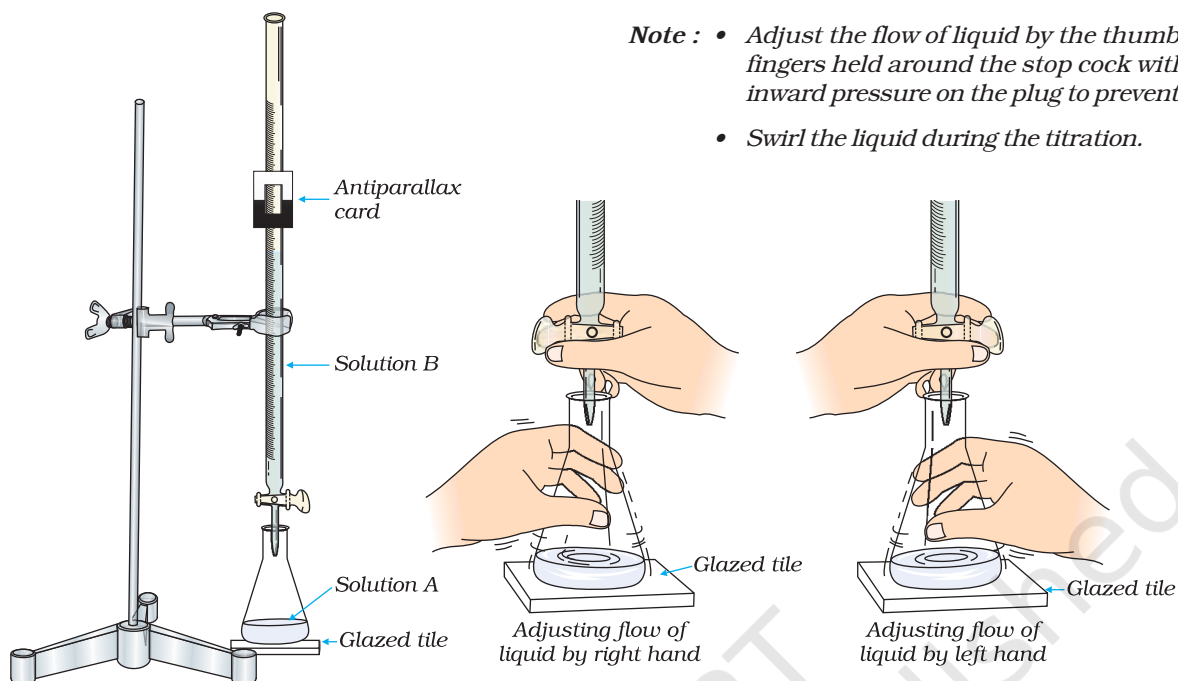
Note : • *Adjust the flow of liquid by the thumb and two fingers held around the stop cock with a slight inward pressure on the plug to prevent leakage.*

• *Swirl the liquid during the titration.*

Fig. 6.3 : Titrating the solution

(viii) Read the lower meniscus of the solution in the burette again and record it as final reading.

(ix) Repeat the procedure until three concordant readings are obtained. Record your readings as in Table 6.1.

Table 6.1 : Titration of sodium hydroxide vs oxalic acid solution

Sl. No.	Volume of oxalic acid solution taken in conical flask each time V_1 mL	Burette readings		Volume of sodium hydroxide solution used V_2 mL = (y–x) mL	Concordant reading in mL
		Initial reading (x)	Final reading (y)		

Calculations

Molarity of NaOH solution can be calculated by using the equation:

Oxalic acid   Sodium hydroxide

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

where, M_1 and V_1 are the molarity and volume of the oxalic acid solution.

M_2 and V_2 are the molarity and volume of the sodium hydroxide solution.

a_1 and a_2 are respectively the basicity of oxalic acid and acidity of sodium hydroxide. In this case a_1 = 2 and a_2 = 1.

Also, Molar mass of oxalic acid, $(COOH)_2.2H_2O = 126 \text{ g mol}^{-1}$ and Molar mass of sodium hydroxide $(NaOH) = 40 \text{ g mol}^{-1}$

Calculate the concentration of sodium hydroxide solution in g/L by using the equation given below.

Concentration (strength) in g/L = Molarity Molar mass

Result

Concentration of NaOH solution is ——————— g/L.

Precautions

(a) Always rinse the burette with the solution, which is to be taken in it.

(b) Remove the air gap if any, from the burette before titrating the solution. Make sure that the nozzle of burette is also filled.

(c) Never forget to remove the funnel from the burette before noting the readings of the burette and ensure that no drop is hanging from the nozzle of the burette.

(d) Always read the lower meniscus for all transparent solutions and upper meniscus for coloured solutions.

(e) To note the burette readings place the eye exactly at the level of the meniscus.

(f) Never hold the pipette at the bulb.

(g) Never use the pipette and burette with a broken nozzle.

(h) Never suck a strong acid or an alkali with the pipette.

(i) Always keep the lower end of the pipette dipped in the liquid while sucking the liquid.

(j) Do not blow out the last drop of the solution from the jet end of the pipette into the flask.

(k) The concentration (strength) of the solution must be calculated up to the fourth place of decimal.

Discussion Questions

(i) Why are the burette and the pipette rinsed with the solution with which these are filled?

(ii) What is an indicator? Which indicator is used in the titration of oxalic acid vs sodium hydroxide? Can the titration be performed by using some other indicator?

(iii) Why should one read the lower meniscus in the case of colourless and transparent solutions and the upper meniscus for solutions of dark colour?

(iv) Explain the term 'end point'?

(v) What do you mean by 1.0 M solution?

(vi) Why should the last drop of the solution not be blown out of a pipette?

(vii) Explain the term basicity of an acid and acidity of a base?

(viii) For titrating NaOH vs HCl, phenolphthalein and methyl orange, both are suitable indicators. Why?

(ix) What is meant by the term , 'concordant readings'?

(x) Can one take oxalic acid solution in the burette and sodium hydroxide solution in the titration flask? Point out the limitations of doing so if any.

KNOW THIS ALSO

The complete neutralisation is possible only when the amount of alkali is in equivalent proportion to the amount of acid. Therefore, at the end point equivalent mass of acid dissolved in volume V_1 of solvent should be equal to the equivalent mass of the base dissolved in Volume V_2 of solvent. If N_1 and N_2 are equivalent masses of acid and base respectively dissolved in per litre of solution then $N_1V_1 = N_2V_2$ … (i)

Equivalent mass of acids and bases is given by the following expression:

$$\text{Equivalent mass of acid} = \frac{\text{molar mass}}{\text{basicity}} \quad \text{… (ii)}$$

$$\text{Equivalent mass of base} = \frac{\text{molar mass}}{\text{acidity}} \quad \text{… (iii)}$$

The number of gram equivalent mass of solute dissolved in one litre of the solution is called the normality of the solution. For acids and bases

$$\text{Normality (N)} = \frac{\text{Number of gram equivalent mass}}{\text{Volume of solution in litre } (V)} = \frac{w/\text{Equivalent mass}}{\text{Volume of solution in litre } (V)} \quad \text{… (iv)}$$

Where w = mass of substance in grams

Relationship between Normality and Molarity

From definition of normality (N) [(equation (iv)]

$$\text{Equivalent mass} = \frac{w}{N \, V} \quad \text{… (v)}$$

If acidity or basicity is 'a', then by definition of equivalent mass

$$\text{Equivalent mass} = \frac{\text{Molar mass}}{a} \qquad \dots \text{(vi)}$$

From equations (v) and (vi) we can write

$$\frac{w}{N \quad V} \qquad \frac{\text{Molar mass}}{a}$$

Or

$$N \qquad \frac{a\,(w/\text{Molar mass})}{V}$$

But

$$\frac{w/\text{Molar mass}}{V} \text{ is the molarity } (M)$$

Therefore, $N = a\,M$ ... (vii)

Equation (vii) is the expression for the relationship between normality and molarity.

By using equation (vii) in equation (i) we have $a_1 M_1 V_1 = a_2 M_2 V_2$ .... (viii)

Where a_1 and a_2 are basicity and acidity of acid and base respectively and M_1 and M_2 are the molar masses of acid and base respectively. Thus we see that equation (i) can also be used to calculate the strength of the solution. Equation (viii) can be used for making the solution by dilution. For solutions of the same substance $a_1 = a_2$. Therefore for using equation (viii) for dilution of solution –

$$M_1 V_1 = M_2 V_2 \qquad \dots \text{(ix)}$$

Therefore, to obtain V_2 volume of a solution of molarity M_2 from a solution of molarity M_1, the volume V_1 of the solution of molarity M_1 which is required for dilution, can be calculated from equation (ix). $(V_2 - V_1)$ volume of solvent will be required to be added to V_1 volume of the solution of molarity M_1.

EXPERIMENT 6.2

Aim

Preparation of 0.1 M standard solution of sodium carbonate.

Theory

Sodium carbonate has characteristics nearer to the primary standards therefore its standard solution can be made by direct weighing.

To prepare 0.1 M Na_2CO_3 solution, 10.6000g of sodium carbonate should be dissolved per litre of the solution (Molar mass of sodium carbonate is 106 g mol^{-1}).

Therefore, to prepare 100 mL of 0.1M Na_2CO_3 solution 1.0600 g of sodium carbonate is dissolved in minimum quantity of water and the solution is diluted to exactly 100 mL by adding water to it.

Material Required

• Measuring flask (100 mL) :	One	
• Watch glass	:	One
• Funnel	:	One
• Wash bottle	:	One

• Sodium carbonate : As per need

Procedure

Follow the same procedure as in Experiment 2.1.

EXPERIMENT 6.3

Aim

Determination of the strength of a given solution of dilute hydrochloric acid by titrating it against a standard solution of sodium carbonate.

Theory

The strength of hydrochloric acid is determined by titrating it against a standard solution of sodium carbonate. The following reaction takes place:

$$Na_2CO_3 + 2HCl \longrightarrow 2\ NaCl + CO_2 + H_2O$$
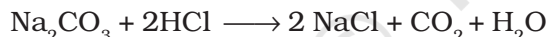
In this titration, methyl orange, a weak base (yellow in the unionised form) is used as an indicator.

In this experiment also, the titration follows the usual course, i.e., the proton furnished by the addition of the acid first neutralises sodium carbonate solution. When the entire sodium carbonate solution is neutralised, the last drop of the acid added from the burette produces the pinkish red colour change, which is the end point.

The concentration (strength) of the unknown solution is calculated in g/L. It is calculated from the molarity of the solution.

Here, the molarity equation is written as

Base Acid
$$a_1M_1V_1 = a_2M_2V_2$$

where, a_1 and a_2 are the acidity and basicity of the alkali and the acid respectively. M_1 and M_2 are the molarities, V_1 and V_2 are the volumes of the base and acid respectively used to neutralise each other.

Material Required
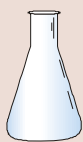
- Burette (50 mL)   : One
- Pipette (10 mL)   : One
- Conical flask (100 mL)   : One
- Burette stand   : One
- Funnel   : One
- Glazed tile (white)   : One
- Measuring flask (100 mL) : One

- Hydrochloric acid   : As per need
- Sodium carbonate   : As per need
- Methyl orange solution   : As per need

Procedure

Hydrochloric acid

(A) Preparation of 0.1 M standard solution of sodium carbonate

Follow the procedure as described in Experiment 2.1.

(B) Titration of hydrochloric acid and standard sodium carbonate solution.

Follow the procedure as given in the Experiment 6.1.

In this case, hydrochloric acid is taken in the burette and sodium carbonate solution in the conical flask. Methyl orange is used as an indicator. The colour change at the end point will be from yellow to pinkish-red. Record your observations in Table 6.2.

Table 6.2 : Titration of Hydrochloric acid with standard sodium carbonate solution

Sl. No.	Volume V_1 of Na_2CO_3 solution taken in the conical flask each time in mL	Burette readings		Volume of HCl solution used V_2 mL = (y–x) mL	Concordant reading in mL
		Initial reading (x)	Final reading (y)		

Calculations

Calculate the strength of HCl solution by using the equation

$$\text{Na}_2\text{CO}_3 \text{ solution} \qquad \text{HCl solution}$$
$$a_1 M_1 V_1 \qquad = \qquad a_2 M_2 V_2$$

where M_1 and V_1 are the molarity and volume of sodium carbonate solution respectively and a_1 is the number of moles of OH⁻ (aq) ions supplied by one mole of the base (i.e. the acidity of the Na_2CO_3 solution).

$$\therefore \quad a_1 = 2$$

M_2 and V_2 are the molarity and volume respectively of hydrochloric acid solution.

a_2 is the number of moles of H⁺ (aq) ions supplied by one mole of the acid (i.e. the basicity of HCl).

$$\therefore \quad a_2 = 1$$

Molar mass of $\text{Na}_2\text{CO}_3 = 106 \text{ g mol}^{-1}$, Molar mass of HCl = 36.5 g mol^{-1},

$\therefore$ Concentration (Strength) of HCl solution in g/L = Molarity $\times$ Molar mass

Result

The concentration (strength) of the given HCl solution is _____ g/L.

Precautions

(a) Care should be taken while handling the acid and base.
(b) Always rinse the burette and the pipette with the solution which is to be taken in them.
(c) Remove the air gap if any, from the burette before titration.
(d) Never forget to remove the funnel from the burette before noting the initial reading of the burette and ensure that no drop is hanging from the nozzle.
(e) Always read the lower meniscus for all transparent solutions and upper meniscus for the coloured solutions.
(f) Never use burette and pipette with a broken nozzle.
(g) Never suck a strong acid or an alkali with the pipette, use pipette bulb.
(h) Always keep the lower end of the pipette dipped in the liquid while sucking the liquid.
(i) While transferring the solution to the flask, do not blow out the last drop of the solution from the jet of the pipette.
(j) The strength of the solution must be calculated up to the fourth decimal place.

KNOW THIS ALSO

Potassium hydrogenphthalate is primary standard for standardisation of sodium hydroxide solution. Formula of potassium hydrogen phthalate is $C_6H_5O_4K$. It behaves as a monobasic acid. Sodium hydroxide reacts with potassium hydrogenphthalate according to the following equation.

$$\text{(aq) + NaOH(aq)} \longrightarrow \text{(aq) + } H_2O\ (l)$$
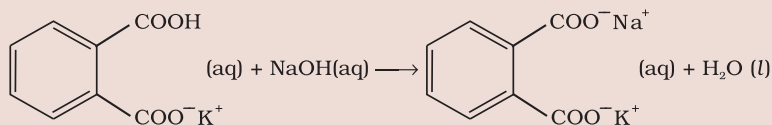
Phenolphthalein can be used as an indicator in this titration.

Discussion Questions

(i) Which indicator is used in the titration of sodium carbonate against hydrochloric acid and what is the colour change at the end point?

(ii) How will you prepare 250 mL of 0.05 M solution of sodium carbonate?

(iii) Though sodium carbonate is a salt yet its aqueous solution is weakly alkaline in nature. Explain why?

(iv) How can you determine the acidity of sodium carbonate solution?

(v) Why is methyl orange not an Arrhenius base?

(vi) How can you titrate a solution of the mixture of Na_2CO_3 and $NaHCO_3$ against HCl?

(vii) What is the difference between an end point and an equivalence point?

(viii) Can you directly prepare standard solution of HCl, HNO_3 and H_2SO_4 ?