CHAPTER 14

VOLUMETRIC ANALYSIS

Volumetric analysis is a method of quantitative analysis. It involves the measurement of the volume of a known solution required to bring about the completion of the reaction with a measured volume of the unknown solution whose concentration or strength is to be determined. By knowing the volume of the known solution, the concentration of the solution under investigation can be calculated. Volumetric analysis is also termed as **titrimetric analysis.**

14.1 IMPORTANT TERMED USED IN VOLUMETRIC ANALYSIS

(i) Titration: The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete, is termed as **titration.** Thus, a titration involves two solutions:

(a) Unknown solution and (b) Known solution or standard solution.

(ii) Titrant: The reagent or substance whose solution is employed to estimate the concentration of unknown solution is termed **titrant.** There are two types of reagents or titrants:

(a) Primary titrants: These reagents can be accurately weighed and their solutions are not to be standardised before use. Oxalic acid, potassium dichromate, silver nitrate, copper sulphate, ferrous ammonium sulphate, sodium thiosulphates, etc., are the examples of primary titrants.

(b) Secondary titrants: These reagents cannot accurately weighed and their solutions are to be standardised before use. Sodium hydroxide, potassium hydroxide, hydrochloric acid, sulphuric acid, iodine, potassium permanganate, etc., are the examples of secondary titrants.

(iii) Standard solution: The solution of exactly known concentration of the titrant is called the standard solution.

(iv) Titrate: The solution consisting the substance to be estimated is termed unknown solution. The substance is termed **titrate.**

(v) Equivalence point: The point at which the reagent (titrant) and the substance (titrate) under investigation are chemically equivalent is termed **equivalence point or stoichiometric end point** or **simply end point.**

(vi) Indicator: It is the auxiliary substance used for physical (visual) detection of the completion of titration or detection of end point is termed as indicator. Indicators show change in colour or turbidity at the stage of completion of titration.

14.2 CONCENTRATION REPRESENTATION OF SOLUTION

1. Concentration Representation in Physical Units

(a) Strength of solution: Number of grams of solute dissolved per litre of solution is called strength of solution.

(b) Parts Per Million (ppm): Number of grams of solute dissolved per 10^6 grams of solvent is called concentration of solution in the unit of Parts Per Million (ppm). This unit is used to represent hardness of water and concentration of very dilute solutions.

(c) Percentage by mass: Number of grams of solute dissolved per 100 grams of solution is called percentage by mass.

(d) Percentage by volume: Number of millilitres of solute per 100 mL of solution is called percentage by volume.

For example, if 25 mL ethyl alcohol is diluted with water to make 100 mL solution then the solution thus obtained is 25% ethyl alcohol by volume.

(e) Percentage mass by volume: Number of grams of solute present per 100 mL of solution is called percentage mass by volume.

For example, let 25 g glucose is dissolved in water to make 100 mL solution then the solution is 25% glucose mass by volume.

2. Concentration Representation in Chemical Units

(a) Normality: Number of gram equivalents of solute dissolved per litre of solution is called the normality of the solution. It is denoted by *N* and it can be calculated as,

$$N = \frac{w_B \times 1000}{E_B \times V} \quad \text{... (i)}$$

where, w_B = mass of solute in grams

E_B = gram equivalent mass of solute

V = volume of solution in mL

Another relation for calculation of normality is

$$N = \frac{x \times d \times 10}{E_B} \quad \text{... (ii)}$$

where, d = density of solution is g/mL

x = percentage by mass of solute

Symbol	Normality	Physical significance
(i) N	Normal solution, *i.e.*, Normality = 1	1 g equivalent of solute per litre of solution
(ii) $0.1\,N$ or $\frac{N}{10}$	Decinormal solution, *i.e.*, Normality = 0.1	0.1 g equivalent of solute per litre of solution
(iii) $0.01\,N$ or $\frac{N}{100}$	Centinormal solution, *i.e.*, Normality = 0.01	0.01 g equivalent of solute per litre of solution
(iv) $0.001\,N$ or $\frac{N}{1000}$	Millinormal solution, *i.e.*, Normality = 0.001	0.001 g equivalent of solute per litre of solution
(v) $0.5\,N$ or $\frac{N}{2}$	Seminormal solution, *i.e.*, Normality = 0.5	0.5 g equivalent of solute per litre of solution

Note: If normality of a solution is given then number of equivalents of solute in a definite volume of solution may be calculated easily.

Number of equivalents of solute $= \frac{N \times V}{1000}$

where, V = volume of solution in mL.

(b) Molarity: Number of moles of solute dissolved per litre of solution is called molarity. It is denoted by 'M'. It may be calculated using the following relations:

$$M = \frac{w_B \times 1000}{m_B \times V} \quad \text{... (i)}$$

or

$$M = \frac{x \times d \times 10}{m_B} \quad \text{... (ii)}$$

where, w_B = mass of solute in grams

m_B = gram molecular mass of solute

x = percentage by mass of solute

d = density of solution in g mL^{-1}

In the problems of volumetric analysis, concept of molarity is very useful. Let us consider an equation of the following type :

$$n_1 A + n_2 B \longrightarrow m_1 C + m_2 D$$

Let molar of A and B are M_1 and M_2 respectively, then

$$\frac{M_1 V_1}{n_1}(A) = \frac{M_2 V_2}{n_2}(B)$$

(c) Molality: Number of moles of solute dissolved per 1000 g (per kg) of solvent is called molality of solution. It is denoted by 'm'. It can be calculated as,

$$m = \frac{w_B \times 1000}{m_B \times w_A}$$

where, w_B = mass of solute in grams

m_B = gram molecular mass of solute

[illegible] = mass of solvent in grams

Principle of Volumetric Analysis

Volumetric analysis is based on the **principle of equivalence.** According to this principle, substances combine together in the ratio of their equivalent masses.

Let x g of a compound 'A' completely react with y g of another compound 'B'.

Then, $$\frac{\text{Equivalent mass of '}A\text{'}}{\text{Equivalent mass of '}B\text{'}} = \frac{x}{y}$$

$$\frac{x}{\text{Equivalent mass of '}A\text{'}} = \frac{y}{\text{Equivalent mass of '}B\text{'}}$$

Number of gram equivalents of 'A' = Number of gram equivalents of 'B'

Thus, **one gram equivalent of a substance 'A' completely reacts with one gram equivalent of another substance 'B'.**

According to the principle of equivalence,

Number of gram equivalents of A

= No. of gram equivalents of B

Number of gram equivalents of $A = \frac{N_A \times V_A}{1000}$;

where, V_A = volume of A in mL

Number of gram equivalents of $B = \frac{N_B \times V_B}{1000}$;

where, V_B = volume of B in mL

$$\therefore \quad \frac{N_A \times V_A}{1000} = \frac{N_B \times V_B}{1000}$$

$$N_A \times V_A = N_B \times V_B$$

The above equation is called normality equation and it is very useful in numerical calculations of volumetric analysis.

14.3 CLASSIFICATION OF REACTIONS INVOLVED IN VOLUMETRIC ANALYSIS

1. Neutralisation Reactions

The reaction in which acids and bases react to form salt is called neutralisation.

e.g., $$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$H^+_{(acid)} + OH^-_{(base)} \longrightarrow H_2O\,(\text{feebly ionised})$$

The titration based on neutralisation is called acidimetry or alkalimetry.

2. Oxidation-Reduction Reactions

The reactions involving simultaneous loss and gain of electrons among the reacting species are called oxidation-reduction or redox reactions, *e.g.*, let us consider oxidation of ferrous sulphate (Fe^{2+} ion) by potassium permanganate (MnO_4^- ion) in acidic medium.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad \text{(Gain of electrons or reduction)}$$

$$5 \times [Fe^{2+} \longrightarrow Fe^{3+} + e^-] \quad \text{(Loss of electrons or oxidation)}$$

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

In the given reaction, MnO_4^- acts as oxidising agent and Fe^{2+} acts as reducing agent.

The titrations involving redox reactions are called redox titrations. These titrations are also called according to the reagent used in the titration, *e.g.*, iodometric, iodimetric, cerimetric, permanganometric and dichromometric titrations.

3. Precipitation Reaction

A chemical reaction in which cations and anions combine to form a compound of very low solubility (in the form of residue or precipitate), is called precipitation.

e.g., $BaCl_2 + Na_2SO_4 \longrightarrow \underset{\text{(White precipitate)}}{BaSO_4} + 2NaCl$

$$AgNO_3 + NaCl \longrightarrow \underset{\text{(White precipitate)}}{AgCl} + NaNO_3$$

The titrations involving precipitation reactions are called **precipitation titrations.**

4. Complex Formation Reactions

These are ion combination reactions in which a soluble slightly dissociated complex ion or compound is formed. Complex compounds retain their identity in the solution and have the properties of the constituent ions and molecules.

e.g., $CuSO_4 + 4NH_3 \longrightarrow \underset{\text{(Complex compound)}}{[Cu(NH_3)_4]SO_4}$

$$AgNO_3 + 2KCN \longrightarrow \underset{\text{(Complex compound)}}{K[Ag(CN)_2]} + KNO_3$$

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Complex compound)}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

The titrations involving complex formation reactions are called **complexometric titrations.**

14.4 CALCULATION OF EQUIVALENT MASS OF DIFFERENT SUBSTANCES

The equivalent mass of a substance is defined as the number of parts by mass of it which combine with or displace 1.0078 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine.

The equivalent mass of a substance expressed in grams is called **gram equivalent mass.**

The equivalent mass of a substance is not constant. It depends upon the reaction in which the substance is participating. A compound may have different equivalent mass in different chemical reactions and under different experimental conditions.

(A) Equivalent Mass of an Acid

It is the mass of an acid in grams which contains 1.0078 g of replaceable H^+ ions or it is the mass of acid which contains one mole of replaceable H^+ ions. It may be calculated as:

$$\text{Equivalent mass of acid} = \frac{\text{Molecular mass of acid}}{\text{Basicity of acid}}$$

Basicity of acid = number of replaceable hydrogen atoms present in one molecule of acid

Acid	Basicity	Molecular mass	Equivalent mass
HNO_3	1	63	$\frac{63}{1} = 63$
HCl	1	36.5	$\frac{36.5}{1} = 36.5$
CH_3COOH	1	60	$\frac{60}{1} = 60$
H_3PO_2	1	66	$\frac{66}{1} = 66$
H_2SO_4	2	98	$\frac{98}{2} = 49$
COOH | $\cdot 2H_2O$ COOH	2	126	$\frac{126}{2} = 63$
H_3PO_3	2	82	$\frac{82}{2} = 41$

Note: Phosphoric acid may act as monobasic or dibasic or tribasic acid, *e.g.*,

(i) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

Here, phosphoric acid acts as monobasic acid.

$$\therefore \text{ Equivalent mass of } H_3PO_4 = \frac{\text{Molecular mass}}{\text{Basicity}} = \frac{98}{1} = 98$$

(ii) $H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4 + 2H_2O$

Here, Basicity of $H_3PO_4 = 2$

$$\text{Equivalent mass of } H_3PO_4 = \frac{\text{Molecular mass}}{\text{Basicity}} = \frac{98}{2} = 49$$

(iii) $H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + 3H_2O$

Here, Basicity of $H_3PO_4 = 3$

$$\text{Equivalent mass of } H_3PO_4 = \frac{\text{Molecular mass}}{\text{Basicity}} = \frac{98}{3} = 32.66$$

(B) Equivalent Mass of a Base

It is the mass of the base which contains one mole of replaceable OH^- ions in a molecule.

$$\text{Equivalent mass of base} = \frac{\text{Molecular mass of base}}{\text{Acidity of the base}}$$

Acidity of base = Number of replaceable OH^- ions present in one molecule of the base

or

It is the mass of a base which completely reacts with one gram equivalent mass of an acid,

e.g.,
$$\underset{74\,g}{Ca(OH)_2} + \underset{73\,g}{2HCl} \longrightarrow CaCl_2 + 2H_2O$$

$$= 2\text{ g equivalent of HCl}$$

2 gram equivalent of HCl reacts with 74 g $Ca(OH)_2$

∴ 1 gram equivalent of HCl will react with 37 g $Ca(OH)_2$

Thus, equivalent mass of $Ca(OH)_2 = 37$

Base	Acidity	Molecular mass	Equivalent mass
NaOH	1	40	40/1 = 40
KOH	1	56	56/1 = 56
$Ca(OH)_2$	2	74	74/2 = 37
NH_4OH	1	35	35/1 = 35

(C) Equivalent Mass of Salt

Let us consider a salt of weak acid (H_2CO_3) and strong base (NaOH). This salt undergoes hydrolysis in water to form basic solution.

$$Na_2CO_3 + 2H_2O \rightleftharpoons H_2CO_3 + 2Na^+ + 2OH^-$$

Such salts react with mineral acids like HCl

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

In the above reaction one mole of Na_2CO_3 reacts with 2 equivalents of HCl

$$\therefore \text{ Equivalent mass of } Na_2CO_3 = \frac{\text{Molecular mass of } Na_2CO_3}{2}$$

$$= \frac{106}{2} = 53$$

Thus, *mass of the salt which reacts with one gram equivalent of acid or base is called its equivalent mass, e.g.*,

(i) $\underset{1\text{ mol}}{NH_4Cl} + \underset{1\text{ g equivalent}}{NaOH} \longrightarrow NH_3 + NaCl + H_2O$

$$\text{Equivalent mass of } NH_4Cl = \frac{\text{Molecular mass of } NH_4Cl}{1}$$

(ii) $\underset{1\text{ mol}}{AgNO_3} + \underset{1\text{ g equivalent}}{HCl} \longrightarrow AgCl + HNO_3$

$$\text{Equivalent mass of } AgNO_3 = \frac{\text{Molecular mass of } AgNO_3}{1}$$

Alternatively,

$$\text{Equivalent mass of salt} = \frac{\text{Molecular mass of salt}}{\text{Total positive or negative valency}}$$

Salt	Valency	Equivalent mass
NaCl	1	molecular mass/1
$CaCl_2$	2	molecular mass/2
$Ca_3(PO_4)_2$	6	molecular mass/6
$AlCl_3$	3	molecular mass/3

(D) Equivalent Mass of an Oxidising Agent

(a) Available oxygen concept: The mass of oxidising agent which contains 8 g of available oxygen (*i.e.*, the oxygen which can be used for oxidation) is called the equivalent mass of oxidising agent.

Examples:

(i) $\underset{294.2\,g}{K_2Cr_2O_7} + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + \underset{\substack{3\times 16\,g\\ = 48\,g}}{3[O]}$

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{294.2}{48} \times 8 = 49.03$$

(ii) Equivalent mass of $KMnO_4$: Potassium permanganate is a powerful oxidising agent in acid, base and in neutral medium.

(1) Acid medium:

$$\underset{2\times 158\,g}{2KMnO_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + \underset{5\times 16\,g}{5[O]}$$

80 g oxygen is furnished by 316 g $KMnO_4$

∴ 8 g oxygen is furnished by 31.6 g $KMnO_4$

i.e., equivalent mass of $KMnO_4$ in acidic medium is 31.6.

(2) Neutral medium:

$$\underset{2\times 158\,g}{2KMnO_4} + H_2O \longrightarrow 2MnO_2 + 2KOH + \underset{3\times 16\,g}{3[O]}$$

$$\text{Equivalent mass of } KMnO_4 = \frac{316}{48} \times 8 = 52.66$$

(3) Alkaline medium:

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

$$2 \times 158\text{ g } KMnO_4 \equiv 16\text{ g 'O'}$$

$$\text{Equivalent mass of } KMnO_4 = \frac{316}{16} \times 8 = 158$$

(b) Electron concept:

Equivalent mass of oxidising agent

$$= \frac{\text{Molecular mass of oxidising agent}}{\text{Number of electrons gained by one molecule}}$$

Examples: (i) Equivalent mass of potassium dichromate:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{\text{Molecular mass}}{6} = \frac{294}{6} = 49$$

(ii) Equivalent mass of $KMnO_4$ in acid medium:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molecular mass}}{5} = \frac{158}{5} = 31.6$$

Similarly, equivalent mass of $KMnO_4$ in neutral and alkaline medium can be calculated.

$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ (Neutral medium)

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ (Alkaline medium)

(c) Oxidation number concept:

Equivalent mass of oxidising agent

$$= \frac{\text{Molecular mass of oxidising agent}}{\text{Total change in oxidation number per molecule of oxidising agent}}$$

Examples:

(i) Equivalent mass of $K_2Cr_2O_7$:

$$K_2\overset{+2}{} \overset{+12}{\underline{Cr}_2}\overset{-14}{O_7} + 4H_2SO_4 \rightarrow K_2SO_4 + \overset{+6}{\underline{Cr}_2}\overset{-6}{(SO_4)_3} + 4H_2O + 3[O]$$

Change in oxidation number of chromium = 12 − 6 = 6

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{\text{Molecular mass}}{6} = \frac{294}{6} = 49$$

(ii) Equivalent mass of $KMnO_4$ in acid medium:

$$2\overset{+1}{K}\overset{+7}{\underline{Mn}}\overset{-8}{O_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2\overset{+2}{\underline{Mn}}\overset{-2}{SO_4} + 3H_2O + 5[O]$$

Change in oxidation number of manganese = 7 − 2 = 5

Equivalent mass of $KMnO_4$

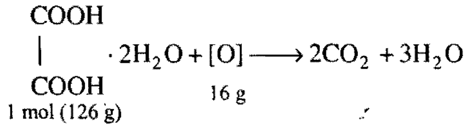
$$= \frac{\text{Molecular mass}}{5} = \frac{158}{5} = 31.6$$

(E) Equivalent Mass of a Reducing Agent

(a) Available oxygen concept: The amount of reducing agent in gram which reacts with 8 g of available oxygen is called gram equivalent mass of reducing agent.

Examples:

(i) Oxalic acid:



$$\underset{\text{1 mol (126 g)}}{\begin{array}{c}COOH\\ |\\ COOH\end{array}} \cdot 2H_2O + \underset{16\text{ g}}{[O]} \longrightarrow 2CO_2 + 3H_2O$$

$$\text{Equivalent mass of oxalic acid} = \frac{126}{16} \times 8 = 63$$

(ii) Ferrous sulphate:

$$\underset{\text{2 mol } (2\times152\text{ g})}{2FeSO_4} + H_2SO_4 + \underset{16\text{ g}}{[O]} \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$\text{Equivalent mass of ferrous sulphate} = \frac{2\times152}{16} \times 8 = 152$$

Similarly, equivalent mass of Mohr salt can be determined.

$$2 \text{ mol } FeSO_4(NH_4)_2SO_4 \cdot 6H_2O \equiv 1 \text{ gram atom of oxygen}$$

$$\therefore \text{Equivalent mass of Mohr salt} = \frac{392\times2\times8}{16} = 392$$

(b) Electron loss concept:

Equivalent mass of a reducing agent

$$= \frac{\text{Molecular mass}}{\text{Number of electrons lost by one molecule}}$$

Example: Ferrous ammonium sulphate (Mohr salt). Oxidation of Mohr salt involves the following ionic reaction:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Equivalent mass = Molecular mass

(c) Oxidation number concept:

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{\begin{array}{c}\text{Total change in oxidation number}\\ \text{of the oxidised element per molecule}\end{array}}$$

The oxidation number of iron in ferrous salt is +2 while the oxidation number of iron in ferric salt is +3. The change in oxidation number per atom of iron is 1, *i.e.*, one unit.

∴ Equivalent mass of ferrous ammonium sulphate

$$= \frac{\text{Molecular mass}}{1} = \frac{392}{1} = 392$$

SOME SOLVED EXAMPLES

Example 1. *When hydrogen gas was passed over 8.08 g of heated metal oxide, it was completely reduced and 1.8 g of water was formed:*

(a) What is weight of oxygen in the metal oxide?

(b) What is the equivalent mass of the metal?

Solution: (a) When hot metal oxide is treated with hydrogen, 1.8 g water is formed.

18 g H_2O contains 16 g oxygen.

Thus, 1.8 g H_2O will contain 1.6 g oxygen.

(b) Equivalent mass may be defined as weight of the metal that combines with 8 parts of oxygen to form its oxide.

Mass of metal in its oxide = 8.08 − 1.6
= 6.48 g

∵ 1.6 g oxygen combines with 6.48 g of metal

$$\therefore 8 \text{ g oxygen will combine with } = \frac{6.48}{1.6} \times 8 \text{ g of metal}$$
$$= 32.4 \text{ g}$$

Thus, equivalent mass of metal = 32.4

Example 2. *SO_2 is oxidised to SO_4^{2-} in acid medium. Calculate equivalent mass of SO_2.*

$$\textbf{Solution: } \overset{+4}{S}O_2(g) + 2H_2O \longrightarrow \overset{+2}{H_2}\overset{+6}{S}\overset{-8}{O_4} + 2H^+ + 2e^-$$

Change in oxidation number of sulphur = 6 − 4 = 2

$$\text{Equivalent mass of } SO_2 = \frac{\text{Molecular mass}}{2} = \frac{64}{2} = 32$$

Example 3. *What is the equivalent mass of:*

(a) H_3PO_4 when neutralised to HPO_4^{2-}

(b) $HClO_4$

(c) $NaIO_3$ when reduced to I^-

(d) $NaIO_3$ when reduced to I_2

(e) $Al(OH)_3$.

Solution: (a) Molecular mass of $H_3PO_4 = (3 + 31 + 64) = 98$ g. H_3PO_4 when neutralised to HPO_4^{2-}, two H^+ ions have been replaced.

$$\text{Thus, eq. mass} = \frac{\text{Mol. mass}}{\text{No. of replaceable hydrogen atoms}}$$
$$= \frac{98}{2} = 49.0 \text{ g}$$

(b) $HClO_4$ molecule contains one replaceable hydrogen atom.

$$\text{Thus, eq. mass} = \frac{\text{Mol. mass}}{1} = \frac{100.5}{1} = 100.5$$

(c) $NaIO_3 \longrightarrow I^-$

Oxidation no. $+5 \qquad -1$

Change in oxidation number = 6

Mol. mass of $NaIO_3 = (23 + 127 + 48) = 198$ g

$$\text{Eq. mass of } NaIO_3 = \frac{\text{Mol. mass}}{\text{Change in O.N.}} = \frac{198}{6} = 33.0$$

(d) $NaIO_3 \longrightarrow I_2$

Oxidation no. $+5 \qquad 0$

Change in oxidation number = 5

$$\text{Eq. mass of } NaIO_3 = \frac{198}{5} = 39.6$$

(e) The acidity of $Al(OH)_3$ is 3.

$$\text{Eq. mass of } Al(OH)_3 = \frac{\text{Mol. mass}}{\text{Acidity}} = \frac{78}{3} = 26.0 \text{ g}$$

Example 4. *Calculate the number of millimoles and milliequivalents of $Cr_2O_7^{2-}$ ions in acid medium when 100 mL of 0.01 M $Cr_2O_7^{2-}$ is reduced to Cr^{3+} by Fe^{2+}.*

Solution: $\underset{1 \text{ mol}}{Cr_2O_7^{2-}} + 14H^+ + \underset{6 \text{ mol}}{6e^-} \longrightarrow 2Cr^{3+} + 7H_2O$

$$\therefore \quad 0.01\,M\ Cr_2O_7^{2-} \equiv 0.06\,N\ Cr_2O_7^{2-}$$

Number of millimoles $= M \times V = 0.01 \times 100 = 1$
Number of milliequivalents $= N \times V = 0.06 \times 100 = 6$

Example 5. *Give the relation between molecular mass (M) and equivalent mass (E) of the underlined species in the following reactions:*

(a) $\underline{H_3PO_4} + Ca(OH)_2 \longrightarrow CaHPO_4 + 2H_2O$

(b) $\underline{H_2O_2} + MnO_4^- \longrightarrow Mn^{2+} + O_2 + H_2O$

(c) $\underline{4H_3PO_3} \longrightarrow 3H_3PO_4 + PH_3$

(d) $\underline{HC{\equiv}CH} + 2Na \longrightarrow NaC{\equiv}CNa + H_2$

Solution: (a) $\underline{H_3PO_4} + Ca(OH)_2 \longrightarrow CaHPO_4 + 2H_2O$

Basicity of $H_3PO_4 = 2$

$$\therefore \text{ Equivalent mass of } H_3PO_4(E) = \frac{\text{Molecular mass } (M)}{2}$$

(b) $\underline{\overset{+2}{H_2}\overset{-2}{O_2}} \longrightarrow \overset{0}{O_2}$

Change in oxidation number of $H_2O_2 = 2$

$$\therefore \text{ Equivalent mass of } H_2O_2\ (E) = \frac{\text{Molecular mass } (M)}{2}$$

(c) $\underline{\overset{+3}{H_3}\,\overset{+3}{P}\,\overset{-6}{O_3}} \longrightarrow \overset{+3}{H_3}\,\overset{+5}{P}\,\overset{-8}{O_4}$

Change in oxidation number of 'P' = 2

$$\therefore \text{ Equivalent mass } (E_1) = \frac{\text{Molecular mass } (M)}{2}$$

$$\overset{+3}{H_3}\,\overset{+3}{P}\,\overset{-6}{O_3} \longrightarrow \overset{-3}{P}\,\overset{+3}{H_3}$$

Change in oxidation number of 'P' = + 3 − (−3) = + 6

$$\text{Equivalent mass } (E_2) = \frac{\text{Molecular mass } (M)}{6}$$

$$\text{Overall equivalent mass} = E_1 + E_2 = \frac{M}{2} + \frac{M}{6} = \frac{4M}{6} = \frac{2M}{3}$$

(d) $\underline{H{-}C{\equiv}C{-}H} + 2Na \longrightarrow NaC{\equiv}CNa + H_2$

Basicity of acetylene = 2

$$\therefore \quad \text{Equivalent mass } (E) = \frac{\text{Molecular mass } (M)}{2}$$

Example 6. *Determine the number of g equivalents of solute in (a) 100 mL of 5 N HCl (b) 250 mL of 0.1 N Na_2CO_3.*

Solution : We know that

Number of g equivalents = Normality × Vol. of solution (litres)

(a) Number of g equivalents of HCl $= 5 \times \frac{100}{1000} = 0.5$

(b) Number of g equivalents of $Na_2CO_3 = 0.1 \times \frac{250}{1000} = 0.025$

Example 7. *What volumes of 12 N HCl and 3 N HCl must be mixed to form one litre 6 N HCl?*

Solution: Let x mL of 12 N HCl and y mL of 3 N HCl be mixed to form one litre 6 N HCl.

So, $\quad x + y = 1000 \quad$ ... (i)

Applying the formula $N_1V_1 + N_2V_2 = N_3V_3$,

$N_1 = 12\,N, V_1 = x, N_2 = 3\,N, V_2 = y, N_3 = 6\,N, V_3 = 1000$

So, $\quad 12x + 3y = 6 \times 1000 \quad$ ... (ii)

Putting the value of $y = (1000 - x)$ from eq. (i) in eq. (ii),

$$12x + 3(1000 - x) = 6000$$

or $\quad 12x - 3x + 3000 = 6000$

or $\quad 9x = 3000$

$$x = \frac{3000}{9} = 333.3 \text{ mL}$$

So, $\quad y = (1000 - x) = (1000 - 333.3) = 666.7$ mL

i.e., 333.3 mL 12 N HCl and 666.7 mL 3 N HCl are mixed.

Example 8. *(a) What is the normality of a 96 per cent solution of H_2SO_4 of specific gravity 1.84?*

(b) How many mL of 96 per cent sulphuric acid solution is necessary to prepare one litre 0.1 N H_2SO_4?

(c) To what volume should 10 mL of 96 per cent H_2SO_4 be diluted to prepare 2 N solution?

Solution: Mass of 1 litre of H_2SO_4 solution

= Vol. × Density
= 1000 × 1.84 = 1840 g

Mass of H_2SO_4 present in one litre 96% H_2SO_4 solution

$$= \frac{96}{100} \times 1840 = 1766.4 \text{ g}$$

Strength of H_2SO_4 solution $= 1766.4$ g/L

(a) Normality $= \frac{\text{Strength}}{\text{Eq. mass}} = \frac{1766.4}{49} = 36.05\ N$

(b) Let the volume taken be V_1 mL

Applying $N_1V_1 = N_2V_2$

$N_1 = 36.05N,\quad V_1 = ?,\quad N_2 = \frac{N}{10},\quad V_2 = 1000\text{ mL}$

$$36.05 \times V_1 = \frac{1}{10} \times 1000$$

So, $V_1 = \frac{1000}{36.05 \times 10} = 2.77\text{ mL}$

i.e., 2.77 mL of H_2SO_4 is diluted to one litre.

(c) $\underset{\text{Before dilution}}{N_BV_B} = \underset{\text{After dilution}}{N_AV_A}$

$$10 \times 36.05 = V_A \times 2$$

$$V_A = 180.25\text{ mL}$$

i.e., 10 mL of given H_2SO_4 is diluted to 180.25 mL.

Example 9. *250 mL of x M solution and 500 mL of y M solution of a solute A are mixed and diluted to 2 litre to produce a final concentration of 1.6 M.*

If $x : y = 5 : 4$, calculate x and y.

Solution: We know that,

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$x \times 250 + y \times 500 = 1.6(2000)$$

$$x + 2y = 1.6 \times 8$$

$$x + 2y = 12.8$$

$$\frac{x}{y} + 2 = \frac{12.8}{y}$$

$$\frac{5}{4} + 2 = \frac{12.8}{y}$$

$$\frac{13}{4} = \frac{12.8}{y}$$

$$y = \frac{12.8 \times 4}{13} = 3.94$$

Similarly, $x = 4.92$

Example 10. *2.68×10^{-3} mol of a solution containing an ion A^{n+} required 1.6×10^{-3} mol of MnO_4^- for oxidation of A^{n+} to AO_3^- ion in acid medium. What is the value of n?*

Solution: A^{n+} is oxidised to AO_3^-

Change in oxidation number $= 5(\text{in } AO_3^-) - n(\text{in } A^{n+})$

$= 5 - n$ ... (i)

2.68×10^{-3} mol of A^{n+} ion react with 1.6×10^{-3} mol of MnO_4^- ions

$\therefore$ 1 mol of A^{n+} ion will react with $\frac{1.6 \times 10^{-3}}{2.68 \times 10^{-3}}$ mol of MnO_4^- ions

$= 0.579$ mol of MnO_4^- ions

$$2K\overset{+7}{Mn}O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 3H_2O + 5[O]$$

Number of equivalents of MnO_4^- used in oxidation of A^{n+} to $AO_3^- = 0.597 \times 5 = 2.985 \approx 3$

Thus, from equation (i), $5 - n = 3$

$n = 2$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. An element X having equivalent mass E forms a general oxide X_mO_n, its atomic mass should be:

(a) $\frac{2En}{m}$ (b) $2mEn$ (c) $\frac{E}{n}$ (d) $\frac{ME}{2n}$

[Ans. (a)]

[Hint: Amount of X that combines with 8 g of oxygen,

i.e., $E = \frac{m \times \text{Atomic mass}}{n \times 2}$

$\therefore$ Atomic mass $= \frac{2En}{m}$]

2. In the reaction,

$$FeS_2 + KMnO_4 + H^+ \longrightarrow Fe^{3+} + SO_2 + Mn^{2+} + H_2O$$

the equivalent mass of FeS_2 would be equal to:

(a) molar mass (b) $\frac{\text{molar mass}}{10}$

(c) $\frac{\text{molar mass}}{11}$ (d) $\frac{\text{molar mass}}{13}$

[Ans. (c)]

[Hint: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$; $S_2^{2-} \longrightarrow 2S^{4+} + 10e^-$

$\therefore$ $FeS_2 \longrightarrow 2S^{4+} + Fe^{3+} + 11e^-$

Equivalent mass of $FeS_2 = \frac{\text{Molar mass}}{11}$]

3. The equivalent mass of H_3BO_3 in its reaction with NaOH to form $Na_2B_4O_7$ is equal to:

(a) molar mass/4 (b) molar mass/3

(c) molar mass/2 (d) molar mass

[Ans. (d)]

[Hint: Boric acid is a monobasic acid.

Hence, Equivalent mass = Molar mass]

4. For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, if molecular masses of NH_3 and N_2 are M_1 and M_2, their equivalent masses are E_1 and E_2, then $(E_1 - E_2)$ is:

(a) $\frac{2M_1 - M_2}{6}$ (b) $M_1 - M_2$

(c) $3M_1 - M_2$ (d) $M_1 - 3M_2$

[Ans. (a)]

[Hint: Equivalent mass of N_2, *i.e.*, $E_2 = \frac{M_2}{6}$

Equivalent mass of NH_3, *i.e.*, $E_1 = \frac{M_1}{3}$

Then, $E_1 - E_2 = \frac{M_1}{3} - \frac{M_2}{6} = \frac{2M_1 - M_2}{6}$]

5. X g metal gave Y g of its oxide. Hence, equivalent mass of the metal is:

(a) $\left(\frac{X}{Y-X}\right) \times 8$ (b) $\left(\frac{Y-X}{X}\right) \times 8$

(c) $\left(\frac{Y+X}{X}\right) \times 8$ (d) $\frac{X}{Y} \times 8$

[**Ans.** (a)]

[**Hint:** Mass of oxygen in the oxide = $(Y - X)$

$\therefore$ 8 g oxygen will combine with $\frac{X}{Y-X} \times 8$ g metal.

$$\therefore \quad E = \left(\frac{X}{Y-X}\right) \times 8]$$

6. $KMnO_4$ (m.w. = 158) oxidises oxalic acid in acid medium to CO_2 and water as follows:

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

What is the equivalent weight of $KMnO_4$? **[CET (J&K) 2006]**

(a) 158 (b) 31.6 (c) 39.5 (d) 79

[**Ans.** (b)]

[**Hint:** $MnO_4^- \longrightarrow Mn^{2+}$

(Oxidation number of Mn = + 7) (Oxidation number of Mn = + 2)

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molecular mass}}{\text{Change in oxidation number}}$$

$$= \frac{158}{5} = 31.6]$$

7. The formula mass of Mohr's salt is 392. The iron present in it is oxidised by $KMnO_4$ in acid medium. The equivalent mass of Mohr's salt is:

(a) 392 (b) 31.6 (c) 278 (d) 156

[**Ans.** (a)]

[**Hint:** Formula of Mohr's salt: $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Oxidation of Fe^{2+} ions take place as:

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

Change in oxidation number of Fe = + 3 − (+2) = + 1

$$\text{Equivalent mass of Mohr's salt} = \frac{\text{Molecular mass}}{\text{Change in oxidation number}}$$

$$= \frac{392}{1} = 392]$$

8. In a redox reaction, dichromate ion ($Cr_2O_7^{2-}$) is reduced to Cr^{3+} ion, the equivalent mass of $K_2Cr_2O_7$ in this reaction is: **(EAMCET 2007)**

(a) $\frac{\text{molecular mass}}{3}$ (b) $\frac{\text{molecular mass}}{6}$

(c) $\frac{\text{molecular mass}}{1}$ (d) $\frac{\text{molecular mass}}{2}$

[**Ans.** (b)]

[**Hint:** $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

Change in oxidation number = 6

$$\therefore \text{Equivalent mass} = \frac{\text{Molecular mass}}{6}]$$

14.5 ACID-BASE TITRATIONS

The determination of concentration of bases by titration with a standard acid is called **acidimetry** and the determination of concentration of acids by titration with a standard base is called **alkalimetry.**

The substances which give different colours with acids and bases are called acid-base indicators. These indicators are used in the visual detection of the equivalence point in acid-base titrations. The acid-base indicators are also called pH indicators because their colour change according to pH of the solution.

pH Range of Indicators

Indicators	pH range	Colour of indicator	
		Acid medium	Basic medium
Methyl orange	3.1 – 4.4	Red	Orange
Bromo phenol blue	3 – 4.6	Yellow	Blue
Methyl red	4.2 – 6.3	Red	Yellow
Litmus	5 – 8	Red	Blue
Bromo-thymol blue	6 – 7.6	Yellow	Blue
Phenol red	8.3 – 10	Colourless	Pink
Thymol phthalein	8.3 – 10.5	Colourless	Blue

In the selection of indicator for a titration, following two informations are taken into consideration:

(i) pH range of indicator.

(ii) pH change near the equivalence point in the titration.

The indicator whose pH range is included in the pH change of the solution near the equivalence point, is taken as suitable indicator for the titration.

(i) Strong acid-strong base titration: In the titration of HCl with NaOH, the equivalence point lies in the pH change of 4 –10. Thus, methyl orange, methyl red and phenolphthalein will be suitable indicators.

(ii) Weak acid-strong base titration: In the titration of CH_3COOH with NaOH the equivalence point lies between 7.5 and 10. Hence, phenolphthalein (8.3–10) will be the suitable indicator.

(iii) Weak base-strong acid titration: In the titration of NH_4OH (weak base) against HCl (strong acid), the pH at equivalence point is about 6.5 and 4. Thus, methyl orange (3.1–4.4) or methyl red (4.2–6.3) will be suitable indicators.

(iv) Weak acid-weak base titration: In the titration of a weak acid (CH_3COOH) with weak base (NH_4OH) the pH at the equivalence point is about 7, *i.e.*, lies between 6.5 and 7.5 but no sharp change in pH is observed in these titrations. Thus, no simple indicator can be employed for the detection of the equivalence point.

(v) Titration of a salt of a weak acid and a strong base with strong acid:

$$\underset{\text{Weak acid}}{H_2CO_3} + \underset{\text{Strong base}}{2NaOH} \longrightarrow Na_2CO_3 + 2H_2O$$

Na_2CO_3 when titrated with HCl, the following two stages are involved:

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl \qquad \text{(First stage)}$$

pH = 8.3, near equivalence point

$NaHCO_3 + HCl \longrightarrow NaCl + H_2CO_3$ (Second stage)
pH = 4, near equivalence point

For first stage, phenolphthalein and for second stage, methyl orange will be the suitable indicator.

14.6 TITRATION OF MIXTURE OF NaOH, Na_2CO_3 AND $NaHCO_3$ BY STRONG ACID LIKE HCl

In this titration the following indicators are mainly used:

(i) Phenolphthalein (weak organic acid): It shows colour change in the pH range (8–10).

(ii) Methyl orange (weak organic base): It shows colour change in the pH range (3.1–4.4). Due to lower pH range, it indicates complete neutralisation of whole of the base.

S.No.	Base	Phenolphthalein	Methyl orange
1.	NaOH	Shows complete neutralisation, $NaOH + HCl \rightarrow NaCl + H_2O$	Shows complete neutralisation, $NaOH + HCl \rightarrow NaCl + H_2O$
2.	Na_2CO_3	Shows half neutralisation due to following reaction: $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$	Shows complete neutralisation, $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
3.	$NaHCO_3$	Shows no reaction	Show complete reaction, $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

Let for complete neutralisation of Na_2CO_3, $NaHCO_3$ and NaOH, x, y and z mL of standard HCl are required. The titration of the mixture may be carried by two methods as summarised below:

Mixture	Volume of HCl used with		Volume of HCl used	
	Phenol-phthalein from beginning	Methyl orange from beginning	Phenol-phthalein from beginning	Methyl orange after first end point
1. NaOH + Na_2CO_3	$z + (x/2)$	$(x + z)$	$z + \frac{x}{2}$	$x/2$ (for remaining 50% Na_2CO_3)
2. NaOH + $NaHCO_3$	$z + 0$	$(z + y)$	$(z + 0)$	y (for 100% remaining $NaHCO_3$)
3. Na_2CO_3 + $NaHCO_3$	$(x/2) + 0$	$(x + y)$	$(x/2) + 0$	$(x/2) + y$ (for remaining 50% of Na_2CO_3 and 100% $NaHCO_3$ are indicated)

SOME SOLVED EXAMPLES

Example 11. *What is the strength in g per litre of a solution of sulphuric acid, 12 mL of which neutralise 15 mL of N/10 sodium hydroxide solution?*

Solution: Applying

$$\underset{(NaOH)}{N_1V_1} = \underset{(H_2SO_4)}{N_2V_2}$$

$$\frac{1}{10} \times 15 = N_2 \times 12$$

$$N_2 = \frac{15}{10 \times 12} = 0.125$$

Normality × Eq. mass = Strength (g/L)

Strength = 0.125 × 49 = 6.125 g/L

Example 12. *4.9 g of H_2SO_4 is present in 100 mL of the solution. What is the molarity of the solution? Calculate its normality also.*

Solution: $\text{Strength (g/L) of } H_2SO_4 = \frac{4.9}{100} \times 1000 = 49$

$$\text{Molarity} = \frac{\text{Strength}}{\text{Mol. mass}} = \frac{49}{98} = 0.5\,M$$

$$\text{Normality} = n \times \text{Molarity}$$

$$n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2$$

$$\text{Normality} = 2 \times 0.5 = 1.0$$

Hence, the H_2SO_4 solution is 1 N.

Example 13. *25 mL of N/10 caustic soda solution exactly neutralises 20 mL of an acid solution containing 7.875 g of acid per litre. Calculate the equivalent mass of the acid.*

Solution:

$$\underset{(NaOH)}{N_1V_1} = \underset{(Acid)}{N_2V_2}$$

$$\frac{1}{10} \times 25 = N_2 \times 20$$

$$N_2 = \frac{25}{10 \times 20} = 0.125$$

Strength = Normality × Eq. mass

$$\text{Eq. mass of the acid} = \frac{7.875}{0.125} = 63.00$$

Example 14. *150 mL of N/10 HCl is required to react completely with 1.0 g of a sample of limestone. Calculate the percentage purity of calcium carbonate.*

Solution: $150\text{ mL}\,\frac{N}{10}\,\text{HCl} \equiv 150\text{ mL}\,\frac{N}{10}\,CaCO_3$

$$\underset{\text{Mol. mass}}{CaCO_3} + \underset{2g\text{ eq.}}{2HCl} \longrightarrow CaCl_2 + H_2O + CO_2$$

$$\text{Eq. mass of } CaCO_3 = \frac{40 + 12 + 48}{2} = \frac{100}{2} = 50$$

Mass of $CaCO_3$ present in 150 mL $N/10$ solution,

$$\left[N \times E \times \frac{V}{1000}\right] = 50 \times \frac{1}{10} \times \frac{150}{1000} = 0.75\text{ g}$$

$$\text{Purity} = \frac{0.75}{1} \times 100 = 75\%$$

Example 15. *0.63 g of dibasic acid was dissolved in water. The volume of the solution was made 100 mL. 20 mL of this acid solution required 10 mL $\frac{N}{5}$ NaOH solution. What is the equivalent mass and molecular mass of the acid?*

Solution: $\underset{(\text{Acid})}{N_1V_1} \equiv \underset{(\text{NaOH})}{N_2V_2}$

$$N_1 \times 20 = \frac{1}{5} \times 10$$

$$N_1 = \frac{1}{5} \times \frac{10}{20} = \frac{1}{10}$$

Strength of the acid solution = Eq. mass of the acid × Normality

$$= E \times \frac{1}{10} = \frac{E}{10}\ \text{g/L}$$

Mass of acid in 100 mL of the solution $= \frac{E}{10} \times \frac{100}{1000} = \frac{E}{100}$

Mass of acid in 100 mL of the solution = 0.63 g (given)

So, $\frac{E}{100} = 0.63$ or $E = 63$

Mol. mass = Basicity × Eq. mass

$$= 2 \times 63 = 126$$

Example 16. *10.875 g of a mixture of NaCl and Na_2CO_3 was dissolved in water and the volume made up to 250 mL, 20 mL of this solution required 75.5 mL of $\frac{N}{10}$ H_2SO_4. Find out the percentage composition of the mixture.*

Solution: Only Na_2CO_3 will react with H_2SO_4.

Applying $\underset{(Na_2CO_3)}{N_1V_1} \equiv \underset{(H_2SO_4)}{N_2V_2}$

$$N_1 \times 20 = 75.5 \times \frac{1}{10}$$

$$N_1 = \frac{75.5}{20 \times 10} = 0.3775$$

$$\underset{\text{1 mol. mass}}{Na_2CO_3} + \underset{\text{2g eq.}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O + CO_2$$

$$\text{Eq. mass of } Na_2CO_3 = \frac{106}{2} = 53$$

Mass of Na_2CO_3 present in 250 mL 0.3775 *N* solution

$$= \frac{N \times E \times V}{1000} = \frac{0.3775 \times 53 \times 250}{1000}$$

$$= 5.0018\ \text{g}$$

$$\text{Mass of NaCl} = (10.875 - 5.0018) = 5.8732\ \text{g}$$

$$Na_2CO_3 = \frac{5.0018}{10.875} \times 100 = 45.99\%$$

$$NaCl = \frac{5.8732}{10.875} \times 100 = 54.0\%$$

Example 17. *A quantity of ammonium chloride was heated with 100 mL of 0.8 N NaOH solution till the reaction was complete. The excess of NaOH was neutralised with 12.5 mL of 0.75 N H_2SO_4. Calculate the quantity of ammonium chloride.*

Solution:

12.5 mL of 0.75 *N* H_2SO_4 ≡ 12.5 mL of 0.75 *N* NaOH

12.5 mL of 0.75 *N* NaOH ≡ 11.72 mL of 0.8 *N* NaOH

NaOH solution used by NH_4Cl

= (100 − 11.72) mL of 0.8 N NaOH

= 88.28 mL of 0.8 *N* NaOH

≡ 88.28 mL of 0.8 *N* NH_4Cl

Mass of NH_4Cl present in 88.28 mL of 0.8 *N* NH_4Cl solution

$$= \frac{N \times E \times V}{1000} = \frac{0.8 \times 53.5 \times 88.28}{1000} = 3.7783\ \text{g}$$

[Eq. mass of NH_4Cl = 53.5]

Example 18. *A sample of $Na_2CO_3 \cdot H_2O$ weighing 0.62 g is added to 100 mL of 0.1 N sulphuric acid. Will the resulting solution be acidic, basic or neutral? (At. mass H = 1, C = 12, O = 16, Na = 23, S = 32)*

Solution: Mass of $Na_2CO_3 \cdot H_2O$ = 0.62 g

$$\text{No. of g equivalents} = \frac{\text{Mass}}{\text{Eq. mass}} = \frac{0.62}{62} = 0.01$$

$$[\text{Eq. mass of } Na_2CO_3 \cdot H_2O = \frac{124}{2} = 62]$$

$$\text{No. of g equivalents of } H_2SO_4 \text{ in 100 mL} = \frac{0.1}{1000} \times 100$$

$$= \frac{0.1}{10} = 0.01$$

Both the substances are present in same equivalent; they will completely neutralise each other and hence, the resulting solution will be neutral.

Example 19. *A solution containing 4.2 g of KOH and $Ca(OH)_2$ is neutralised by an acid. If it consumes 0.1 g equivalents of the acid, calculate the composition of the sample.*

Solution: Let mass of KOH be present in mixture = *a* g

and Mass of $Ca(OH)_2$ = (4.2 − *a*) g

$$\text{Eq. mass of KOH} = 56; \quad \text{Eq. mass of } Ca(OH)_2 = \frac{74}{2} = 37$$

g equivalent of KOH + g equivalent of $Ca(OH)_2$

= g equivalent of the acid

$$\frac{a}{56} + \frac{(4.2 - a)}{37} = 0.1$$

or $37a - 56a = 0.1 \times 56 \times 37 - 4.2 \times 56$

or $19a = 28$

$$a = \frac{28}{19} = 1.47$$

Mass of KOH in the sample = 1.47 g

Percentage of KOH = 35

and Percentage of $Ca(OH)_2$ = 100 − 35 = 65

Example 20. *40 mL of HCl is exactly neutralised by 20 mL of NaOH solution. The resulting neutral solution is evaporated to dryness and the residue is found to have a mass of 0.117 g. Calculate the normality of the HCl and NaOH.*

Solution: $\underset{\underset{\text{1g eq.}}{36.5}}{HCl} + \underset{\underset{\text{1g eq.}}{40}}{NaOH} \longrightarrow \underset{\underset{\text{1g eq.}}{58.5}}{NaCl} + H_2O$

$$\text{Mass of NaCl obtained} = 0.117\ \text{g}$$

$$\text{Eq. mass of NaCl} = 58.5$$

$$\text{No. of g equivalents of NaCl} = \frac{0.117}{58.5} = 0.002$$

Thus, 0.002 g eq. of HCl will react with 0.002 g eq. of NaOH to form 0.002 g eq. NaCl.

$$\text{Normality of HCl} = \frac{0.002}{40} \times 1000 = 0.05\ N$$

$$\text{Normality of NaOH} = \frac{0.002}{20} \times 1000 = 0.10\ N$$

Example 21. *1.03 g mixture of sodium carbonate and calcium carbonate require 20 mL N HCl for complete neutralisation. Calculate the percentage of sodium carbonate and calcium carbonate in the given mixture.*

Solution:

$$\underset{106}{Na_2CO_3} + \underset{2 \times 36.5}{2HCl} \longrightarrow 2NaCl + H_2O + CO_2$$

Eq. mass 53 36.5

1 g eq. 1 g eq.

$$\underset{100}{CaCO_3} + \underset{2 \times 36.5}{2HCl} \longrightarrow CaCl_2 + H_2O + CO_2$$

Eq. mass 50 36.5

1 g eq. 1 g eq.

Let x g $CaCO_3$ be present in the mixture.

Mass of Na_2CO_3 in the mixture $= (1.03 - x)$ g

$$\text{No. of g equivalents of } CaCO_3 = \frac{x}{50}$$

$$\text{No. of g equivalents of } Na_2CO_3 = \frac{(1.03 - x)}{53}$$

$$\text{No. of g equivalents in 20 mL } N \text{ HCl} = \frac{\text{Normality} \times \text{Vol.}}{1000}$$

$$= \frac{1 \times 20}{1000} = \frac{1}{50}$$

At equivalence point,

No. of g equivalents of $CaCO_3$ + No. of g equivalents of Na_2CO_3 = No. of gram equivalents of HCl

$$\frac{x}{50} + \frac{1.03 - x}{53} = \frac{1}{50}$$

or

$$x = 0.50$$

$$CaCO_3 = 0.50\ \text{g}, \quad \%\ CaCO_3 = \frac{0.50}{1.03} \times 100 = 48.54$$

$$Na_2CO_3 = 0.53\ \text{g}, \%\ Na_2CO_3 = \frac{0.53}{1.03} \times 100 = 51.46$$

Example 22. *1.325 g of anhydrous sodium carbonate are dissolved in water and the solution made up to 250 mL. On titration 25 mL of this solution neutralise 20 mL of a solution of sulphuric acid. How much water should be added to 450 mL of this acid solution to make it exactly N/12?*

Solution: $\text{Eq. mass of } Na_2CO_3 = \frac{\text{Mol. mass}}{2} = \frac{106}{2} = 53$

250 mL of the sodium carbonate solution contains = 1.325 g

1000 mL of the sodium carbonate solution contains

$$= \frac{1.325\ \text{g}}{250} \times 1000 = 5.300\ \text{g}$$

$$\text{Normality of } Na_2CO_3 \text{ solution} = \frac{\text{Strength (g/L)}}{\text{Eq. mass}}$$

$$= \frac{5.30}{53} = \frac{1}{10} N$$

Applying

$$\underset{(Na_2CO_3)}{N_1V_1} \equiv \underset{(H_2SO_4)}{N_2V_2}$$

$$\frac{1}{10} \times 25 = N_2 \times 20$$

$$N_2 = \frac{25}{10 \times 20} = \frac{1}{8}$$

Applying

$$\underset{\text{(Before dilution)}}{N_BV_B} \equiv \underset{\text{(After dilution)}}{N_AV_A}$$

$$\frac{1}{8} \times 450 = \frac{1}{12} \times V_A$$

$$V_A = \frac{450 \times 12}{8} = 675\ \text{mL}$$

Water to be added for dilution = (675 − 450) = 225 mL

Example 23. *A sample of sodium carbonate contains sodium sulphate also. 1.5 g of the sample is dissolved in water and volume raised to 250 mL. 25 mL of this solution requires 20 mL of $\frac{N}{10}$ H_2SO_4 solution for neutralisation. Calculate the percentage of sodium carbonate in the sample.*

Solution: Only Na_2CO_3 will react with H_2SO_4.

Applying

$$\underset{(Na_2CO_3)}{N_1V_1} = \underset{(H_2SO_4)}{N_2V_2}$$

$$N_1 \times 25 = 20 \times \frac{1}{10}$$

$$N_1 = \frac{20}{25 \times 10} = 0.08$$

$$\text{Eq. mass of } Na_2CO_3 = \frac{\text{Mol. mass}}{2} = \frac{106}{2} = 53$$

Mass of Na_2CO_3 present in 250 mL 0.08 N solution

$$= \frac{N \times E \times V}{1000} = \frac{0.08 \times 53 \times 250}{1000} = 1.06\ \text{g}$$

$$\text{Percentage of } Na_2CO_3 \text{ in the mixture} = \frac{1.06}{1.50} \times 100 = 70.67$$

Example 24. *In a sample of sodium carbonate some sodium sulphate is also mixed. 1.25 g of this sample is dissolved and the volume made up to 250 mL. 25 mL of this solution neutralises 20 mL of $\frac{N}{10}$ sulphuric acid. Calculate the percentage of sodium carbonate in the sample.*

Solution: 25 mL of sample solution neutralises

$$= 20 \text{ mL } \frac{N}{10} H_2SO_4$$

250 mL of sample solution will neutralise

$$= 200 \text{ mL } \frac{N}{10} H_2SO_4$$

$$200 \text{ mL } \frac{N}{10} H_2SO_4 \equiv 200 \text{ mL } \frac{N}{10} Na_2CO_3 \text{ solution}$$

$$\text{Amount of } Na_2CO_3 \text{ present} = \frac{E \times N \times V}{1000}$$

$$= \frac{53 \times 200}{10 \times 1000} = 1.06$$

$$\% \text{ of } Na_2CO_3 \text{ in the sample} = \frac{1.06}{1.25} \times 100 = 84.8$$

Example 25. *1.725 g of a metal carbonate is mixed with 300 mL of $\frac{N}{10}$ HCl. 10 mL of $\frac{N}{2}$ sodium hydroxide were required to neutralise excess of the acid. Calculate the equivalent mass of the metal carbonate.*

Solution: 10 mL of $\frac{N}{2}$ NaOH solution

$$= 10 \text{ mL of } \frac{N}{2} \text{ HCl solution}$$

$$\equiv 50 \text{ mL of } \frac{N}{10} \text{ HCl solution}$$

$$\text{Volume of } \frac{N}{10} \text{ HCl used for neutralisation} = 300 - 50 = 250 \text{ mL}$$

$$250 \text{ mL of } \frac{N}{10} \text{ HCl} \equiv 250 \text{ mL of } \frac{N}{10} \text{ metal carbonate solution}$$

Let the equivalent mass of metal carbonate be E.

Mass of metal carbonate present in solution

$$= \frac{N \times E \times V}{1000} = 1.725$$

$$= \frac{1 \times E \times 250}{10 \times 1000} = 1.725$$

$$= \frac{E}{40} = 1.725$$

$$E = 40 \times 1.725 = 69$$

Example 26. *1.575 g of oxalic acid $(COOH)_2 \cdot xH_2O$ are dissolved in water and the volume made up to 250 mL. On titration 16.68 mL of this solution requires 25 mL of $\frac{N}{15}$ NaOH solution for complete neutralisation. Calculate x.*

Solution:

$$25 \text{ mL of } \frac{N}{15} \text{ NaOH solution} \equiv 25 \text{ mL of } \frac{N}{15} \text{ oxalic acid solution}$$

$$\text{Mass of oxalic acid present in 25 mL of } \frac{N}{15} \text{ oxalic acid solution}$$

$$= \frac{N \times E \times V}{1000} = \frac{1 \times (90 + 18x) \times 25}{15 \times 2 \times 1000}$$

$$= \frac{(90 + 18x)}{1200} \text{ g}$$

Actually $\frac{(90 + 18x)}{1200}$ g oxalic acid is present in 16.68 mL solution.

250 mL of the solution contains oxalic acid

$$= \frac{(90 + 18x) \times 250}{1200 \times 16.68} = 1.575 \text{ (given)}$$

$$\text{or} \quad 90 + 18x = \frac{1.575 \times 1200 \times 16.68}{250} = 126$$

$$\text{or} \quad 18x = 126 - 90 = 36$$

$$x = 2$$

Example 27. *25 mL of a mixture of NaOH and Na_2CO_3 when titrated with N/10 HCl using phenolphthalein indicator required 25 mL HCl. The same volume of mixture when titrated with N/10 HCl using methyl orange indicator required 30 mL of HCl. Calculate the amount of Na_2CO_3 and NaOH in one litre of this mixture.*

Solution: When phenolphthalein is the indicator, whole of NaOH has been neutralised and carbonate converted into bicarbonate, *i.e.*,

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

So, 25 mL $\frac{N}{10}$ HCl ≡ NaOH + 1/2 Na_2CO_3 present in 25 mL of mixture

In another titration when methyl orange is the indicator, whole of NaOH has been neutralised and carbonate converted into carbonic acid, *i.e.*,

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2CO_3$$

$$30 \text{ mL } \frac{N}{10} \text{ HCl} \equiv NaOH + Na_2CO_3 \text{ present in 25 mL of mixture}$$

Hence,

$$(30 - 25) \text{ mL } \frac{N}{10} \text{ HCl} \equiv \frac{1}{2} Na_2CO_3 \text{ present in 25 mL of mixture}$$

Hence,

$$10 \text{ mL } \frac{N}{10} \text{ HCl} \equiv Na_2CO_3 \text{ present in 25 mL of mixture}$$

$$\equiv 10 \text{ mL } \frac{N}{10} Na_2CO_3 \text{ solution}$$

$$\text{Amount of } Na_2CO_3 = \frac{53 \times 10}{10 \times 1000} = 0.053 \text{ g}$$

This amount of Na_2CO_3 is present in 25 mL of mixture.

The amount present in one litre of mixture

$$= \frac{0.053}{25} \times 1000 = 2.12 \text{ g}$$

$$(30-10)\,\text{mL}\,\frac{N}{10}\,\text{HCl} \equiv \text{NaOH present in 25 mL mixture}$$

$$\equiv 20\,\text{mL}\,\frac{N}{10}\,\text{NaOH}$$

$$\text{Amount of NaOH in 25 mL of mixture} = \frac{40\times 20}{10\times 1000} = 0.08\,\text{g}$$

$$\text{The amount present in one litre of mixture} = \frac{0.08}{25}\times 1000 = 3.20\,\text{g}$$

Example 28. *25 mL of a mixture of NaOH + Na_2CO_3, when titrated with $\frac{N}{10}$ HCl using phenolphthalein indicator required 25 mL HCl to decolourise phenolphthalein. At this stage methyl orange was added and addition of acid was continued. The second end point was reached after further addition of 5 mL of the acid. Calculate the amount of Na_2CO_3 and NaOH in one litre of the solution.*

Solution: Between first and second end points,

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2CO_3$$

$$5\,\text{mL}\,\frac{N}{10}\,\text{HCl} \equiv \frac{1}{2}\,Na_2CO_3 \text{ present in 25 mL of a mixture}$$

$$\text{or } 10\,\text{mL}\,\frac{N}{10}\,\text{HCl} \equiv Na_2CO_3 \text{ present in 25 mL of a mixture}$$

$$\equiv 10\,\text{mL}\,\frac{N}{10}\,Na_2CO_3 = 0.053\,\text{g } Na_2CO_3$$

$$\text{Amount of } Na_2CO_3 \text{ in one litre of mixture} = \frac{0.053}{25}\times 1000$$

$$= 2.12\,\text{g}$$

$$(25-5)\,\text{mL}\,\frac{N}{10}\,\text{HCl} \equiv \text{NaOH present in 25 mL of mixture}$$

$$\equiv 25\,\text{mL}\,\frac{N}{10}\,\text{NaOH}$$

$$\equiv 0.08\,\text{g NaOH}$$

$$\text{Amount of NaOH in one litre of mixture} = \frac{0.08}{25}\times 1000$$

$$= 3.2\,\text{g}$$

Example 29. *A solution contains Na_2CO_3 and $NaHCO_3$. 10 mL of the solution required 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in one litre of the solution.*

Solution: 2.5 mL of 0.1 M H_2SO_4 = 2.5 mL of 0.2 N H_2SO_4

$$= \frac{1}{2}\,Na_2CO_3 \text{ present in 10 mL of mixture}$$

So,

5 mL of 0.2 N H_2SO_4 = Na_2CO_3 present in 10 mL of mixture

$$\equiv 5 \text{ mL of } 0.2\,N\,Na_2CO_3$$

$$\equiv \frac{0.2\times 53}{1000}\times 5 = 0.053\,\text{g}$$

$$\text{Amount of } Na_2CO_3 = \frac{0.053}{10}\times 1000 = 5.3\,\text{g/L of mixture}$$

Between first and second end points,

= 2.5 mL of 0.2 M H_2SO_4 used

= 2.5 mL of 0.4 N H_2SO_4 used

= 5 mL of 0.2 N H_2SO_4 used

$$\equiv \frac{1}{2}\,Na_2CO_3 + NaHCO_3 \text{ present in 10 mL of mixture}$$

$$(5-2.5)\,\text{mL } 0.2\,N\,H_2SO_4$$

$$\equiv NaHCO_3 \text{ present in 10 mL of mixture}$$

$$\equiv 2.5\,\text{mL } 0.2\,N\,NaHCO_3$$

$$\equiv \frac{0.2\times 84}{1000}\times 2.5 = 0.042\,\text{g}$$

$$\text{Amount of } NaHCO_3 = \frac{0.042}{10}\times 1000 = 4.20\,\text{g/L of mixture.}$$

Example 30. *Calculate the normality of a solution obtained by mixing 100 mL $\frac{N}{10}$ H_2SO_4, 50 mL $\frac{N}{2}$ HNO_3 and 25 mL $\frac{N}{5}$ HCl solutions.*

Solution: Let the final normality be N.

$$\text{Total volume} = (100+50+25) = 175\,\text{mL}$$

$$\text{So,}\quad 175\times N = \underset{(H_2SO_4)}{N_1V_1} + \underset{(HNO_3)}{N_2V_2} + \underset{(HCl)}{N_3V_3}$$

$$= \left(100\times\frac{1}{10}\right) + \left(50\times\frac{1}{2}\right) + \left(25\times\frac{1}{5}\right)$$

$$= (10+25+5) = 40$$

$$N = \frac{40}{175} = 0.2286$$

Hence, normality of solution = 0.2286 N

Example 31. *0.5 g of fuming H_2SO_4 (oleum) is diluted with water. This solution is completely neutralised by 26.7 mL of 0.4 N NaOH. Find the percentage of free SO_3 in the sample solution.*

Solution: Oleum consists of SO_3 and H_2SO_4.

Let the mass of SO_3 in the given sample of oleum be = x g

Mass of H_2SO_4 in the given sample of oleum = $(0.5-x)$ g

$$\text{Eq. mass of } SO_3 = \frac{80}{2} = 40$$

$$\text{No. of g equivalents of } SO_3 = \frac{x}{40}$$

$$[2NaOH + SO_3 \longrightarrow Na_2SO_4 + H_2O$$

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O]$$

$$\text{Eq. mass of } H_2SO_4 = \frac{98}{2} = 49$$

$$\text{No. of g equivalents of } H_2SO_4 = \frac{(0.5-x)}{49}$$

$$\text{Total no. of g equivalents} = \frac{x}{40} + \frac{(0.5-x)}{49}$$

26.7 mL of 0.4 N NaOH contain no. of equivalents of NaOH

$$= \frac{0.4}{1000} \times 26.7$$

At equivalence point,

$$\text{No. of g equivalents of NaOH} = \frac{x}{40} + \frac{(0.5-x)}{49}$$

So, $$\frac{0.4 \times 26.7}{1000} = \frac{49x + (40 \times 0.5 - 40x)}{40 \times 49}$$

$$x = \frac{0.9328}{9} = 0.1036$$

$$\text{Hence, \% of free } SO_3 = \frac{0.1036}{0.5} \times 100$$

$$= 20.72$$

Example 32. *0.789 g of crystalline barium hydroxide is dissolved in water. For the neutralisation of this solution, 20 mL of $\frac{N}{4}$ HNO_3 is required. How many molecules of water are present in one g mole of this base? ($Ba = 137.4$, $O = 16$, $N = 14$, $H = 1$)*

Solution: Let the molecular formula be $Ba(OH)_2 \cdot xH_2O$

$$\text{Mol. mass of } Ba(OH)_2 \cdot xH_2O = 137.4 + (2 \times 16) + 2 \times 1 + 18x$$

$$= 171.4 + 18x$$

$$\text{Eq. mass of } Ba(OH)_2 \cdot xH_2O = \frac{171.4 + 18x}{2}$$

$$20 \text{ mL } \frac{N}{4} \text{ } HNO_3 \equiv 20 \text{ mL } \frac{N}{4} \text{ } Ba(OH)_2 \cdot xH_2O$$

$$\text{Amount of } Ba(OH)_2 \cdot xH_2O = \frac{(171.4 + 18x)}{2 \times 4} \times \frac{20}{1000}$$

$$= \frac{171.4 + 18x}{400} \text{ g}$$

$$\text{Amount of } Ba(OH)_2 \cdot xH_2O = 0.789 \text{ g}$$

Hence, $$\frac{171.4 + 18x}{400} = 0.789$$

or $$171.4 + 18x = 0.789 \times 400$$

$$x = \frac{144.2}{18} = 8.01 \approx 8$$

Thus, 8 g moles of water molecules are present in one g mole of the base.

Example 33. *A piece of aluminium weighing 2.7 g is heated with 75 mL of H_2SO_4 (sp. gr. 1.18, containing 24.7% H_2SO_4 by mass). After the metal is carefully dissolved, the solution is diluted to 400 mL. Calculate the molarity of the free H_2SO_4 in the resulting solution.*

Solution: $$\text{Mass of } H_2SO_4 = \frac{24.7}{100} \times 75 \times 1.18$$

$$= 21.8595 \text{ g}$$

$$\text{Reaction: } \underset{2 \times 27}{2Al} + \underset{3 \times 98}{3H_2SO_4} \longrightarrow Al_2(SO_4)_3 + 3H_2$$

H_2SO_4 required for dissolving 2.7 g Al

$$= \frac{3 \times 98}{2 \times 27} \times 2.7 = 14.7 \text{ g}$$

H_2SO_4 left unreacted = (21.895 – 14.7) g = 7.1595 g

7.1595 g H_2SO_4 is present in 400 mL

$$\text{Amt. of } H_2SO_4 \text{ present in one litre} = \frac{7.1595}{400} \times 1000 \text{ g}$$

$$= 17.898 \text{ g}$$

$$\text{No. of g moles of } H_2SO_4 = \frac{17.898}{98} = 0.1826$$

Hence, molarity of $H_2SO_4 = 0.1826$ M

Example 34. *0.50 g of a mixture of K_2CO_3 and Li_2CO_3 requires 30 mL of a 0.25 N HCl solution for neutralisation. What is the percentage composition of the mixture?*

Solution: $$\underset{\substack{138 \\ 69}}{K_2CO_3} + \underset{\substack{2 \times 36.5 \\ 36.5}}{2HCl} \longrightarrow 2KCl + H_2O + CO_2$$

Eq. mass

$$\underset{\substack{74 \\ 37}}{Li_2CO_3} + \underset{\substack{2 \times 36.5 \\ 36.5}}{2HCl} \longrightarrow 2LiCl + H_2O + CO_2$$

Eq. mass

Let x g of K_2CO_3 be present in the mixture.

$$\text{Mass of } Li_2CO_3 = (0.50 - x)$$

$$\text{No. of g equivalents of } K_2CO_3 = \frac{x}{69}$$

$$\text{No. of g equivalents of } Li_2CO_3 = \frac{(0.50 - x)}{37}$$

No. of g equivalents in 30 mL of 0.25 N HCl

$$= \frac{\text{Normality} \times \text{Volume}}{1000} = \frac{0.25 \times 30}{1000}$$

$$= \frac{3}{400}$$

At equivalence point,

$$\frac{x}{69} + \frac{(0.50 - x)}{37} = \frac{3}{400}$$

So, $$x = 0.48$$

$$K_2CO_3 = 0.48 \text{ g; or } 96\%$$

$$Li_2CO_3 = 0.02 \text{ g; or } 4\%$$

Example 35. *5 mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 litres. Thirty mL of this acid mixture exactly neutralise 42.9 mL of sodium carbonate solution containing one gram of $Na_2CO_3 \cdot 10H_2O$ in 100 mL of water. Calculate the amount in grams of the sulphate ions in solution.*

Solution: Molecular mass of $Na_2CO_3 \cdot 10H_2O = 286$

$$\text{Equivalent mass of } Na_2CO_3 \cdot 10H_2O = \frac{286}{2} = 143$$

100 mL solution of sodium carbonate contains = 1 g
1000 mL solution of sodium carbonate contains = 10 g

$$\text{Normality of the solution} = \frac{10}{143}$$

Applying the formula,
Normality of acid solution × its volume
= Normality of sodium carbonate solution × its volume,

$$\text{Normality of the acid solution} = \frac{10 \times 42.9}{143 \times 30} = 0.1$$

Let V mL be the volume of H_2SO_4 taken.

$$8 \times 5 + 4.8 \times 5 + 34 \times V = 0.1 \times 2000$$

$$V = 4 \text{ mL}$$

$$\text{Amount of } SO_4^{2-} = \frac{\text{Normality} \times \text{Eq. mass} \times \text{Volume}}{1000}$$

$$= \frac{34 \times 48 \times 4}{1000} = 6.528 \text{ g}$$

Example 36. *2.26 g of an ammonium salt were treated with 100 mL of normal NaOH solution and boiled till no more of ammonia gas was given off. The excess of NaOH solution left over required 60 mL normal sulphuric acid. Calculate the percentage of ammonia in the salt.*

Solution: 60 mL normal $H_2SO_4 \equiv$ 60 mL normal NaOH

Thus, (100 − 60) mL normal NaOH were consumed by ammonium salt.

So, 40 mL normal NaOH ≡ 40 mL normal NH_3

Amount of NH_3 in 40 mL normal NH_3

$$= \frac{\text{Eq. mass of } NH_3 \times 40}{1000}$$

$$= \frac{17 \times 40}{1000} = 0.68$$

$$\text{So, \% of ammonia in the ammonium salt} = \frac{0.68}{2.26} \times 100$$

$$= 30.09$$

Example 37. *10 mL of a solution containing sulphuric acid and hydrochloric acid required 16 mL $\frac{N}{8}$ caustic soda solution for neutralisation. On adding excess of barium chloride to 20 mL of the same solution of the mixture of the two acids it gives 0.3501 g barium sulphate. What is the amount of hydrochloric acid per litre in the mixture of acids? (Ba = 137.4, S = 32, O = 16, Cl = 35.5)*

Solution: Mol. mass of $BaSO_4$ = (137.4 + 32 + 64) = 233.4

$$\underset{98\text{ g}}{H_2SO_4} + BaCl_2 \longrightarrow \underset{233.4\text{ g}}{BaSO_4} + 2HCl$$

233.4 g of $BaSO_4$ is obtained from = 98 g of H_2SO_4

$$0.3501 \text{ g of } BaSO_4 \text{ is obtained from} = \frac{98}{233.4} \times 0.3501$$

$$= 0.147 \text{ g of } H_2SO_4$$

20 mL of acid mixture contains 0.147 g of H_2SO_4

So, 10 mL of acid mixture contains 0.0735 g of H_2SO_4

Amount of NaOH in 16 mL $\frac{N}{8}$ NaOH solution

$$= \frac{E \times N \times V}{1000}$$

$$= \frac{40 \times 16}{8 \times 1000} = 0.08 \text{ g}$$

$$\underset{98\text{ g}}{H_2SO_4} + \underset{2 \times 40 = 80\text{ g}}{2NaOH} \longrightarrow Na_2SO_4 + 2H_2O$$

Thus, 98 g of H_2SO_4 require = 80 g of NaOH

$$0.07. \,.\, \text{g of } H_2SO_4 \text{ will require} = \frac{80}{98} \times 0.0735 \text{ g of NaOH}$$

$$= 0.06 \text{ g of NaOH}$$

Let the amount of HCl in 10 mL acid mixture be = x g

$$\underset{36.5\text{ g}}{HCl} + \underset{40\text{ g}}{NaOH} \longrightarrow NaCl + H_2O$$

36.5 g HCl require = 40 g of NaOH

$$x \text{ g HCl will require} = \frac{40}{36.5} x \text{ g of NaOH}$$

$$= 1.0958x \text{ g of NaOH}$$

$$1.0958x + 0.06 = 0.08$$

$$x = \frac{(0.08 - 0.06)}{1.0958} = 0.01825 \text{ g}$$

Amount of HCl present in one litre of the acid solution

$$= \frac{0.01825 \times 1000}{10} = 1.825$$

Example 38. *A small amount of $CaCO_3$ completely neutralises 525 mL of 0.1 N HCl and no acid is left in the end. After converting all calcium chloride to $CaSO_4$, how much plaster of Paris can be obtained?* **(Dhanbad 1991)**

Solution:

525 mL of 0.1 N HCl = 525 mL of 0.1 N $CaCl_2$

= 525 mL of 0.1 N plaster of Paris

$$\text{Molecular mass of plaster of Paris} = CaSO_4 \cdot \tfrac{1}{2} H_2O = 145$$

$$\text{Equivalent mass of plaster of Paris} = \frac{145}{2} = 72.5$$

Mass of plaster of Paris in 525 mL of 0.1 N solution

$$= \frac{N \times E \times V}{1000} = \frac{0.1 \times 72.5 \times 525}{1000}$$

$$= 3.806 \text{ g}$$

Example 39. *25 mL of 0.107 M H_3PO_4 was titrated with 0.115 M solution of NaOH to the end point identified by indicator bromocresol green. This required 23.1 mL. The titration was repeated using phenolphthalein as indicator. This time 25 mL of 0.107 M H_3PO_4 required 46.2 mL of the 0.115 M NaOH. What is the coefficient 'n' in the following reaction?*

$$H_3PO_4 + nOH^- \longrightarrow [H_{3-n}PO_4]^{n-} + nH_2O$$

Solution: Number of milliequivalents of H_3PO_4

$$= 25 \times 0.107 \times n$$
$$= 2.675 \times n$$

In first titration: Number of milliequivalents of OH^- used

$$= 23.1 \times 0.115 \times 1 = 2.66$$

(Acidity of NaOH = 1)

In second titration: Number of milliequivalents of OH^- used

$$= 46.2 \times 0.115 \times 1 = 5.313$$

$\therefore$ In first titration: $2.675 \times n = 2.66$

i.e., $n = 1$

$\therefore$ In second titration: $2.675 \times n = 5.313$

$$n = 2$$

Example 40. *11.2 g carbon reacts completely with 19.63 litre O_2 at NTP. The cooled gases are passed through 2 litre of 2.5 N NaOH solution. Calculate concentration of remaining NaOH and Na_2CO_3 in solution. (CO does not react with NaOH under these conditions.)*

Solution: Let x moles of carbon be converted into CO and y moles of carbon be converted into CO_2.

$$\underset{x}{C} + \underset{x/2}{\tfrac{1}{2}O_2} \longrightarrow CO$$

$$\underset{y}{C} + \underset{y}{O_2} \longrightarrow CO_2$$

Total volume of oxygen used $= \frac{x}{2} \times 22.4 + y \times 22.4$

$$= 19.63$$

$$11.2x + 22.4y = 19.63 \qquad \text{... (i)}$$

$$x + y = \frac{11.2}{12}; \text{ i.e., } 12x + 12y = 11.2 \qquad \text{... (ii)}$$

Solving eqs. (i) and (ii), we get

$$x = 0.11, y = 0.82$$

Number of moles of CO_2 formed = 0.82

Number of milliequivalents of NaOH solution through which CO_2 is massed $= N \times V = 2.5 \times 2000 = 5000$.

Number of milliequivalents of CO_2 passed $= 0.82 \times 2 \times 1000$

$$= 1640$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Number of milliequivalents of $Na_2CO_3 = 1640$

$$N_{Na_2CO_3} = \frac{1640}{2000} = 0.82$$

Number of milliequivalents of remaining NaOH

$$= 5000 - 1640 = 3360$$

Normality of remaining NaOH $= \frac{3360}{2000} = 1.68$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

9. How many grams of $NaHCO_3$ are required to neutralise 1 mL of 0.0902 *N* vinegar?

(a) 8.4×10^{-3} g (b) 1.5×10^{-3} g

(c) 0.758×10^{-3} g (d) 1.07×10^{-3} g

[Ans. (c)]

[Hint: Number of equivalents of $NaHCO_3$

$$= \text{Number of equivalents of acid}$$
$$= \frac{NV}{1000} = \frac{0.0902 \times 1}{1000}$$

Mass of $NaHCO_3 = \frac{0.0902 \times 1 \times 84}{1000}$

$$= 0.758 \times 10^{-3} \text{ g}]$$

10. 0.7 g of $Na_2CO_3 \cdot xH_2O$ was dissolved in water and the volume made up to 100 mL, 20 mL of it required 19.8 mL of $\frac{N}{10}$ HCl for complete neutralisation. The value of x is:

(a) 7 (b) 3

(c) 2 (d) 5

[Ans. (c)]

[Hint: Number of milliequivalents of $Na_2CO_3 \cdot xH_2O$ in 20 mL

$$= 19.8 \times \frac{1}{10}$$
$$= 1.98$$

$\therefore$ Number of milliequivalents in 100 mL $= 1.98 \times 5 = 9.9$

$$\frac{\text{Mass}}{\text{Equivalent mass}} \times 1000 = 9.9$$

$$\frac{0.7}{M/2} \times 1000 = 9.9$$

$$M = 141.40$$

(Molar mass of $Na_2CO_3 \cdot xH_2O$)

$$106 + 18x = 141.40$$
$$x = 2]$$

11. Calculate the equivalent mass of Na_2CO_3 when it is titrated against HCl in presence of phenolphthalein.

(a) 106 (b) 53

(c) 26.5 (d) 212

[Ans. (a)]

[Hint: The reaction involved is,

$$Na_2CO_3 + HCl \longrightarrow NaCl + NaHCO_3$$

Equivalent mass of $Na_2CO_3 = \frac{106}{1} = 106]$

12. 1 mol H_2SO_4 will exactly neutralise:

(a) 2 mol of ammonia (b) 1 mol of $Ba(OH)_2$

(c) 0.5 mol of $Ba(OH)_2$ (d) 2 mol of KOH

[Ans. (a, b, d)]

[Hint: $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$$Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2H_2O$$
$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O]$$

13. Which of the following gives equivalent mass of Na_2CO_3 when titrated against HCl in the presence of methyl orange?

(a) 5.3 (b) 53
(c) 10.6 (d) 106
[**Ans.** (b)]

[**Hint:** $Na_2CO_3 + 2HCl \xrightarrow{\text{Methyl orange}} 2NaCl + H_2O + CO_2$
Equivalent mass = molecular mass/2 = 106/2 = 53]

14.7 REDOX TITRATIONS

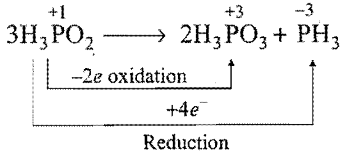
Oxidimetry: The determination of the strength of a solution of a reducing agent by titration with a standard solution of an oxidising agent is called oxidimetry.

Reductimetry: The determination of the strength of a solution of an oxidising agent by titration with standard solution of reducing agent is called reductimetry.

(Species) Oxidising Agent (OA) Or Reducing Agent (RA)	Reaction involved	Change in oxidation number Or Number of electrons involved	Equivalent mass
MnO_4^- (Acidic medium OA)	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	5	M.w./5
MnO_4^- (Neutral medium OA)	$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	3	M.w./3
MnO_4^- (Basic medium OA)	$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	1	M.w./1
H_2O_2 (OA)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	2	M.w./2
H_2O_2 (RA)	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	2	M.w./2
$S_2O_3^{2-}$ (RA)	$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$	1 (per molecule)	M.w./1
Cl_2 (OA) (Obtained from bleaching powder)	$Cl_2 + 2e^- \rightarrow 2Cl^-$	2	M.w./2
$Cr_2O_7^{2-}$ (OA)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	6	M.w./6
MnO_2 (OA)	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+}$	2	M.w./2
Fe^{2+} (RA)	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	1	M.w./1

Equivalent Mass of Substance Undergoing Disproportionation

Let us consider, disproportionation of H_3PO_2.



$$3H_3\overset{+1}{P}O_2 \longrightarrow 2H_3\overset{+3}{P}O_3 + \overset{-3}{P}H_3$$

$$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2} = \frac{4 \times 2}{4+2} = \frac{4}{3}$$

$$\text{Equivalent mass of } H_3PO_2 = \frac{\text{Molecular mass}}{n\text{-factor}}$$

$$= \frac{m}{4/3} = \frac{3m}{4}$$

14.8 IODOMETRIC AND IODIMETRIC TITRATIONS

(Titrating solution is $Na_2S_2O_3 \cdot 5H_2O$ called hypo.)

(i) *Estimation of I_2:*

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

Eq. mass of $Na_2S_2O_3 \cdot 5H_2O$ = M. w./1

(ii) *Estimation of $CuSO_4$:*

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

Eq. mass of $CuSO_4$ = M. w./1

(iii) *Estimation of MnO_2 present in pyrolusite:*

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

or $$MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$$

$$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$$

Eq. mass of MnO_2 = M. w./2

(iv) *Estimation of available chlorine in bleaching powder:*

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

Eq. mass of $CaOCl_2$ = M. w./2

(v) *Estimation of H_2O_2:*

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$$

Eq. mass of H_2O_2 = M. w./2

(vi) *Estimation of ozone:*

$$O_3 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

Eq. mass of O_3 = M. w./6

(vii) *Estimation of $Cr_2O_7^{2-}$:*

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$$

Eq. mass of $Cr_2O_7^{2-}$ = M. w./6

(viii) *Estimation of ClO^-:*

$$ClO^- + 2I^- + 2H^+ \longrightarrow H_2O + Cl^- + I_2$$

Eq. mass of ClO^- = M. w./2

(ix) *Estimation of* IO_3^-:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

Eq. mass of IO_3^- = M. w./5

SOME SOLVED EXAMPLES

Example 41. *0.5 g of an oxalate was dissolved in water and the solution made to 100 mL. On titration 10 mL of this solution required 15 mL of* $\frac{N}{20}$ $KMnO_4$. *Calculate the percentage of oxalate in the sample.*

Solution:

$$15\text{ mL } \frac{N}{20}\ KMnO_4 = 10 \times \text{Normality of oxalate solution.}$$

$$\text{Normality of oxalate solution} = \frac{15}{10} \times \frac{1}{20} = \frac{3}{40}$$

Strength of oxalate solution = Normality × Eq. mass of oxalate

$$= \frac{3}{40} \times 44 = 3.3\text{ g/L} \quad \left[\text{Eq. mass of } C_2O_4^{2-} = \frac{88}{2} = 44\right]$$

$$\text{Amount of oxalate in 100 mL solution} = \frac{3.3}{1000} \times 100 = 0.33\text{ g}$$

$$\%\text{ of oxalate} = \frac{0.33}{0.5} \times 100 = 66.0$$

Example 42. *How many mL of a 0.05 M* $KMnO_4$ *solution are required to oxidise 2.0 g of* $FeSO_4$ *in a dilute solution (acidic)?*

Solution:

$$\underset{10\times151.8}{10FeSO_4} + \underset{2\times158}{2KMnO_4} + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

10×151.8 g of $FeSO_4$ require $KMnO_4 = 2 \times 158$ g

$$2\text{ g of } FeSO_4 \text{ will require } KMnO_4 = \frac{2 \times 158 \times 2}{10 \times 151.8}\text{ g}$$

Suppose, V mL of $KMnO_4$ solution (0.05 M) is required.

$$\text{Amount of } KMnO_4 \text{ in this solution} = \frac{158 \times 0.05}{1000} \times V$$

Thus,
$$\frac{158 \times 0.05 \times V}{1000} = \frac{2 \times 158 \times 2}{10 \times 151.8}$$

$$V = 52.7\text{ mL}$$

Example 43. *5.5 g of a mixture of* $FeSO_4 \cdot 7H_2O$ *and* $Fe_2(SO_4)_3 \cdot 9H_2O$ *required 5.4 mL of 0.1 N* $KMnO_4$ *solution for complete oxidation. Calculate the gram mole of hydrated ferric sulphate in the mixture.*

(At. mass $H = 1, O = 16, S = 32, Fe = 56$*)*

Solution: Only $FeSO_4 \cdot 7H_2O$ will be oxidised by $KMnO_4$.

$$\text{Mol. mass of } FeSO_4 \cdot 7H_2O = 278$$

As the conversion involves one electron,

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-,$$

$$\text{The eq. mass of } FeSO_4 \cdot 7H_2O = \frac{278}{1} = 278$$

5.4 mL of 0.1 N $KMnO_4$

$\equiv$ 5.4 mL of 0.1 N $FeSO_4 \cdot 7H_2O$ solution

$$\text{Amount of } FeSO_4 \cdot 7H_2O = \frac{0.1 \times 278}{1000} \times 5.4 = 0.15\text{ g}$$

Amount of $Fe_2(SO_4)_3 \cdot 9H_2O = (5.5 - 0.15) = 5.35$ g

Mol. mass of $Fe_2(SO_4)_3 \cdot 9H_2O = 562$

$$\text{No. of g moles of } Fe_2(SO_4)_3 \cdot 9H_2O = \frac{\text{Mass}}{\text{Mol. mass}}$$

$$= \frac{5.35}{562} = 0.00952$$

$$= 9.52 \times 10^{-3}$$

Example 44. *0.5 g mixture of* $K_2Cr_2O_7$ *and* $KMnO_4$ *was treated with excess of KI in acidic medium. Iodine liberated required* 100 cm^3 *of 0.15 N sodium thiosulphate solution for titration. Find the per cent amount of each in the mixture.* (IIT 1995)

Solution: Let 'a' g of $K_2Cr_2O_7$ be present in the mixture.

$$\text{Mass of } KMnO_4 = (0.5 - a)\text{ g}$$

$$\text{Eq. mass of } K_2Cr_2O_7 = \frac{\text{Mol. mass}}{6} = \frac{294}{6} = 49.0$$

$$\text{Eq. mass of } KMnO_4 = \frac{\text{Mol. mass}}{5} = \frac{158}{5} = 31.6$$

$$\text{No. of equivalents of } K_2Cr_2O_7 = \frac{a}{49.0}$$

$$\text{No. of equivalents of } KMnO_4 = \frac{(0.5 - a)}{31.6}$$

No. of equivalents of $Na_2S_2O_3$ in 100 cm^3 of 0.15 N solution

$$= \frac{100 \times 0.15}{1000} = 0.015$$

Equivalents of $K_2Cr_2O_7$ + Equivalents of $KMnO_4$

$\equiv$ Equivalents of iodine

$\equiv$ Equivalents of $Na_2S_2O_3$

$$\frac{a}{49.0} + \frac{(0.5 - a)}{31.6} = 0.015$$

$$17.4a = 1.274$$

$$a = 0.0732$$

$$\%\text{ of } K_2Cr_2O_7 = \frac{0.0732 \times 100}{0.5} = 14.64$$

$$\%\text{ of } KMnO_4 = 85.36$$

Example 45. *Calculate the percentage of available chlorine in a given sample of bleaching powder from the following data:*

3.55 g of bleaching powder when treated with acetic acid and xcess of KI liberated iodine which required 60 mL of 0.5 N odium thiosulphate solution.

Solution: $60 \text{ mL } 0.5\,N\ Na_2S_2O_3 \equiv 60 \text{ mL } 0.5\,N\ I_2$

$$\equiv 60 \text{ mL } 0.5\,N\ Cl_2$$

$$\text{Amount of chlorine} = \frac{35.5 \times 0.5}{1000} \times 60 = 1.065 \text{ g}$$

$$\%\text{ available chlorine} = \frac{1.065}{3.55} \times 100 = 30.0$$

Example 46. *0.261 g of a sample of pyrolusite was heated with excess of HCl and the chlorine evolved was passed in a solution of KI. The liberated iodine required 90 mL $\frac{N}{30}$ $Na_2S_2O_3$. Calculate the percentage of MnO_2 in the sample.*

Solution: $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

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

$$90 \text{ mL } \frac{N}{30}\ Na_2S_2O_3 \equiv 90 \text{ mL } \frac{N}{30}\ I_2$$

$$\equiv 90 \text{ mL } \frac{N}{30}\ Cl_2$$

$$\equiv 90 \text{ mL } \frac{N}{30}\ MnO_2$$

$$\text{Eq. mass of } MnO_2 = \frac{\text{Mol. mass}}{2} = \frac{87}{2}$$

[Since, change in O.N. is from 4 to 2]

$$\text{Amount of } MnO_2 = \frac{87}{2 \times 30} \times \frac{90}{1000} = 0.1305 \text{ g}$$

$$\%\text{ of } MnO_2 = \frac{0.1305}{0.261} \times 100 = 50$$

Example 47. (*i*) *What is the mass of sodium bromate and molarity of the solution necessary to prepare 85.4 mL of 0.672 N solution when the half reaction is,*

$$BrO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$$

(*ii*) *What would be the mass as well as molarity if the half cell reaction is,*

$$2BrO_3^- + 12H^+ + 10e \longrightarrow Br_2 + 6H_2O$$

Solution:

(i) Molecular mass of $NaBrO_3 = 23 + 80 + (3 \times 16) = 151$

Each bromate ion takes-up 6 electrons; therefore,

$$\text{Eq. mass of } NaBrO_3 = \frac{\text{Mol. mass}}{6} = \frac{151}{6}$$

Amount of $NaBrO_3$ in 85.5 mL 0.672 N solution

$$= \frac{0.672}{1000} \times \frac{151}{6} \times 85.5 = 1.446 \text{ g}$$

$$\text{Molarity} = \frac{\text{Normality}}{n} = \frac{0.672}{6} = 0.112\,M$$

(ii) Each bromate ion takes-up 5 electrons; therefore,

$$\text{Eq. mass of } NaBrO_3 = \frac{\text{Mol. mass}}{5} = \frac{151}{5}$$

Amount of $NaBrO_3$ in 85.5 mL 0.672 N solution

$$= \frac{151}{5} \times \frac{0.672}{1000} \times 85.5$$

$$= 1.7352 \text{ g}$$

$$\text{Molarity} = \frac{\text{Normality}}{n} = \frac{0.672}{5} = 0.1344\,M$$

Example 48. *50 mL of an aqueous solution of H_2O_2 was treated with an excess of KI solution and dilute H_2SO_4. The liberated iodine required 20 mL 0.1 N $Na_2S_2O_3$ solution for complete interaction. Calculate the concentration of H_2O_2 in g/L.*

Solution: $H_2O_2 + 2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O + I_2$

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

$$\text{Eq. mass } H_2O_2 = \frac{34}{2} = 17$$

$$20 \text{ mL } 0.1\,N\ Na_2S_2O_3 = 20 \text{ mL } 0.1\,N\ I_2 \text{ solution}$$

$$\equiv 20 \text{ mL } 0.1\,N\ H_2O_2 \text{ solution}$$

Amount of H_2O_2 in 50 mL *aq.* solution

$$= \frac{0.1 \times 17}{1000} \times 20 = 0.034 \text{ g}$$

$$\text{Concentration in g/L} = \frac{0.034}{50} \times 1000 = 0.68$$

Example 49. *0.124 g of iron wire was dissolved in dilute H_2SO_4 in oxygen free atmosphere and the resultant solution was titrated against 0.09672 N solution of $KMnO_4$. The titre value was 22.90 mL. Calculate the percentage purity of iron wire.*

Solution:

$$22.90 \text{ mL } 0.09672\,N\ KMnO_4 \equiv 22.90 \text{ mL } 0.09672\,N\ FeSO_4$$

$$\text{Amount of } FeSO_4 \text{ in the solution} = \frac{0.09672 \times 152 \times 22.90}{1000}$$

$$= 0.3366 \text{ g}$$

$$\text{Amount of iron in 0.3366 g of } FeSO_4 = \frac{56}{152} \times 0.3366$$

$$= 0.124 \text{ g}$$

Thus, $\text{percentage} = \frac{0.124}{0.124} \times 100 = 100$

The iron wire is 100% pure.

Example 50. *A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 mL of water. 10 mL of this solution was* *reacted with excess of $FeCl_3$ solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 mL of $\frac{M}{50}$ $KMnO_4$. Estimate the amount of hydrazine sulphate in one litre of solution.*

Reactions: $4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$

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

Solution: $20\text{ mL } \frac{M}{50}\text{ KMnO}_4 = 20\text{ mL } \frac{N}{10}\text{ KMnO}_4$

$$\left[\text{Equivalent mass of KMnO}_4 = \frac{\text{Molecular mass}}{5}\right]$$

$$20\text{ mL } \frac{N}{10}\text{ KMnO}_4 \equiv 20\text{ mL } \frac{N}{10}\text{ Ferrous ion}$$

$$\equiv 20\text{ mL } \frac{N}{10}\text{ FeCl}_3$$

$$\equiv 20\text{ mL } \frac{N}{10}\text{ N}_2\text{H}_6\text{SO}_4$$

$$\text{Eq. mass N}_2\text{H}_6\text{SO}_4 = \frac{\text{Mol. mass}}{4} = \frac{130}{4} = 32.5$$

[Since, change in O.N. ($N_2H_4 \rightarrow N_2$) per molecule = 4]

Amount of hydrazine sulphate in 10 mL of solution

$$= \frac{1}{10} \times \frac{32.5}{1000} \times 20 = 0.065\text{ g}$$

Amount of hydrazine sulphate in one litre of solution

$$= \frac{0.065}{10} \times 1000 = 6.50\text{ g}$$

Example 51. *0.1M $KMnO_4$ is used for the following titration. What volume of the solution in mL will be required to react with 0.158 g of $Na_2S_2O_3$?*

$$S_2O_3^{2-} + MnO_4^- + H_2O \longrightarrow MnO_2(s) + SO_4^{2-} + OH^-$$

(not balanced) (MLNR 1992)

Solution: $S_2O_3^{2-} \longrightarrow 2SO_4^{2-}$

Change in oxidation number of sulphur per molecule of $S_2O_3^{2-} = 2 \times (6-2) = 8$

Change in oxidation number of Mn per molecule of MnO_4^- $= 7 - 4 = 3$

$$\text{No. of moles in 0.158 g of Na}_2\text{S}_2\text{O}_3 = \frac{0.158}{158} = 1 \times 10^{-3}$$

$$\text{No. of equivalents} = 8 \times 10^{-3}$$

Normality of 0.1 M $KMnO_4$ solution $= 0.1 \times 3 = 0.3$

Let V mL of volume of $KMnO_4$ be required; then

$$\frac{V}{1000} \times 0.3 = 8 \times 10^{-3}$$

or

$$V = \frac{8}{0.3} \times 10^{-3} \times 10^3$$

$$= 26.7\text{ mL}$$

Example 52. *25 mL of H_2O_2 solution were added to excess of acidified solution of KI. The iodine so liberated required 20 mL of 0.1 N $Na_2S_2O_3$ for titration. Calculate the strength of H_2O_2 in terms of normality, percentage and volume.* (MLNR 1996)

Solution: 20 mL of 0.1 N $Na_2S_2O_3$

$= 20$ mL of 0.1 N I_2 solution

$= 20$ mL of 0.1 N H_2O_2 solution

$\equiv 25$ mL of 0.08 N H_2O_2 solution

$$\text{Mass of H}_2\text{O}_2\text{ in 100 mL solution} = \frac{0.08 \times 17 \times 100}{1000} = 0.136\text{ g}$$

$$\% = 0.136$$

68 g H_2O_2 evolve oxygen at NTP = 22400 mL

0.00136 g H_2O_2 evolve oxygen at NTP

$$= \frac{22400}{68} \times 0.00136 = 0.448$$

The solution is of 0.448 volume.

Example 53. *0.804 g sample of iron ore was dissolved in acid. Iron was reduced to +2 state and it required 47.2 mL of 0.112 N $KMnO_4$ solution for titration. Calculate the percentage of iron and Fe_3O_4 in the ore.*

Solution: The titration involves the conversion of ferrous into ferric.

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

47.2 mL of 0.112 N $KMnO_4$ $\equiv$ 47.2 mL of 0.112 N Fe^{2+} ions

$$= \frac{47.2 \times 0.112 \times 55.5}{1000} = 0.2934$$

Mass of iron = 0.2934 g

$$\% \text{ of iron in the ore} = \frac{0.2934}{0.804} \times 100 = 36.49$$

$$\underset{(3\times55.5)}{3\text{Fe}} \longrightarrow \underset{(3\times55.5+64)}{\text{Fe}_3\text{O}_4}$$

3×55.5 g of iron form 230.5 g of Fe_3O_4.

$$\text{0.2934 g of iron will form} = \frac{230.5}{166.5} \times 0.2934 = 0.406\text{ g}$$

$$\% \text{ of Fe}_3\text{O}_4\text{ in the ore} = \frac{0.406}{0.804} \times 100 = 50.5$$

Example 54. *An equal volume of a reducing agent is treated separately with 1 M $KMnO_4$ in acid, neutral and alkaline media. The volume of $KMnO_4$ required are 20 mL in acid, 33.4 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reaction product. Give the balanced equations for all the three half reactions. Find out the volume of 1 M $K_2Cr_2O_7$ consumed, if the same volume of the reducing agent is treated in acid medium.*

Solution: Let N_1, N_2 and N_3 be the normalities of $1\,M$ $KMnO_4$ solution in acid, neutral and alkaline mediums, respectively.

$$20\,\text{mL}\ N_1 \equiv 33.4\,\text{mL}\ N_2 \equiv 100\,\text{mL}\ N_3$$

In acidic medium, the half reaction is:

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

$$1\,M\ KMnO_4 = 5\,N\ KMnO_4$$

Thus, from above relation,

$$N_2 = \frac{20}{33.4} \times N_1 = \frac{20}{33.4} \times 5\,N = 3\,N$$

and $$N_3 = \frac{20}{100} \times N_1 = \frac{20}{100} \times 5\,N = 1\,N$$

The equations in the three media are:

$$MnO_4^- + 5e^- \xrightarrow{\text{Acid}} Mn^{2+}$$

$$MnO_4^- + 3e^- \xrightarrow{\text{Neutral}} Mn^{4+}$$

$$MnO_4^- + e^- \xrightarrow{\text{Alkaline}} Mn^{6+}$$

The balanced equations are:

$$MnO_4^- + 8H^+ + 5e^- \xrightarrow{\text{Acid}} Mn^{2+} + 4H_2O$$

$$MnO_4^- + 2H_2O + 3e^- \xrightarrow{\text{Neutral}} MnO_2 + 4OH^-$$

$$MnO_4^- + e^- \xrightarrow{\text{Alkaline}} MnO_4^{2-}$$

The balanced equation in the case of acidified $K_2Cr_2O_7$ solution can be written as:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 3Cr^{3+} + 7H_2O$$

$$1\,M\ K_2Cr_2O_7 = 6\,N\ K_2Cr_2O_7$$

The volume required for the titration of the same volume of reducing agent with acidified $K_2Cr_2O_7$ solution as follows:

$$20\ \text{mL}\ 5\,N\ KMnO_4 \equiv V\ 6\,N\ K_2Cr_2O_7$$

$$V = \frac{20 \times 5}{6} = 16.66\,\text{mL}$$

Example 55. *1.6 g of pyrolusite ore was treated with $50\,cm^3$ of $1.0\,N$ oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to $250\,cm^3$ in a flask. $25\,cm^3$ of this solution when titrated with $0.1\,N$ $KMnO_4$ required $32\,cm^3$ of the solution. Find the percentage of pure MnO_2 in the sample and also the percentage of available oxygen.* (IIT 1996)

Solution: $25\ cm^3$ of undecomposed oxalic acid required

$$= 32\ cm^3\ 0.1\,N\ KMnO_4 \text{ solution}$$

Thus, $250\,cm^3$ of undecomposed oxalic acid required

$$= 320\ cm^3\ 0.1\,N\ KMnO_4 \text{ solution}$$

$$\equiv 32\ cm^3\ 1\,N\ KMnO_4 \text{ solution}$$

$$= 32\ cm^3\ 1\,N \text{ oxalic acid solution}$$

Oxalic acid used by pyrolusite

$$= (50 - 32)\ cm^3\ 1\,N \text{ solution}$$

$$= 18\ cm^3\ 1\,N \text{ solution}$$

$$\equiv 18\ cm^3\ 1\,N\ MnO_2 \text{ solution}$$

$$\text{Mass of } MnO_2 = \frac{N \times E \times V}{1000} = \frac{1 \times 18 \times 87}{1000 \times 2} = 0.783\ \text{g}$$

$$\text{Percentage of } MnO_2 = \frac{0.783}{1.6} \times 100 = 48.9$$

$$\underset{87\,g}{MnO_2} \longrightarrow MnO + \overset{16\,g}{O}$$

$$\text{Oxygen given by } 0.783\ \text{g}\ MnO_2 = \frac{16}{87} \times 0.783 = 0.144\ \text{g}$$

$$\%\ \text{of available oxygen} = \frac{0.144}{1.6} \times 100 = 9.0$$

Example 56. *A mixture of $H_2C_2O_4$ and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and the solution made up to one litre. 10 mL of this solution required 3.0 mL of $0.1\,N$ NaOH solution for complete neutralisation. In another experiment 10 mL of same solution in hot dilute H_2SO_4 medium required 4 mL of $0.1\,N$ $KMnO_4$ for complete neutralisation. Calculate the amount of $H_2C_2O_4$ and $NaHC_2O_4$ in the mixture.* (IIT 1990)

Solution: Let mass of $H_2C_2O_4$ present in the mixture be $= a$ g in 1 litre

and mass of $NaHC_2O_4$ present in the mixture be $= b$ g in 1 litre

For acid-base reaction

$$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$$

$$\text{Eq. mass of } H_2C_2O_4 = \frac{\text{Mol. mass}}{2} = \frac{90}{2} = 45$$

$$NaHC_2O_4 + NaOH \longrightarrow Na_2C_2O_4 + H_2O$$

$$\text{Eq. mass of } NaHC_2O_4 = \frac{\text{Mol. mass}}{1} = 112$$

Now,

$$\underset{\text{in 10 mL solution}}{\text{Equivalents of } H_2C_2O_4} + \underset{\text{in 10 mL solution}}{\text{Equivalents of } NaHC_2O_4} = \frac{3 \times 0.1}{1000}$$

$$\frac{a \times 10}{45 \times 1000} + \frac{b \times 10}{112 \times 1000} = \frac{3 \times 0.1}{1000}$$

or $$112a + 45b = \frac{3 \times 0.1 \times 45 \times 112}{10} = 151.2 \qquad \text{... (i)}$$

For redox reaction

$$\text{Eq. mass of } H_2C_2O_4 = \frac{90}{2} = 45;$$

$$\text{Eq. mass of } NaHC_2O_4 = \frac{112}{2} = 56$$

(Change in oxidation number of carbon per molecule = 2; $C_2^{3+} \longrightarrow 2C^{4+}$)

Now,

$$\underset{\text{in 10 mL solution}}{\text{Equivalents of } H_2C_2O_4} + \underset{\text{in 10 mL solution}}{\text{Equivalents of } NaHC_2O_4} = \frac{4\times 0.1}{1000}$$

$$\frac{a\times 10}{45\times 1000}+\frac{b\times 10}{56\times 1000}=\frac{4\times 0.1}{1000}$$

or $$56a+45b=100.8 \qquad \dots\text{(ii)}$$

Solving equations (i) and (ii),

$$a=0.9\text{ g} \quad \text{and} \quad b=1.12\text{ g}$$

Example 57. *A 3.0 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted to Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the dilute solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the diluted solution after complete extraction of iodine requires 12.8 mL of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for oxidation of Fe^{2+}. Calculate the percentage of Fe_2O_3 and Fe_3O_4 in the original sample.* **(IIT 1996)**

Solution: Fe_3O_4 is an equimolar mixture of Fe_2O_3 and FeO. Thus, the sample contains Fe_2O_3, FeO and impurities. The amount of iodine liberated depends on the amount of Fe_2O_3 and the entire iron is converted into Fe^{2+}.

$$Fe_3O_4+2KI+H_2SO_4 \longrightarrow 3FeO+H_2O+K_2SO_4+I_2$$

$$Fe_2O_3+KI+H_2SO_4 \longrightarrow 2FeO+H_2O+K_2SO_4+I_2$$

5×11.0 mL of 0.5 M $Na_2S_2O_3 \equiv$ 55.0 mL of 0.5 N $Na_2S_2O_3$ soln.

$\equiv$ 55.0 mL of 0.5 N I_2 soln.

$\equiv$ 55.0 mL of 0.5 N Fe_2O_3 soln.

$= 27.5\times 10^{-3}$ equivalent Fe_2O_3 soln.

$= 13.75\times 10^{-3}$ moles Fe_2O_3

2×12.8 mL of 0.25 M $KMnO_4$ soln.

$\equiv$ 25.6 mL of 1.25 N $KMnO_4$ soln.

$\equiv$ 25.6 mL of 1.25 N FeO soln.

$= 32.0\times 10^{-3}$ equivalent FeO

$= 32.0\times 10^{-3}$ moles FeO

Moles of FeO in $Fe_3O_4 = 0.032-0.0275=0.0045$

Mass of $Fe_3O_4 = 0.0045\times 232 = 1.044$ g

Moles of Fe_2O_3 existing separately

$= 0.01375-0.0045=0.00925$

Mass of $Fe_2O_3 = 0.00925\times 160 = 1.48$ g

$$\%\, Fe_3O_4 = \frac{1.044}{3}\times 100 = 34.8$$

$$\%\, Fe_2O_3 = \frac{1.48}{3}\times 100 = 49.33$$

Example 58. *Hydroxylamine reduces iron (III) according to the equation,*

$$2NH_2OH+4Fe^{3+} \longrightarrow N_2O(g)\uparrow + H_2O+4Fe^{2+}+4H^+$$

Iron (II) thus produced is estimated by titration with a standard permanganate solution. The reaction is:

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

A 10 mL sample of hydroxylamine solution was diluted to one litre. 50 mL of this diluted solution was boiled with excess of iron (III) solution. The resulting solution required 12 mL of 0.02 M $KMnO_4$ solution for complete oxidation of iron (II). Calculate the mass of hydroxylamine in one litre of the original solution.

Solution:

12 mL of 0.02 M $KMnO_4 \equiv$ 12 mL of 0.1 N $KMnO_4$

$\equiv$ 12 mL of 0.1 N Fe^{2+}

$\equiv$ 12 mL of 0.1 N NH_2OH

$$\text{Eq. mass of } NH_2OH = \frac{\text{Mol. mass}}{2} = \frac{33}{2} = 16.5$$

Mass of NH_2OH in 12 mL of 0.1 N NH_2OH soln.

$$= \frac{N\times E\times V}{1000} = \frac{0.1\times 16.5\times 12}{1000} = 0.0198\text{ g}$$

50 mL of diluted solution contains NH_2OH = 0.0198 g

1000 mL of diluted solution contains NH_2OH

$$= \frac{0.0198}{50}\times 1000 = 0.396\text{ g}$$

10 mL of original solution contains NH_2OH = 0.396 g

1000 mL of original solution contains NH_2OH

$$= 100\times 0.396 = 39.6\text{ g}$$

Example 59. *0.56 g of limestone was treated with oxalic acid to give CaC_2O_4. The precipitate decolourised 45 mL of 0.2 N $KMnO_4$ in acid solution. Calculate the % of CaO in limestone.*

Solution:

45 mL of 0.2 N $KMnO_4$ = 45 mL of 0.2 N CaC_2O_4

= 45 mL of 0.2 N $CaCO_3$

= 45 mL of 0.2 N CaO

$$\text{Mass of CaO} = \frac{N\times E\times V}{1000} = \frac{0.2\times 28\times 45}{1000} = 0.252\text{ g}$$

$$\%\text{ of CaO in limestone} = \frac{0.252}{0.56}\times 100 = 45$$

Example 60. *A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL oxidant. The resulting solution is neutralised by Na_2CO_3, acidified with dilute acetic acid and titrated with excess of KI. The liberated iodine required 11.3 mL of 0.05 M $Na_2S_2O_3$ for complete reduction. Find out the mole ratio of Cu^{2+} and $C_2O_4^{2-}$ in the compound.* **(IIT 1991)**

Solution: 1st case: Only $C_2O_4^{2-}$ ions are oxidised by $KMnO_4$ solution.

Normality of $KMnO_4$ solution = $0.02\times 5 = 0.1\,N$

22.6 mL of 0.1 N $KMnO_4$ = 22.6 mL of 0.1 N $C_2O_4^{2-}$ soln.

$$\text{Mass of } C_2O_4^{2-} \text{ ions in the solution} = \frac{N \times E \times V}{1000} = \frac{N \times M \times V}{1000 \times 2}$$

$$\text{No. of moles of } C_2O_4^{2-} \text{ ions in the solution} = \frac{N \times M \times V}{1000 \times 2 \times M}$$

$$= \frac{N \times V}{2000}$$

$$= \frac{0.1 \times 22.6}{2000}$$

$$= 11.3 \times 10^{-4}$$

2nd case: Only Cu^{2+} ions are reduced by KI and iodine liberated is neutralised by $Na_2S_2O_3$ solution.

$$11.3 \text{ mL of } 0.05\,M\ Na_2S_2O_3 \equiv 11.3 \text{ mL of } 0.05\,N\ Na_2S_2O_3$$

$$= 11.3 \text{ mL of } 0.05\,N\ I_2$$

$$= 11.3 \text{ mL of } 0.05\,N\ Cu^{2+}$$

$$\text{Mass of } Cu^{2+} \text{ ions in the solution} = \frac{N \times E \times V}{1000} = \frac{N \times M \times V}{1000}$$

$$\text{No. of moles of } Cu^{2+} \text{ ions in the solution} = \frac{N \times M \times V}{1000 \times M}$$

$$= \frac{N \times V}{1000}$$

$$= \frac{0.05 \times 11.3}{1000}$$

$$= 5.65 \times 10^{-4}$$

$$\text{Molar ratio of } \frac{Cu^{2+}}{C_2O_4^{2-}} = \frac{5.65 \times 10^{-4}}{11.3 \times 10^{-4}} = \frac{1}{2}$$

Example 61. *12 g of an impure sample of arsenious oxide was dissolved in water containing 7.5 g of sodium bicarbonate and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidised by 22.4 mL of a solution of iodine. 25 mL of this iodine solution reacted with same volume of a solution containing 24.8 g of sodium thiosulphate solution ($Na_2S_2O_3 \cdot 5H_2O$) in one litre. Calculate the percentage of arsenious oxide in the sample. (Atomic mass of As = 75)* (IIT 1999)

Solution: Normality of $Na_2S_2O_3$ soln. $= \frac{24.8}{248} = 0.1\,N$

Applying $N_1V_1 = N_2V_2$

Volume of As_2O_3 soln. in $NaHCO_3$ × Normality of this soln.

= Volume of iodine soln. × Normality of iodine soln.

$$25 \times N_1 = 22.4 \times 0.1$$

$$\therefore \quad N_1 = \frac{22.4 \times 0.1}{25}$$

Amt. of As_2O_3 present in 250 mL of the solution

$$= N_1 \times \frac{\text{Equivalent mass of } As_2O_3}{1000} \times 250$$

$$= \frac{22.4 \times 0.1}{25} \times \frac{198}{4} \times \frac{250}{1000} = 1.1088 \text{ g}$$

$$\text{Percentage of } As_2O_3 = \frac{1.1088}{12} \times 100 = 9.24$$

Example 62. *Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolourised by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2.* (IIT 2001)

Solution:

$$\text{(i)}\ \underset{\substack{\text{ppt.}\\ 1 \text{ mole}}}{MnO_2} + \underset{1 \text{ mole}}{Na_2C_2O_4} + 2H_2SO_4 \longrightarrow MnSO_4 + Na_2SO_4 + 2CO_2 + 2H_2O$$

$$\text{mM of } MnO_2 = \text{mM of } Na_2C_2O_4 = 10 \times 0.2 = 2$$

$$\text{(ii)}\ \underset{2 \text{ mole}}{2KMnO_4} + 3MnSO_4 + 2H_2O \longrightarrow \underset{\substack{\text{ppt.}\\ 5 \text{ mole}}}{5MnO_2} + K_2SO_4 + 2H_2O$$

$$\text{mM of } KMnO_4 = \text{mM of } MnO_2 \times \frac{2}{5} = 2 \times \frac{2}{5} = \frac{4}{5}$$

$$\text{(iii)}\ \underset{2 \text{ mole}}{2KMnO_4} + 3H_2SO_4 + \underset{5 \text{ mole}}{5H_2O_2} \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$\therefore \quad \text{mM of } H_2O_2 = \text{mM of } KMnO_4 \times \frac{5}{2} = \frac{4}{5} \times \frac{5}{2} = 2$$

$$\therefore \quad M \times 20 = 2$$

$$\text{or} \quad M_{H_2O_2} = \frac{2}{20} = 0.1\,M$$

Example 63. *The Mn_3O_4 formed on strong heating of a sample of $MnSO_4 \cdot 4H_2O$ was dissolved in 100 cm^3 of 0.1 N $FeSO_4$ containing dilute H_2SO_4. The resulting solution reacted completely with 50 cm^3 of $KMnO_4$ solution. 25 cm^3 of this $KMnO_4$ solution requires 30 cm^3 of 0.1 N $FeSO_4$ solution for complete reaction. Calculate the amount of $MnSO_4 \cdot 4H_2O$ in the sample.* (IIT 2001)

Solution: $MnSO_4 \cdot 4H_2O \xrightarrow{\text{Heat}} Mn_3O_4$

Mn_3O_4 is dissolved in ferrous sulphate solution and is reduced from $Mn^{(8/3)+}$ to Mn^{2+}. The excess of $FeSO_4$ is estimated by doing titration with $KMnO_4$ solution. The normality of $KMnO_4$ solution is determined by another ferrous sulphate solution.

For normality of $KMnO_4$ solution:

$$25 \times N = 30 \times 0.1$$

$$N = \frac{30 \times 0.1}{25} = \frac{3}{25}$$

Let the volume of unreacted $FeSO_4$ solution be V mL

$$V \text{ mL of } 0.1\,N\ FeSO_4 = 50 \text{ mL of } \frac{3}{25}\,N\ KMnO_4$$

or $$V = \frac{50 \times 3}{0.1 \times 25} = 60 \text{ mL}$$

$$\therefore \text{Volume of } FeSO_4 \text{ used for } Mn_3O_4 = (100 - 60) \text{ mL} = 40 \text{ mL}$$

$$40 \text{ mL of } 0.1\,N\ FeSO_4 \equiv 40 \text{ mL of } 0.1\,N\ Mn_3O_4 \equiv 40 \text{ mL of } 0.1\,N\ MnSO_4 \cdot 4H_2O$$

$$\text{Mass of } MnSO_4 \cdot 4H_2O = \frac{E \times 0.1 \times 40}{1000} = \frac{E}{250} \text{ g}$$

Equivalent mass of

$$MnSO_4 \cdot 4H_2O = \frac{M}{\left(\frac{8}{3} - 2\right)} = \frac{3M}{2} = \frac{3 \times 223}{2}$$

$$\therefore \text{Mass of } MnSO_4 \cdot 4H_2O = \frac{3 \times 223}{2 \times 250} = 1.338 \text{ g}$$

Example 64. *0.96 g of hydrogen iodide was heated to 450°C till the equilibrium was reached. It was then quickly cooled and the amount of iodine liberated required 15.7 cc of $N/10$ sodium thiosulphate. Calculate the percentage of hydrogen iodide dissociated at 450°C.*

Solution: Reactions involved

$$2HI \rightleftharpoons H_2 + I_2$$

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

$$1 \text{ mole } I_2 \equiv 2 \text{ mole hypo}$$

$$\text{No. of moles of hypo} = \frac{\text{Mass}}{\text{Molecular mass (158)}} = \frac{E \times N \times V}{1000 \times 158}$$

where, E, N and V are equivalent weight, normality and volume of hypo used.

$$E = 158, N = 1/10, V = 15.7$$

$$\therefore \quad \text{No. of moles of } Na_2S_2O_3 = \frac{158 \times 1/10 \times 15.7}{1000 \times 158} = 1.57 \times 10^{-3} \text{ mole}$$

Moles of I_2 produced by decomposition of HI

$$= \frac{1}{2} \text{ mole of } Na_2S_2O_3$$

$$= \frac{1}{2} \times 1.57 \times 10^{-3} = 0.785 \times 10^{-3} \text{ mole} \quad \text{... (i)}$$

$$\text{Moles of HI} = \frac{\text{Mass}}{\text{M.w.}} = \frac{0.96}{128} = 7.5 \times 10^{-3}$$

$$\begin{array}{llll} & HI & \rightleftharpoons \frac{1}{2}H_2 & + \frac{1}{2}I_2 \\ \text{At } t = 0 & C & 0 & 0 \\ \text{At equilibrium} & C(1-\alpha) & \frac{C\alpha}{2} & \frac{C\alpha}{2} \end{array}$$

where, $C = 7.5 \times 10^{-3}$, α = degree of dissociation

$$\text{Moles of } I_2 = \frac{C\alpha}{2} = \frac{7.5 \times 10^{-3}\alpha}{2} \quad \text{... (ii)}$$

Equating eqs. (i) and (ii), we get

$$\frac{7.5 \times 10^{-3}\alpha}{2} = 0.785 \times 10^{-3}$$

$$\alpha = 0.209$$

$$\text{\% dissociation of HI} = \text{Degree of dissociation} \times 100 = 0.209 \times 100 = 20.9\%$$

Example 65. *50 mL sample of ozonised oxygen at NTP was passed through a solution of potassium iodide. The liberated iodine required 15 mL of 0.08 N $Na_2S_2O_3$ solution for complete titration. Calculate the volume of ozone at NTP in the given sample.*

Solution: Reactions involved may be given as:

$$2KI + H_2O + O_3 \longrightarrow 2KOH + I_2 + O_2 \uparrow$$

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

$$1 \text{ mole } O_3 = 2 \text{ mole } Na_2S_2O_3 \quad \text{... (i)}$$

$$\text{No. of moles of hypo} = \frac{\text{Mass}}{\text{Molecular mass (158)}} = \frac{E \times N \times V}{1000 \times 158}$$

where, $E_{Na_2S_2O_3} = 158, N = 0.08, V = 15$

$$\therefore \quad \text{No. of moles of hypo} = \frac{158 \times 0.08 \times 15}{1000 \times 158} = 1.2 \times 10^{-3}$$

$$\text{No. of moles of } O_3 = \frac{1}{2} \text{ mole of hypo} \quad \text{[from eq. (i)]}$$

$$= \frac{1}{2} \times 1.2 \times 10^{-3}$$

$$= 6 \times 10^{-4} \text{ mole}$$

$$\text{Volume of } O_3 \text{ at NTP} = \text{No. of moles} \times 22400 = 6 \times 10^{-4} \times 22400 = 13.44 \text{ mL at NTP}$$

Example 66. *10 mL of a potassium dichromate solution liberates iodine from potassium iodide solution. When the iodine was titrated with hypo solution ($N/20$), the titre value was 15 mL. Find the concentration of dichromate solution in g per litre.*

Solution: The reactions involved may be given as

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$3[I_2 + 2Na_2S_2O_3] \longrightarrow 3[2NaI + Na_2S_4O_6]$$

$$1 \text{ mole } K_2Cr_2O_7 \equiv 6 \text{ moles of } Na_2S_2O_3 \quad \text{... (i)}$$

$$\text{No. of moles of hypo} = \frac{\text{Mass}}{\text{M.w. (158)}} = \frac{E \times N \times V}{1000 \times 158}$$

$$=\frac{158\times 1/20\times 15}{1000\times 158}$$

$$=7.5\times 10^{-4}\text{ mole}$$

$$\text{No. of moles of } K_2Cr_2O_7=\frac{1}{6}[\text{No. of moles of } Na_2S_2O_3]$$

$$=1.25\times 10^{-4}\text{ mole}$$

$$\text{Mass of } K_2Cr_2O_7 \text{ in 10 mL solution}=1.25\times 10^{-4}\times 294$$

$$=0.03675\text{ g}$$

$$\text{Weight of } K_2Cr_2O_7 \text{ in 10 mL solution}=3.675\text{ g/L}$$

Example 67. *1.5 g of sample of impure potassium dichromate was dissolved in water and made up to 500 mL solution. 25 mL of this solution required iodometrically 24 mL of a sodium thiosulphate solution. 26 mL of this sodium thiosulphate solution required 25 mL of N/20 solution of pure potassium dichromate. Find the percentage purity of impure sample of potassium dichromate.*

Solution: Normality of sodium thiosulphate solution may be determined as:

$$N_1V_1(Na_2S_2O_3)=N_2V_2\ (\text{pure } K_2Cr_2O_7)$$

$$N_1\times 26=25\times\frac{1}{20}$$

$$N_1=0.048\,(\text{hypo})$$

The reaction involved may be given as:

$$Cr_2O_7^{2-}+6I^-+4H^+\longrightarrow 2Cr^{3+}+3I_2+7H_2O$$

$$3[I_2+2Na_2S_2O_3\longrightarrow 2NaI+Na_2S_4O_6]$$

$$1\text{ mole } K_2Cr_2O_7\equiv 6\text{ mole } Na_2S_2O_3 \qquad \ldots(i)$$

25 mL of solution of $K_2Cr_2O_7$ is treated by 24 mL of 0.048 N hypo

∴ 500 mL of solution will be titrated by 480 mL of 0.048 N hypo

$$\text{No. of moles of hypo}=\frac{\text{Mass}}{\text{M.w. (158)}}=\frac{E\times N\times V}{1000\times 158}$$

$$=\frac{158\times 0.048\times 480}{1000\times 158}$$

$$=0.02304\text{ mole}$$

$$\text{No. of moles of } K_2Cr_2O_7=\frac{1}{6}[\text{No. of moles of hypo}]$$

$$=\frac{1}{6}[0.02304]=3.84\times 10^{-3}$$

$$\text{Mass of } K_2Cr_2O_7=3.84\times 10^{-3}\times 294$$

$$=1.12896$$

$$\%\text{ purity}=\frac{1.12896}{1.5}\times 100=75.26\%$$

Example 68. *5 g of a sample of brass were dissolved in 1 litre dil. H_2SO_4. 20 mL of this solution were mixed with KI and liberated iodine required 20 mL of 0.0327 N hypo solution for titration. Calculate the amount of copper in the alloy.*

Solution: When brass is extracted with concentrated H_2SO_4, it gives copper sulphate.

$$2[Cu+2H_2SO_4\longrightarrow CuSO_4+SO_2+2H_2O]$$

$$2CuSO_4+4KI\longrightarrow 2K_2SO_4+2CuI_2$$

$$2CuI_2\longrightarrow Cu_2I_2+I_2$$

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

$$2\text{ mole Cu}\equiv 1\text{ mole } I_2\equiv 2\text{ mole hypo}$$

20 mL of solution reacts with 20 mL of 0.0327 N hypo

∴ 1000 mL of solution will react with 1000 mL of 0.0327 N hypo

$$\text{No. of moles of hypo used}=\frac{\text{Mass}}{\text{Molecular mass (158)}}$$

$$=\frac{E\times N\times V}{1000\times 158}$$

where, $E=158$, $N=0.0327$ given, $V=1000$ mL

$$\therefore\ \text{No. of moles of hypo used}=\frac{158\times 0.0327\times 1000}{1000\times 158}$$

$$=0.0327$$

$$\text{No. of moles of Cu}=\text{No. of moles of hypo}$$

$$=0.0327\text{ mole}$$

$$\text{Mass of copper in brass}=0.0327\times 63.5=2.07645$$

$$\%\text{ of copper in brass}=\frac{2.07645}{5}\times 100$$

$$=41.529\%$$

Example 69. *An excess KI solution is mixed in a solution of $K_2Cr_2O_7$ and liberated iodine required 72 mL of 0.05 N $Na_2S_2O_3$ for complete reaction. How many grams of $K_2Cr_2O_7$ were present in the solution of $K_2Cr_2O_7$? The reaction occurs as:*

$$Cr_2O_7^{2-}+6I^-+14H^+\longrightarrow 2Cr^{3+}+3I_2+7H_2O$$

Solution: The reaction involved may be given as:

$$Cr_2O_7^{2-}+6I^-+14H^+\longrightarrow 2Cr^{3+}+3I_2+7H_2O$$

$$3[I_2+2Na_2S_2O_3\longrightarrow 2NaI+Na_2S_4O_6]$$

$$1\text{ mole } K_2Cr_2O_7=6\text{ mole } Na_2S_2O_3 \qquad \ldots(i)$$

$$\text{No. of moles of hypo}=\frac{\text{Mass}}{\text{M.w. (158)}}=\frac{E\times N\times V}{1000\times 158}$$

$$N_{Na_2S_2O_3}=\frac{158\times 0.05\times 72}{1000\times 58}=3.6\times 10^{-3}$$

$$\text{No. of moles of } K_2Cr_2O_7 = \frac{1}{6}[\text{No. of moles of } Na_2S_2O_3]$$

$$= \frac{1}{6}[3.6 \times 10^{-3}] = 6 \times 10^{-4} \text{ mole}$$

Mass of $K_2Cr_2O_7$ in the given solution

$$= \text{No. of moles} \times \text{Molecular weight}$$

$$= 6 \times 10^{-4} \times 294 = 0.1764$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

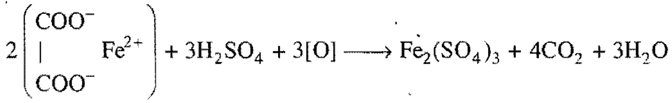
14. How many moles of MnO_4^- ions will react with 1 mole of ferrous oxalate in acid medium?

(a) 1/5 (b) 2/5 (c) 3/5 (d) 5/3

[Ans. (c)]

[Hint:

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



$$2\begin{pmatrix} COO^- & \\ | & Fe^{2+} \\ COO^- & \end{pmatrix} + 3H_2SO_4 + 3[O] \longrightarrow Fe_2(SO_4)_3 + 4CO_2 + 3H_2O$$

$$\therefore \quad 6 \text{ mole } KMnO_4 \equiv 10 \text{ mole } FeC_2O_4$$

$$\therefore 1 \text{ mole } FeC_2O_4 \text{ will react with } \frac{3}{5} \text{ mole of } KMnO_4]$$

15. The molecular mass of $K_2Cr_2O_7$ is 294 amu. It acts as oxidising agent in a redox titration. Its equivalent mass in acid medium will be:

(a) 294 (b) 49 (c) 147 (d) 74

[Ans. (b)]

[Hint: $\overset{+12}{K_2Cr_2O_7} + 4H_2SO_4 \rightarrow K_2SO_4 + \overset{+6}{Cr_2}(SO_4)_3 + 4H_2O + 3[O]$

Change in oxidation number = 6

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{6} = \frac{294}{6} = 49]$$

16. In acid medium, both $KMnO_4$ and $K_2Cr_2O_7$ act as oxidising agents. Which among the following is correct about the oxidising behaviour?

(a) $KMnO_4 > K_2Cr_2O_7$ (b) $KMnO_4 < K_2Cr_2O_7$

(c) $KMnO_4 = K_2Cr_2O_7$ (d) Cannot be predicted

[Ans. (a)]

[Hint:

$$2\overset{+7}{KMnO_4} + 3H_2SO_4 \rightarrow K_2SO_4 + 2\overset{+2}{MnSO_4} + 3H_2O + 5[O]$$

Change in oxidation number = 10

$$\overset{+12}{K_2Cr_2O_7} + 4H_2SO_4 \rightarrow K_2SO_4 + \overset{+6}{Cr_2}(SO_4)_3 + 4H_2O + 3[O]$$

Change in oxidation number = 6]

17. $KMnO_4$ reacts with oxalic acid according to the equation,

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Here, 20 mL of 0.1 M $KMnO_4$ is equivalent to:

(a) 120 mL of 0.25 M $H_2C_2O_4$

(b) 150 mL of 0.1 M $H_2C_2O_4$

(c) 50 mL of 0.1 M $H_2C_2O_4$

(d) 50 mL of 0.2 M $H_2C_2O_4$

[Ans. (c)]

[Hint: $\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}(H_2C_2O_4)$

$$\frac{0.1 \times 20}{2} = \frac{M_2V_2}{5}$$

$$M_2V_2 = 5$$

It is possible in the option (c).]

18. A solution of H_2O_2 is titrated against a solution of $KMnO_4$. The reaction is:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

If it requires 46.9 mL of 0.145 M $KMnO_4$ to oxidise 20 g of H_2O_2, the mass percentage of H_2O_2 in this solution is:

(a) 2.9 (b) 29 (c) 21 (d) 4.9

[Ans. (a)]

[Hint: Number of moles of $KMnO_4 = \frac{MV}{1000} = \frac{0.145 \times 46.9}{1000}$

$$= 6.8 \times 10^{-3}$$

Number of moles of $H_2O_2 = 6.8 \times 10^{-3} \times 2.5 = 0.017$

$$\text{Mass of } H_2O_2 = 0.017 \times 34 = 0.578$$

$$\text{Mass \% of } H_2O_2 = \frac{0.578}{20} \times 100 \approx 2.9]$$

19. In an oxidation-reduction, MnO_4^- ion is converted to Mn^{2+}, what is the number of equivalents of $KMnO_4$ (mol. wt. = 158) present in 250 mL of 0.04 M $KMnO_4$ solution ?

(CPMT 2008)

(a) 0.02 (b) 0.05 (c) 0.04 (d) 0.07

[Ans. (b)]

[Hint : In redox-reaction :

$$8H^+ + MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

Change in oxidation state of $MnO_4^- = (+7) - (+2) = +5$

$$\therefore \quad N_{KMnO_4} = M_{KMnO_4} \times 5$$

$$= 0.04 \times 5 = 0.20$$

$$\text{Number of equivalents} = \frac{NV}{1000} = \frac{0.2 \times 250}{1000} = 0.05\,]$$

20. The strength of 10 volume of H_2O_2 solution is :

(AMU Engg. 2009)

(a) 10 (b) 68 (c) 60.70 (d) 30.36

[Ans. (d)]

[Hint : 10 volume H_2O_2 means, 1 litre of H_2O_2 will give 10 litre oxygen at STP.

$$\underset{68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4\text{ L at STP}}{O_2}$$

$\because$ 22.4 L O_2 is obtained at STP from 68 g H_2O_2

$\therefore$ 10 L O_2 is obtained at STP from $\frac{68}{22.4} \times 10$ g H_2O_2

$$= 30.36\text{ g}$$

Thus, strength of H_2O_2 = 30.36 g/L.]

Questions

1. Calculate the equivalent mass of underlined species:
   (i) $Na_2SO_3 + \underline{Na_2CrO_4} \rightarrow Na_2SO_4 + Cr(OH)_3$
   (ii) $Fe_3O_4 + \underline{KMnO_4} \rightarrow Fe_2O_3 + MnO_2$
   (iii) $\underline{2Na_2S_2O_3} + I_2 \rightarrow Na_2S_4O_6 + 2NaI$
   (iv) $\underline{As_2S_3} + 10NO_3^- + 4H^+ \rightarrow 10NO_2 + 2AsO_4^{3-} + 3S + 2H_2O$
   (v) $\underline{H_3PO_3} \rightarrow H_3PO_4 + PH_3$
   (vi) $\underline{5SO_2} + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$
2. 12 mL of 0.25 *N* sulphuric acid is neutralised with 15 mL of sodium hydroxide solution on titration. Calculate the normality of sodium hydroxide solution.
3. What will be the volume of *N*/10 solution of oxalic acid obtained by dissolving 63 g of oxalic acid?
4. If 1.26 g of oxalic acid is dissolved in 250 mL of solution, find its normality. The equivalent mass of oxalic acid is 63.
5. (a) 50 mL of 0.2 *N* $KMnO_4$ is required for complete oxidation of 0.45 g of anhydrous oxalic acid. Calculate the normality of oxalic acid solution.
   (b) In the titration of Fe^{2+} ions with $KMnO_4$ in acid medium, why is dilute H_2SO_4 used and not dilute HCl? [CBSE (Mains) 2005]

   [**Hint:** The reaction involved in the titration is:
   $$10FeSO_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$
   If HCl is taken in place of H_2SO_4, then HCl will be oxidised to Cl_2.]
6. 30 mL of sodium carbonate solution is mixed with 20 mL of 0.8 *N* sulphuric acid. The resultant solution needed 20 mL of 0.7 *N* hydrochloric acid solution for complete neutralisation. Determine the strength of the sodium carbonate in gram per litre. (Take sodium carbonate to be anhydrous.)
7. 0.25 g of an oxalate salt was dissolved in 100 mL of water. 10 mL of this solution required 8 mL of *N*/20 $KMnO_4$ for its oxidation. Calculate the percentage of oxalate in the salt.
8. 1.13 g of an ammonium sulphate were treated with 50 mL of normal NaOH solution and boiled till no more ammonia was given off. The excess of the alkali solution left over was titrated with normal H_2SO_4. The volume required was 30 mL. Find out the percentage of NH_3 in the salt.
9. The normality of the mixture of HCl and H_2SO_4 solution is *N*/5. 0.287 g of AgCl is obtained when 20 mL of this solution is treated with excess of $AgNO_3$. Calculate the percentage of both the acids in the mixture.
10. 1.17 g of an impure sample of oxalic acid was dissolved and made up to 200 mL with water. 10 mL of this solution in acid medium required 8.5 mL of a solution of potassium permanganate containing 3.16 g per litre of oxidation. Calculate the percentage purity of oxalic acid.
11. What amount of silver chloride will be obtained when 20 mL *N*/20 HCl is made to react with excess of $AgNO_3$?
12. 1.0 g carbonate of a metal was dissolved in 50 mL *N*/2 HCl solution. The resulting liquid required 25 mL of *N*/5 NaOH solution to neutralise it completely. Calculate the equivalent mass of the metal carbonate.
13. 0.35 g of a metal was dissolved in 50 mL *N*-acid. The whole solution then required 20.85 mL of normal alkaline solution to neutralise the excess of the acid. Calculate the equivalent mass of the metal.
14. 2.650 g of anhydrous sodium carbonate are dissolved in water and the solution made up to 500 mL. On titration 50 mL of this solution neutralises 50 mL of a solution of sulphuric acid. How much water should be added to 450 mL of this acid as to make it exactly *N*/12 ?
15. Two acids *A* and *B* are titrated separately each time with 25 mL of *N* Na_2CO_3 solution and require 10 mL and 40 mL respectively for complete neutralisation. What volume of *A* and *B* would you mix to produce one litre of normal acid solution?
16. 1.64 g of a mixture of calcium carbonate and magnesium carbonate were dissolved in 50 mL of 0.8 *N* hydrochloric acid. The excess of the acid required 16 mL *N*/4 sodium hydroxide solution for neutralisation. Find out the percentage composition of the mixture of two carbonates.
17. 30 mL of *N*/10 HCl are required to neutralise 50 mL of a sodium carbonate solution. How many mL of water must be added to 30 mL of this solution so that the solution obtained may have a concentration equal to *N*/50?
18. 2.65 g of diacidic base was dissolved in water and made up to 500 mL. 20 mL of this solution completely neutralised 12 mL of *N*/6 HCl. Find out the equivalent mass and molecular mass of the base.
19. In a sample of sodium carbonate, some sodium sulphate is mixed. 2.50 g of this sample is dissolved and the volume made up to 500 mL. 25 mL of this solution neutralises 20 mL of *N*/10 sulphuric acid. Calculate the percentage of sodium carbonate in the sample.
20. Some amount of NH_4Cl was boiled with 50 mL of 0.75 *N* NaOH solution till the reaction was complete. After the completion of the reaction, 10 mL of 0.75 *N* H_2SO_4 were required for the neutralisation of the remaining NaOH. Calculate the amount of NH_4Cl taken.
21. 25 mL of a mixed solution of sodium carbonate and sodium bicarbonate required 10 mL of *N*/20 HCl when titrated in the presence of phenolphthalein but 25 mL of the same when titrated separately in presence of methyl orange required 25 mL of *N*/10 HCl. Calculate the amount of anhydrous sodium carbonate and bicarbonate in grams per litre of the solution.
22. 4 g of a mixture of NaCl and Na_2CO_3 were dissolved in water and volume made up to 250 mL. 15 mL of this solution required 50 mL of *N*/10 HCl for complete neutralisation. Calculate the percentage composition of the original mixture.
23. 40 mL of a mixture of Na_2CO_3 and NaOH when titrated against *N*/10 HCl, the end point with phenolphthalein was reached at 25 mL of HCl and at this stage methyl orange was added, the quantity of acid further required for second end point was 5 mL. Calculate the amount of Na_2CO_3 and NaOH in g/L of the solution.

24. Find out the percentage of oxalate in a given sample of an oxalate salt of which when 0.3 g were dissolved in 100 mL of water required 90 mL of $N/20$ $KMnO_4$ solution for complete oxidation.

25. A 1.0 g sample of H_2O_2 solution containing 'x' per cent by weight requires x mL of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of the $KMnO_4$ solution.

26. 25 g of a sample of ferrous sulphate was dissolved in water containing dilute H_2SO_4 and the volume made up to one litre. 25 mL of this solution required 20 mL of $N/10$ $KMnO_4$ solution for complete oxidation. Calculate the percentage of $FeSO_4 \cdot 7H_2O$ in the sample.

27. A sample of KCl is contaminated with NaCl. 4.176 g of the sample is dissolved in distilled water and the solution is made to 500 mL. 25 mL of the above solution required 27.50 mL of a solution of silver nitrate (normality factor 0.115) to react completely with it. Calculate the percentage contamination of the sample.

28. The saponification number of fat or oil is defined as the number of mg of KOH required to saponify 1 g oil or fat. A sample of peanut oil weighing 1.5763 g is added to 25 mL of 0.421 M KOH. After saponification is complete, 8.46 mL of 0.2732 M H_2SO_4 is needed to neutralise excess of KOH. What is the saponification number of peanut oil?

29. 500 mL of 2 M HCl, 100 mL of 2 M H_2SO_4 and one gram equivalent of monoacidic alkali are mixed together. 30 mL of this solution required 20 mL of $Na_2CO_3 \cdot xH_2O$ solution obtained by dissolving 143 g $Na_2CO_3 \cdot xH_2O$ in one litre solution. Calculate the water of crystallisation of $Na_2CO_3 \cdot xH_2O$.

30. 1 g of the complex $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ was passed through a cation exchanger to produce HCl. The acid liberated was diluted to 1 litre. What is the normality of this acid solution?

31. 5.0 g of bleaching powder was suspended in water and volume made up to half a litre. 20 mL of this suspension when acidified with acetic acid and treated with excess of KI solution liberated iodine which required 20 mL of a decinormal hypo solution for titration. Calculate percentage of available chlorine in bleaching powder. (IIT 1990)

32. To a solution of excess of KI in dilute H_2SO_4, 25 mL of an unknown solution of $KMnO_4$ were added. The liberated iodine was exactly reduced by 42.5 mL of $N/10$ $Na_2S_2O_3$ solution. Calculate the concentration of $KMnO_4$ solution.

33. In 20 mL of a solution of HCl, 3 g of $CaCO_3$ were dissolved, 0.5 g of $CaCO_3$ being left undissolved. Find out the strength of this solution in terms of (i) normality and (ii) g/L. Find the volume of this acid which would be required to make 1 litre of normal solution of this acid.

34. 1.0 litre of a solution contains 5.3 g of Na_2CO_3 and 8 g of NaOH. 20 mL of this solution are taken and titrated against $N/10$ HCl using separately (a) methyl orange as an indicator and (b) phenolphthalein as an indicator. What will be the titre values in these two cases?

35. To 20 mL of a copper solution after necessary treatment were added excess of KI and the liberated iodine required 11.2 mL decinormal solution of hypo. Express the strength of the original solution in grams of copper per litre of the solution.

36. 0.28 g of a commercial sample of $K_2Cr_2O_7$ was dissolved in water. Excess of KI was added to it along with dilute H_2SO_4. Iodine liberated was then titrated against sodium thiosulphate solution containing 24.82 g of $Na_2S_2O_3 \cdot 5H_2O$ per litre. The thiosulphate solution required was 50 mL. Find the percentage purity of the sample of $K_2Cr_2O_7$.

37. A mixture containing KCl and NaCl was dissolved and total halide was determined by titration with silver nitrate. A sample weighing 0.3250 g required 51 mL of 0.1 N solution. Calculate the percentage of each salt in the sample.

38. 1.355 g of pyrolusite sample are added to 50 mL of 1 N oxalic acid solution containing sulphuric acid. After the reaction is completed, the contents are transferred to a measuring flask and the volume made up to 200 mL. 20 mL of this solution is titrated against $KMnO_4$ solution whose strength is 2 g/L and 31.6 mL of $KMnO_4$ solution are required. Calculate the percentage purity in the given sample of pyrolusite.

39. 0.5 g of bleaching powder was suspended in water an excess of KI added. On acidifying with dilute H_2SO_4 iodine was liberated which required 50 mL of $N/10$ hyposolution. Calculate the percentage of available chlorine in bleaching powder.

40. Calculate the number of oxalic acid molecules in 100 mL of 0.02 N oxalic acid solution. (IIT 1991)

[**Hint :** Molarity $= \dfrac{0.02}{2} = 0.01\,M$

No. of molecules in one molar solution $= 6.02 \times 10^{23}$

No. of molecules in 100 mL of 0.01 M oxalic acid solution

$$= \frac{0.01 \times 6.02 \times 10^{23}}{1000} \times 100 = 6.02 \times 10^{20}\,]$$

41. 1.26 g of a dibasic acid were dissolved in water and made up to 200 mL. 20 mL of this solution were completely neutralised by 10 mL of $N/5$ caustic soda solution. Calculate the equivalent mass and molecular mass of the acid.

42. 3.0 g of a sample of impure ammonium chloride were boiled with excess of caustic soda solution. Ammonia gas so evolved was passed into 120 mL of $N/2$ H_2SO_4. 28 mL of $N/2$ NaOH were required to neutralise residual acid. Calculate the percentage of purity of the given sample of ammonium chloride.

[**Hint :** $(120 - 28)$ mL $N/2$ $H_2SO_4 \equiv 92$ mL $N/2$ NH_4Cl]

43. 2.20 g of an ammonium salt were boiled with 75 mL of N NaOH till the emission of ammonia gas ceased. The excess of unused NaOH solution required 70 mL of $N/2$ sulphuric acid for neutralisation. Calculate the percentage of ammonia in the salt.

44. 3.45 g of a metallic carbonate were mixed with 240 mL of $N/4$ HCl. The excess acid was neutralised by 50 mL of $N/5$ KOH solution. Calculate the equivalent mass of the metal.

Hint : Equivalent mass of metal carbonate

$$= \frac{3.45 \times 4 \times 1000}{200} = 69$$

Equivalent mass of metal = 69 − Eq. mass of carbonate

$$= (69 - 30) = 39]$$

45. (a) 2 g of a metal carbonate were dissolved in 50 mL of N HCl. 100 mL of 0.1 N NaOH were required to neutralise the resultant solution. Calculate the equivalent mass of the metal carbonate.

(b) How much water should be added to 75 mL of 3 N HCl to make it a normal solution?

46. Upon mixing 45.0 mL of 0.25 *M* lead nitrate solution with 25 mL of 0.1 *M* chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. **(IIT 1993)**

[**Hint :** The reaction is:

$$\underset{3\text{ mole}}{3Pb(NO_3)_2} + \underset{1\text{ mole}}{Cr_2(SO_4)_3} \longrightarrow \underset{3\text{ mole}}{3PbSO_4} + \underset{2\text{ mole}}{2Cr(NO_3)_3}$$

$$\text{No. of moles of } Pb(NO_3)_2 = 45 \times 10^{-3} \times 0.25$$
$$= 11.25 \times 10^{-3} \text{ mole}$$

$$\text{No. of moles of } Cr_2(SO_4)_3 = 25 \times 10^{-3} \times 0.1 = 2.5 \times 10^{-3} \text{ mole}$$

Thus, $Cr_2(SO_4)_3$ has limiting concentration. It shall be consumed fully and the number of moles of lead sulphate produced will be

$$= 3 \times 2.5 \times 10^{-3} = 7.5 \times 10^{-3} \text{ mole}$$

$$\text{No. of moles of lead nitrate left} = 11.25 \times 10^{-3} - 7.5 \times 10^{-3}$$
$$= 3.75 \times 10^{-3} \text{ mole}$$

$$\text{Total volume} = (45.0 + 25.0) = 70 \text{ mL or } 70 \times 10^{-3} \text{ litre}$$

$$\text{Molarity} = \frac{3.75 \times 10^{-3}}{70 \times 10^{-3}} = 0.0536\ M$$

$$\text{No. of moles of } Cr(NO_3)_3 \text{ formed} = 2 \times 2.5 \times 10^{-3} = 5 \times 10^{-3} \text{ mole}$$

$$\text{Molarity} = \frac{5 \times 10^{-3}}{70 \times 10^{-3}} = 0.0714\ M$$

$Pb(NO_3)_2$ and $Cr(NO_3)_3$ will be present in solution in ionic form.

Thus, $[Pb^{2+}] = 0.0536\ M$

$$[Cr^{3+}] = 0.0714\ M$$
$$[NO_3^-] = (2 \times 0.0536) + (3 \times 0.0714)$$
$$= 0.3214\ M]$$

47. A sample of hydrazine sulphate ($N_2H_6SO_4$) were dissolved in 250 mL of water. 10 mL of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ions formed were estimated and it required 10 mL of 0.04 *M* potassium permanganate solution. Estimate the amount of hydrazine sulphate dissolved in 250 mL of the solution. Reactions:

$$4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$$
$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(MLNR 1993)

[**Hint :** See example 50]

48. In an ore the only oxidisable material is Sn^{2+}. This ore is titrated with a dichromate solution containing 2.5 g $K_2Cr_2O_7$ in 0.50 litre. A 0.40 g of sample of the ore required 10.0 cm³ of the titrant to reach equivalent point. Calculate the percentage of tin in ore. (K = 39.1, Cr = 52, Sn = 118.7) **(IIT 1993)**

[**Hint :** Mol. mass of $K_2Cr_2O_7 = 2 \times 39.1 + 2 \times 52 + 7 \times 16$

$$= 78.2 + 104.0 + 112.0$$
$$= 294.2$$

$$\text{Eq. mass of } K_2Cr_2O_7 = \frac{294.2}{6} = 49.03$$

$$\text{Normality of } K_2Cr_2O_7 \text{ solution} = \frac{2.5}{49.03} \times \frac{1000}{500} = \frac{5}{49.03}\ N$$

$$10 \text{ mL } \frac{5}{49.03}\ N\ K_2Cr_2O_7 \equiv 10 \text{ mL } \frac{5}{49.03}\ N \text{ stannous ion}$$

$$\text{Eq. mass of } Sn^{2+} = \frac{118.7}{2} = 59.35$$

$$\text{Amount of Sn in the sample} = \frac{5}{49.03} \times \frac{59.35}{1000} \times 10$$
$$= 0.0605 \text{ g}$$

$$\text{Percentage of Sn in the ore} = \frac{0.0605}{0.40} \times 100 = 51]$$

49. 2.26 g of impure ammonium chloride were boiled with 100 mL of *N* NaOH solution till no more ammonia was given off. The excess of NaOH solution left over required 30 mL 2 *N* H_2SO_4 for neutralisation. Calculate the percentage purity of the salt.

(H = 1; N = 14; O = 16; Na = 23; S = 32; Cl = 35.5)

50. Metallic tin in the presence of HCl is oxidised by $K_2Cr_2O_7$ solution to stannic chloride. What volume of decinormal dichromate solution would be reduced by 1 g of Sn? **(MLNR 1994)**

[**Hint :**

$$\underset{3 \times 118.7\text{ g}}{3Sn} + \underset{2 \times 294\text{ g}}{2K_2Cr_2O_7} + 28HCl \longrightarrow 3SnCl_4 + 4KCl + 4CrCl_3 + 14H_2O$$

$$K_2Cr_2O_7 \text{ required for 1 g of Sn} = \frac{2 \times 294}{3 \times 118.7} = 1.65 \text{ g}]$$

51. A 0.5 g sample containing MnO_2 is treated with HCl liberating Cl_2. The Cl_2 is passed into a solution of KI and 30.0 cm³ of 0.1 *M* $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in the sample. **(IIT 1994)**

[**Hint:** 30.0 mL 0.1 $M\ Na_2S_2O_3 \equiv$ 30.0 mL 0.1 $N\ Na_2S_2O_3$

$$\equiv 30.0 \text{ mL } 0.1\ N\ I_2$$
$$\equiv 30.0 \text{ mL } 0.1\ N\ Cl_2$$
$$\equiv 30.0 \text{ mL } 0.1\ N\ MnO_2$$

$$\text{Amount of } MnO_2 \text{ present} = \frac{N \times E \times V}{1000}$$
$$= \frac{1}{10} \times \frac{87}{2} \times \frac{30}{1000}$$

$$\%\ MnO_2 = \frac{87 \times 30 \times 100}{10 \times 2 \times 1000 \times 0.5} = 26.1]$$

52. 3.2 g of a mixture of calcium carbonate and sodium chloride was dissolved in 100 mL of 1.02 *N* HCl. After the reaction the solution was filtered and after separating the precipitate the volume was raised to 200 mL. 20 mL of this solution required 25 mL *N*/5 caustic soda solution for neutralisation. Find out the percentage of calcium carbonate in the mixture.

53. 4 g of a mixture of Na_2SO_4 and anhydrous Na_2CO_3 were dissolved in pure water and volume made up to 250 mL. 20 mL of this solution required 25 mL of *N*/5 H_2SO_4 for complete neutralisation. Calculate the percentage composition of the mixture.

54. A 1.2 g mixture of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 cm³ of a solution. 20 cm³ of this solution required 40 cm³ of 0.1 *N* HCl for neutralisation. Calculate the mass of Na_2CO_3 and K_2CO_3 in the mixture. **(IIT 1997)**

55. One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of $M/10$ sodium thiosulphate solution for titration. What is the weight per cent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?

[**Hint:** Let the total moles of O_2 and O_3 in the mixture be n.

Applying $PV = nRT$

$$1 \times 1 = n \times 0.0821 \times 273$$

$$n = 0.044 \text{ mole}$$

$$\text{Moles of } O_3 = \text{moles of } I_2 = 1/2 \text{ moles of } Na_2S_2O_3$$

$$= \frac{1}{2} \times \frac{1}{10} \times \frac{40}{1000} = 0.002 \text{ moles}$$

Moles of O_2 in the mixture $= 0.044 - 0.002 = 0.042$ moles

Mass of $O_2 = 0.042 \times 32 = 1.344$ g

Mass of $O_3 = 0.002 \times 48 = 0.096$ g

$$\% \; O_3 = \frac{0.096}{1.44} \times 100 = 6.67$$

No. of photons required to decompose 0.002 moles of ozone

$$= 0.002 \times 6.02 \times 10^{23} = 1.204 \times 10^{21}]$$

56. 20 mL of a solution containing 0.2 g of impure sample of H_2O_2 reacts with 0.316 g of $KMnO_4$ (acidic). Calculate:
(a) Purity of H_2O_2
(b) Volume of dry O_2 evolved at 27° C and 750 mm pressure.

57. Five gram of copper alloy was dissolved in one litre of dilute H_2SO_4. 20 mL of this solution was titrated iodometrically and it required 20 mL of a hypo solution. 20 mL of $K_2Cr_2O_7$ which contained 2.4 g per litre, in presence of H_2SO_4 and excess of KI, required 30 mL of the same hypo solution. Calculate the % purity of copper in the alloy.

58. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate?

[**Hint:** $N_1V_1 = N_2V_2$

N_1 = Normality of $H_2SO_4 = 0.5 \times 2 = 1\,N$

V_1 = Vol. of H_2SO_4

N_2 = Normality of copper (II) carbonate $= \dfrac{0.5 \times 2}{123.5} N$

V_2 = Volume of copper (II) carbonate = 1000 mL

Thus, $$1.0 \times V_1 = \frac{0.5 \times 2}{123.5} \times 1000$$

or $$V_1 = 8.09 \text{ mL}]$$

59. An aqueous solution containing 0.10 g KIO_3 (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated iodine consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

[**Hint:** $2KIO_3 + 10KI + 12HCl \longrightarrow 12KCl + 6I_2 + 6H_2O$

$$[2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6] \times 6$$

$$\underset{\text{2 moles}}{2KIO_3} + 10KI + \underset{\text{12 moles}}{12Na_2S_2O_3} + 12HCl \longrightarrow 12KCl + 12NaI + 6Na_2S_4O_6 + 6H_2O$$

$$\text{No. of moles of } KIO_3 = \frac{0.10}{214}$$

No. of moles of $Na_2S_2O_3$ required for $\dfrac{0.10}{214}$ moles of KIO_3

$$= \frac{12}{2} \times \frac{0.10}{214} = \frac{0.60}{214}$$

$$\text{Molarity of } Na_2S_2O_3 = \frac{0.6}{214} \times \frac{1000}{45} = 0.0623\,M]$$

60. Gastric juice contains 3 g of HCl per litre. If a person produces 2.5 litre of gastric juice per day, how many antacid tablets each containing 400 mL of $Al(OH)_3$ are needed to neutralise all the HCl produced in one day?

61. Zinc can be determined volumetrically by the precipitation reactions,

$$3Zn^{2+} + 2K_4[Fe(CN)_6] \longrightarrow K_2Zn_3[Fe(CN)_6] + 6K^+$$

A sample of Zn ore weighing 1.5432 g was prepared for reaction and required 34.68 mL of 0.1043 M $K_4[Fe(CN)_6]$ for titration. What is percentage of zinc in the ore?

62. A mixture of KOH and Na_2CO_3 solution required 15 mL of $N/20$ HCl using phenolphthalein as indicator. The same amount of alkali mixture when titrated using methyl orange as indicator required 25 mL of same acid. Calculate amount of KOH and Na_2CO_3 present in solution.

63. 1000 mL O_2 at NTP was passed through Siemen's ozonizer so that the volume is reduced to 888 mL at same condition. Ozonized oxygen is passed through KI solution. Liberated I_2 was titrated with 0.05 N hypo. Calculate volume of hypo used.

64. 30 mL of $K_2Cr_2O_7$ liberated iodine from KI solution when the iodine was titrated with hypo solution ($N/20$), the titre value was 45 mL. Find the concentration of $K_2Cr_2O_7$ in g per litre.

65. Excess of KI and dil. H_2SO_4 were mixed in 50 mL H_2O_2. The liberated I_2 required 20 mL of 0.1 N $Na_2S_2O_3$. Find out the strength of H_2O_2 in g per litre.

66. 25 mL H_2O_2 were added to excess of acidified solution of KI. The iodine so liberated required 20 mL of 0.1 N sodium thiosulphate for titration. Calculate the strength in terms of normality, percentage and volume.

67. Cl_2 gas can be produced in the lab by the reaction,

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

If a 6.13 g sample that is 96% $K_2Cr_2O_7$ is allowed to react with 320 mL of HCl solution having density 1.15 g/mL and containing 30% by mass of HCl, what mass of Cl_2 is generated?

68. What is the weight in gram of available O_2 per litre from a solution of H_2O_2, 10 mL of which when titrated with $N/20$ $KMnO_4$ solution required 25 mL for the reaction?

$$2KMnO_4 + 5H_2O_2 + 4H_2SO_4 \longrightarrow 5O_2 + 8H_2O + 2KHSO_4 + 2MnSO_4$$

69. A quantity of $KMnO_4$ was boiled with HCl and the gas evolved was led into a solution of KI. When the reaction was complete, the I_2 liberated was titrated with a solution of hypo containing 124 g of $Na_2S_2O_3 \cdot 5H_2O$ per litre. It was found that exactly 60 mL were required to decolourise the solution of I_2. What weight of $KMnO_4$ was used?

70. 0.5 g of a sample of bleaching powder was suspended in water and excess KI is added. On acidifying with dil. H_2SO_4, I_2 was liberated which required 50 mL of $N/10$ hypo ($Na_2S_2O_3 \cdot 5H_2O$). Calculate the percentage of available Cl_2 in bleaching powder.

71. 1.2 g of a sample of $CaOCl_2$ were suspended in water made up to 100 mL. 25 mL of this solution was treated with KI and the I_2 liberated corresponded to 10 mL of $N/25$ hypo. Calculate the percentage of Cl_2 available in $CaOCl_2$.

72. 1.6 g of pyrolusite was treated with 60 mL of normal oxalic acid and some H_2SO_4. The oxalic acid left undecomposed was made up to 250 mL, 25 mL of this solution required 32 mL of 0.1 N potassium permanganate ($KMnO_4$). Calculate the percentage of pure MnO_2 in pyrolusite.

73. A sample of pyrolusite weighing 0.5 g is distilled with conc. HCl. The evolved Cl_2 when passed through a solution of KI liberates sufficient I_2 to react with 125 mL of $N/12.5$ hypo ($Na_2S_2O_3 \cdot 5H_2O$). Calculate the percentage of MnO_2 in pyrolusite.

74. The iodide content of a solution was determined by titration with sodium thiosulphate crystalline containing 11.2% impurity. Calculate the normality of iodide ion solution in 250 mL of the iodide solution required 20 mL hypo (42 g hypo is dissolved in 1 litre).

75. The formula weight of an acid is 82. In a titration, 100 cm^3 of a solution of this acid containing 39.0 g of the acid per litre were completely neutralised by 95.0 cm^3 of aqueous NaOH containing 40.0 g of NaOH per litre. What is the basicity of the acid? (IIT 2000)

[**Hint :** Normality of NaOH = 1

$$\text{Normality of acid} = \frac{1 \times 95}{100} = 0.95$$

Let the eq. mass of the acid be E.

$$\therefore \quad \frac{39}{E} = 0.95 \text{ or } E = 41 \ ; \qquad \text{Basicity} = \frac{82}{41} = 2]$$

76. 20 mL of a solution containing ferrous sulphate and ferric sulphate acidified with H_2SO_4 is reduced by metallic zinc. The solution required 27.4 mL of 0.1 N solution of $K_2Cr_2O_7$ for oxidation. However before reduction with zinc, 20 mL of same solution required 17.96 mL of same $K_2Cr_2O_7$. Calculate the mass of $FeSO_4$ and $Fe_2(SO_4)_3$ per litre of the solution.

[**Hint :** After reduction $Fe_2(SO_4)_3$ is also reduced to $FeSO_4$ and titration gives total concentration of $FeSO_4$ and $Fe_2(SO_4)_3$. Titration before reduction gives only $FeSO_4$.

Milli equiv. of $K_2Cr_2O_7$ after reduction = 27.4 × 0.1 = 2.740
Milli equiv. of $K_2Cr_2O_7$ before reduction = 17.96 × 0.1 = 1.796
Milli equiv. of $Fe_2(SO_4)_3$ in 20 mL = 0.944
Milli equiv. of $FeSO_4$ in 20 mL = 1.796

$$\therefore \quad FeSO_4\ (gL^{-1}) = \frac{1.796}{1000} \times \text{Eq. mass} \times 40$$
$$= \frac{1.796}{1000} \times 152 \times 40 = 10.92$$
$$Fe_2(SO_4)_3\ (gL^{-1}) = \frac{0.944}{1000} \times \text{Eq. mass} \times 40$$
$$= \frac{0.944}{1000} \times 200 \times 40 = 7.55]$$

77. 3.0 g of pyrolusite ore were treated with 20 g of pure ferrous ammonium sulphate (Mol. mass = 392 g mol^{-1}) and dilute H_2SO_4. After the reaction, the solution was diluted to 500 mL. 50 mL of diluted solution required 10 mL of 0.1 N $K_2Cr_2O_7$ solution. Calculate the % of pure MnO_2 in pyrolusite.

[**Hint:** MnO_2 present in pyrolusite oxidises ferrous ammonium sulphate into ferric ammonium sulphate, *i.e.*, $Fe^{2+} \longrightarrow Fe^{3+}$. Unreacted ferrous ammonium sulphate is estimated by potassium dichromate solution.

$$MnO_2 + 2Fe^{2+} + 4H^+ \longrightarrow Mn^{2+} + 2H_2O + 2Fe^{3+}$$
$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

50 mL diluted ferrous ammonium sulphate solution

$$= 10 \text{ mL of } 0.1\ N\ K_2Cr_2O_7$$

500 mL diluted ferrous ammonium sulphate solution

$$= 10 \times 10 \text{ mL of } 0.1\ N\ K_2Cr_2O_7$$
$$= 100 \text{ mL of } 0.1\ N \text{ FeAS}$$
$$= \frac{0.1 \times 392}{1000} \times 100 = 3.92 \text{ g}$$

$$\text{Used FeAS} = (20 - 3.92) = 16.08 \text{ g}$$

$$MnO_2 \text{ present in pyrolusite} = \frac{87}{392 \times 2} \times 16.08 = 1.784 \text{ g}$$

$$\text{Percentage of pure } MnO_2 = \frac{1.784}{3.0} \times 100 = 59.4\%]$$

Answers

1. (i) 54; (ii) 52.66; (iii) 158; (iv) M.w./10; (v) 41; (vi) 32
2. 0.2 *N* **3.** 10 L **4.** 0.08 *N*
5. (a) 0.2 *N* **6.** 45 g/L **7.** 70.4%
8. 30%
9. HCl = 42.69, H_2SO_4 = 57.31 **10.** 91.54%
11. 0.1435 g **12.** 50.0 **13.** 12
14. Vol. of water = 225 mL
15. Vol. of *A* = 200 mL, Vol. of *B* = 800 mL
16. $CaCO_3$ = 48.78%, $MgCO_3$ = 51.22%
17. 60 mL **18.** 53, 106 **19.** Na_2CO_3 = 84.8%
20. 1.605 g **21.** Na_2CO_3 = 2.12 g/L, $NaHCO_3$ = 0.84 g/L
22. NaCl = 33.75%, Na_2CO_3 = 66.25%
23. NaOH = 2.0 g/L, Na_2CO_3 = 1.325 g/L
24. 66% **25.** 0.6 *N* **26.** 88.96%
27. Contamination percentage 46.95%
28. 209.8 **29.** $10H_2O$ **30.** 0.0075 *N*
31. 35.5% **32.** 5.372 g/L **33.** 91.25 g/L, 2.5 *N*, 400 mL
34. With phenolphthalein 50 mL, with methyl orange 60 mL
35. 3.528 g/L **36.** 87.5%
37. NaCl 61.81%; KCl 38.19% **38.** 96.31%
39. 35.5% **41.** 63, 126 **42.** 82%
43. 30.90 **45.** (a) 50, (b) 150 mL
47. 1.625 g **49.** 94.7% **50.** 337 mL
52. 81.25%
53. Na_2CO_3 = 82.8%; Na_2SO_4 = 17.2%
54. Na_2CO_3 = 0.5962; K_2CO_3 = 0.6038
56. % H_2O_2 = 85; Vol. O_2 = 124.79 mL
57. 41.52% **60.** 14 **61.** 22.85
62. Na_2CO_3 = 0.053 g; KOH = 0.014 g
63. 400 mL **64.** 3.675 g **65.** 0.68 g
66. $N = 0.08$, $V = 0.448$
67. 4.263 **68.** 2 g **69.** 0.9486 g
70. 35.5% **71.** 4.7% **72.** 76.125%
73. 87% **74.** 0.024 **77.** 59.4%

OBJECTIVE QUESTIONS

Set–1 : Questions with single correct answer

1. A normal solution:
(a) contains one gram equivalent mass of the substance in one litre solution
(b) contains one gram molecular mass of the substance in one litre solution
(c) contains one gram equivalent mass of the substance in 100 mL of the solution
(d) is that whose concentration is known

2. Which one of the following is a standard solution?
(a) It contains one gram equivalent mass of the substance in one litre solution
(b) Its strength is accurately known
(c) Its strength is to be determined
(d) A solution which has been prepared from pure substance

3. The molecular mass of H_3PO_3 is 82. Its equivalent mass, if it is completely neutralised, is:
(a) 82 (b) 27.3 (c) 41 (d) 246

4. The molecular mass of Mohr's salt, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, is 392. Its equivalent mass is:
(a) 196 (b) 39.2 (c) 98.0 (d) 392

5. According to the following equation,
$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$
the equivalent mass of $K_2Cr_2O_7$ is:
(a) mol. mass/3 (b) mol. mass/6
(c) mol. mass (d) mol. mass/12

6. Amount of oxalic acid required to prepare 250 mL of $N/10$ solution (Mol. mass of oxalic acid = 126) is:
(a) 1.5759 g (b) 3.15 g (c) 15.75 g (d) 63.0 g

7. Normality of 2% H_2SO_4 solution by volume is nearly:
(a) 2 (b) 4 (c) 0.2 (d) 0.4

8. The molecular mass of $KMnO_4$ is M. Its equivalent mass in acidic medium will be:
(a) M (b) $M/2$ (c) $M/5$ (d) $M/4$

9. When $KMnO_4$ is reduced with oxalic acid in acidic medium, the oxidation number of Mn changes from:
(a) 7 to 4 (b) 6 to 4 (c) 7 to 2 (d) 4 to 2

10. For the half cell reaction,

$$2BrO_3^- + 12H^+ + 10e \longrightarrow Br_2 + 6H_2O$$

the equivalent mass of sodium bromate is:
(a) equal to its mol. mass (b) 1/3 of its mol. mass
(c) 1/6 of its mol. mass (d) 1/5 of its mol. mass

11. In the reaction,

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

equivalent mass of iodine is:
(a) equal to its molecular mass
(b) 1/2 the molecular mass
(c) 1/4 the molecular mass
(d) twice the molecular mass

12. A molal solution is one that contains one mole of the solute in:
(a) 1000 g of the solvent (b) one litre of the solvent
(c) one litre of the solution (d) 22.4 litre of the solvent

13. In alkaline conditions, $KMnO_4$ reacts as follows,

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

Therefore, its equivalent mass will be:
(a) 31.6 (b) 52.7 (c) 72.0 (d) 158.0

14. 0.1 N solution of Na_2CO_3 is being titrated with 0.1 N HCl, the best indicator to be used is:
(a) potassium ferricyanide (b) phenolphthalein
(c) methyl orange (d) litmus

15. For the preparation of a litre of $N/10$ solution of H_2SO_4, we need:
(a) 9.8 g (b) 4.9 g (c) 10 g (d) 98 g

16. Molecular mass of a tribasic acid is M. Its equivalent mass will be:
(a) $M/3$ (b) $3M$ (c) $M/2$ (d) $2M$

17. A solution containing Fe^{2+} ions is titrated with $KMnO_4$ solution. Indicator used will be:
(a) phenolphthalein (b) methyl orange
(c) litmus (d) none of these

18. If 200 mL of $N/10$ HCl were added to 1 g calcium carbonate, what would remain after the reaction?
(a) $CaCO_3$ (b) HCl
(c) Neither of the two (d) Part of both

19. How many mL of 1 M H_2SO_4 acid solution is required to neutralise 10 mL of 1 M NaOH?
(a) 5 mL (b) 2.5 mL
(c) 10 mL (d) 20 mL

20. 200 mL of 3 N HCl were mixed with 200 mL of 6 N H_2SO_4 solution. The final normality of H_2SO_4 in the resultant solution will be:
(a) 9 N (b) 3 N (c) 6 N (d) 2 N

21. The volume of water to be added to 400 mL of $N/8$ HCl to make it exactly $N/12$, is:
(a) 400 mL (b) 300 mL
(c) 200 mL (d) 100 mL

22. 100 mL of 0.3 N HCl were mixed with 200 mL of 0.6 N H_2SO_4 solution. The final normality of acid was:
(a) 0.4 N (b) 0.5 N (c) 0.6 N (d) 0.9 N

23. The M mass of NaOH is 40.50 mL of a solution containing 2 g of NaOH in 500 mL will require for complete neutralisation:
(a) 10 mL decinormal HCl (b) 20 mL decinormal HCl
(c) 50 mL decinormal HCl (d) 25 mL decinormal HCl

24. 50 g of a sample of NaOH required for complete neutralisation, 1 litre N HCl. What is the percentage purity of NaOH?
(a) 80 (b) 70 (c) 60 (d) 50

25. Weight of iodine required to oxidise 500 mL N $Na_2S_2O_3$ solution, is:
(a) 6.35 g (b) 63.5 g (c) 127 g (d) 254 g

26. 25 mL *N* $K_2Cr_2O_7$ acidified solution will liberate . . . iodine from KI solution.
(a) 0.3175 g (b) 3.175 g (c) 31.75 g (d) 317.5 g

27. The indicator used in iodometric titrations is:
(a) phenolphthalein (b) litmus
(c) potassium iodide (d) starch

28. Which of the following acids is added in the titration of oxalic acid and potassium permanganate?
(a) HNO_3 (b) HCl
(c) CH_3COOH (d) H_2SO_4

29. In the titration of $K_2Cr_2O_7$ iodometrically, near the end point the colour of the solution becomes:
(a) green (b) red (c) yellow (d) blue

30. In the titration of ferrous ammonium sulphate and potassium dichromate, the external indicator used is:
(a) KCNS (b) NH_4CNS
(c) $K_3Fe(CN)_6$ (d) $K_4Fe(CN)_6$

31. 0.1 *N* solution of a dibasic acid can be prepared by dissolving 0.45 g of the acid in water and diluting to 100 mL. The molecular mass of the acid is:
(a) 45 (b) 90 (c) 135 (d) 180

32. 100 mL of 0.2 *N* HCl solution is added to 100 mL of 0.2 *N* $AgNO_3$ solution. The molarity of nitrate ions in the resulting mixture will be:
(a) 0.05 *M* (b) 0.5 *M* (c) 0.1 *M* (d) 0.2 *M*

33. In an experiment, 20 mL of a decinormal HCl solution was added to 15 mL of a decinormal $AgNO_3$ solution. AgCl was precipitated out and excess of acid was titrated with *N*/20 NaOH solution. The volume of NaOH required was:
(a) 10 mL (b) 20 mL (c) 30 mL (d) 5 mL

34. Iodine solution is prepared by dissolving iodine in:
(a) NaOH (b) Na_2CO_3 (c) H_2O (d) KI

35. Which one of the following is not a primary standard?
(a) Oxalic acid (b) Sodium thiosulphate
(c) Sodium hydroxide (d) Potassium dichromate

36. Which one of the following is a primary standard?
(a) $KMnO_4$ (b) $CuSO_4 \cdot 5H_2O$
(c) I_2 (d) H_2SO_4

37. When 10 mL of 10 *M* solution of H_2SO_4 and 100 mL of 1 *M* solution of NaOH are mixed, the resulting solution will be:
(a) acidic (b) neutral
(c) alkaline (d) cannot be predicted

38. 1.0 g of a metal carbonate neutralises 200 mL of 0.1 *N* HCl. The equivalent mass of the metal will be:
(a) 50 (b) 40 (c) 20 (d) 100

39. The normality of a 26% mass/volume solution of ammonia (density 0.885 g/mL) is approximately:
(a) 1.5 (b) 4.0 (c) 0.4 (d) 15.3

40. The molarity of pure water is:
(a) 18 *M* (b) 50.0 *M* (c) 55.6 *M* (d) 100 *M*

41. 5.0 g of H_2O_2 is present in 100 mL of the solution. The molecular mass of H_2O_2 is 34. The molarity of the solution is:
(a) 1.5 *M* (b) 0.15 *M* (c) 3.0 *M* (d) 50 *M*

42. 2 *N* solution of sodium carbonate is equivalent to a solution of strength:
(a) 106 g per 100 mL (b) 53 g per 100 mL
(c) 10.6 g per 100 mL (d) 5.3 g per 100 mL

43. Which one of these solutions has the highest normality?
(a) 8 g KOH per 100 mL (b) 0.5 *M* H_2SO_4
(c) 6 g of NaOH per 100 mL (d) *N* H_3PO_4

44. 1 g of a metal required 50 mL of 0.5 *N* HCl to dissolve it. The equivalent mass of the metal is:
(a) 25 (b) 50 (c) 20 (d) 40

45. What volume of CO_2 at NTP will be liberated by the action of 100 mL of 0.2 *N* HCl on $CaCO_3$?
(a) 112 mL (b) 224 mL (c) 448 mL (d) 120 mL

46. The equivalent mass of phosphoric acid (H_3PO_4) is 49. It behaves as . . . acid.
(a) monobasic (b) dibasic
(c) tribasic (d) tetrabasic

47. The normality of 10% (mass/volume) acetic acid is:
(a) 1 *N* (b) 10 *N* (c) 1.7 *N* (d) 0.83 *N*

48. Equivalent mass of $KMnO_4$, when it is converted to $MnSO_4$, is: (CBSE [illegible])
(a) *M*/5 (b) *M*/3 (c) *M*/6 (d) *M*/2

49. How many grams of CH_3OH would have to be added to water to prepare 150 mL of a solution that is 2.0 *M* CH_3OH? (CBSE [illegible])
(a) 9.6 (b) 2.4 (c) 9.6×10^3 (d) 4.3×10^2

50. On dissolving 1 mole of each of the following acids in one litre water, the acid which does not give a solution of strength 1 *N* is: [illegible]
(a) HCl (b) $HClO_4$ (c) HNO_3 (d) H_3PO_4

51. 0.16 g a dibasic acid required 25 mL of decinormal NaOH solution for complete neutralisation. The molecular mass of the acid is: [illegible]
(a) 32 (b) 64 (c) 128 (d) 256

52. 5 mL of *N* HCl, 20 mL of *N*/2 H_2SO_4 and 30 mL of *N*/3 HNO_3 are mixed together and volume made to one litre. The normality of the resulting solution is: (MLNR [illegible])
(a) *N*/5 (b) *N*/10
(c) *N*/20 (d) *N*/40

53. The equivalent mass of $MnSO_4$ is half its molecular mass when it is converted to:
(a) Mn_2O_3 (b) MnO_2
(c) MnO_4^- (d) MnO_4^{2-}

54. For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are: [illegible]

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

55. 100 mL solution consists 4 g caustic soda. The normality of the solution is: [illegible]
(a) 1.0 (b) 0.1 (c) 0.5 (d) 4.0

56. The amount of a caustic soda required for complete neutralisation of 100 mL 0.1 N HCl is: [PMT (MP) 1993]
(a) 4.0 g (b) 0.04 g (c) 0.4 g (d) 2.0 g

57. What volume of $N/2$ and $N/10$ HCl should be taken in order to make a 2 litre solution of $N/5$ strength?
(a) 0.5 litre $N/2$ HCl and 1.5 litre of $N/10$ HCl
(b) 1 litre $N/2$ HCl and 1 litre $N/10$ HCl
(c) 1.5 litre $N/2$ HCl and 0.5 litre $N/10$ HCl
(d) 0.7 litre $N/2$ HCl and 1.3 litre $N/10$ HCl

58. The molar concentration of the chloride ion in the solution obtained by mixing 300 mL of 3.0 M NaCl and 200 mL of 4.0 M solution of $BaCl_2$ is:
(a) 1.6 M (b) 1.8 M (c) 5.0 M (d) 0.5 M

59. The normality of 0.3 M phosphorous acid (H_3PO_3) is: [IIT 1990]
(a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6

60. A 100 mL solution of 0.1 N HCl was titrated with 0.2 N NaOH solution. The titration was discontinued after adding 30 mL of NaOH solution. The titration was completed by adding 0.25 N KOH solution. The volume of KOH required for completing the titration is: [illegible]
(a) 70 mL (b) 32 mL (c) 35 mL (d) 16 mL

61. An aqueous solution of 6.3 g of oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is: [IIT 1988]
(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

62. In order to prepare one litre normal solution of $KMnO_4$, how many grams of $KMnO_4$ are required if the solution is to be used in acid medium for oxidation? [PET (MP) 2003]
(a) 158 g (b) 31.6 g (c) 62 g (d) 790 g

63. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. Equivalent weight of the metal is: [illegible]
(a) 33.25 (b) 3.325 (c) 12 (d) 20

64. Phosphoric acid H_3PO_4 can be neutralised to:
(a) HPO_4^{2-} (b) PO_4^{3-} (c) $H_2PO_4^-$ (d) HPO_3^{2-}

65. 'a' g KHC_2O_4 required to reduce 100 mL of 0.02 M $KMnO_4$ in acid medium and 'b' g KHC_2O_4 neutralises 100 mL of 0.05 M $Ca(OH)_2$ then :
(a) $a = b$ (b) $2a = b$
(c) $a = 2b$ (d) none of these

66. Which of the following statements is /are true about H_3PO_2?
(a) It is a tribasic acid
(b) One mole of it is neutralised by 0.5 mole of $Ca(OH)_2$
(c) NaH_2PO_2 is acidic salt
(d) It disproportionates to H_3PO_3 and PH_3 on heating

67. Mixture of 1 mole BaF_2 and 2 mole H_2SO_4 can be neutralised by:
(a) 1 mole KOH (b) 2 mole $Ca(OH)_2$
(c) 4 mole NaOH (d) 2 mole KOH

68. $28\,NO_3^- + 3As_2S_3 + 4H_2O \rightarrow 6AsO_4^{3-} + 28NO + 9SO_4^{2-} + 8H^+$.
What will be the equivalent mass of As_2S_3 in above reaction?
(a) $\frac{\text{M. wt.}}{2}$ (b) $\frac{\text{M. wt.}}{4}$ (c) $\frac{\text{M. wt.}}{24}$ (d) $\frac{\text{M. wt.}}{28}$

69. The number of moles of $KMnO_4$ that will need to react completely with one mole of ferrous oxalate in acidic solution is: [IIT (July) 1997]
(a) 2/5 (b) 3/5 (c) 4/5 (d) 1

70. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is: [IIT (July) 1997]
(a) 2/5 (b) 3/5 (c) 4/5 (d) 1

71. The equivalent weight of KIO_3 in the reaction,
$2Cr(OH)_3 + OH^- + KIO_3 \longrightarrow 2CrO_4^{2-} + 5H_2O + KI$ is: [PET (MP) 2003]
(a) molecular weight (b) $\frac{\text{molecular weight}}{3}$
(c) $\frac{\text{molecular weight}}{6}$ (d) $\frac{\text{molecular weight}}{2}$

72. In the reaction,
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$
equivalent weight of iodine will be equal to: [PMT (MP) 2003]
(a) 4/6 of molecular weight
(b) molecular weight
(c) 2/9 of molecular weight
(d) twice the molecular weight

73. The volume of a concentrated H_2SO_4, mixed with 0.5 N KOH to prepare 150 cm^3 of 0.2 N KOH. Solution is: (KCET 2004)
(a) 50 cm^3 (b) 60 cm^3 (c) 70 cm^3 (d) 80 cm^3

74. For the decolorisation of 1 mole of $KMnO_4$, the number of moles of H_2O_2 required is: (AIIMS 2004)
(a) 1/2 (b) 3/2 (c) 5/2 (d) 7/2

75. The product of oxidation of I^- with MnO_4^- in alkaline medium is: [IIT (S) 2004]
(a) IO_3^- (b) I_2 (c) IO^- (d) IO_4^-

76. Volume of 0.1 M $K_2Cr_2O_7$ required to oxidise 35 mL of 0.5 M $FeSO_4$ solution is: [illegible]
(a) 29.2 mL (b) 17.5 mL
(c) 175 mL (d) 145 mL

77. A commercial sample of H_2O_2 is labelled 10 volume. Its percentage strength is nearly: [illegible]
(a) 1% (b) 3% (c) 10% (d) 90%

78. 50 mL of 10 N H_2SO_4, 25 mL of 12 N HCl and 40 mL of 5 N HNO_3 are mixed and the volume of the mixture is made 1000 mL by adding water. The normality of the resulting solution will be: [illegible]
(a) 1 N (b) 2 N (c) 3 N (d) 4 N
(e) 9 N

[**Hint:** $N_1V_1 + N_2V_2 + N_3V_3 = N_R \times V_R$
$10 \times 50 + 12 \times 25 + 5 \times 40 = N_R \times 1000$
$500 + 300 + 200 = N_R \times 1000$
$N_R = 1$ (Resultant normality)]

79. Acidified $KMnO_4$ oxidizes oxalic acid to CO_2. What is the volume (in litre) of 10^{-4} M $KMnO_4$ required to completely oxidize 0.5 litre of 10^{-2} M oxalic acid in acid medium? [illegible]
(a) 125 (b) 1250 (c) 200 (d) 20

[Hint: $$2KMnO_4 + 3H_2SO_4 + 5\begin{matrix}\text{COOH}\\ | \\ \text{COOH}\end{matrix} \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

$$\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}\begin{pmatrix}\text{COOH}\\ | \\ \text{COOH}\end{pmatrix}$$

$$\frac{10^{-4}\times V_1}{2} = \frac{10^{-2}\times 0.5}{5}$$

$$V_1 = 20\text{ L}]$$

80. The concentration of oxalic acid is 'x' mol litre^{-1}. 40 mL of this solution reacts with 16 mL of 0.05 M acidified $KMnO_4$. What is the pH of 'x' M oxalic acid solution?
(Assume that oxalic acid dissociates completely.) [EAMCET (Engg.) 2006]

(a) 1.3 (b) 1.699 (c) 1 (d) 2

[Hint: $$2KMnO_4 + 3H_2SO_4 + 5\begin{matrix}\text{COOH}\\ | \\ \text{COOH}\end{matrix} \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

$$\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}\begin{pmatrix}\text{COOH}\\ | \\ \text{COOH}\end{pmatrix}$$

$$\frac{0.05\times 16}{2} = \frac{x\times 40}{5}$$

$$x = 0.05\,M$$

$$[H^+] = 2\times 0.05 = 0.1\,M$$

$$pH = -\log(H^+) = -\log(0.1) = 1]$$

81. Consider the titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is: (IIT 2007)

(a) 3 (b) 4 (c) 5 (d) 6

[Hint: $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

1 mole of dichromate oxidises six moles of ferrous ion present in Mohr's salt]

82. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is: [CBSE (Med.) 2007]

(a) $\frac{4}{5}$ (b) $\frac{2}{5}$ (c) 1 (d) $\frac{3}{5}$

[Hint: The redox reaction is:

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

1 mole SO_3^{2-} will be oxidised by $\frac{2}{5}$ mol of MnO_4^-]

83. For the reaction between $KMnO_4$ and H_2O_2, the number of electrons transferred per mole of H_2O_2 is: [PMT (Haryana) 2007]

(a) one (b) two (c) three (d) four

84. Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} is: [PMT (Raj.) 2007]

(a) 1/3 (b) 3 (c) 1/6 (d) 6

85. The formula mass of Mohr's salt is 392. The iron present in it is oxidised by $KMnO_4$ in acid medium. The equivalent mass of Mohr's salt is: [Indraprasth (Engg.) 2007]

(a) 392 (b) 31.6 (c) 278 (d) 156

86. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorus acid (H_3PO_3), the volume of 0.1 M aqueous KOH solution required is: [Jamia Millia Islamia (Engg.) 2008]

(a) 10 mL (b) 20 mL (c) 40 mL (d) 60 mL

[Hint: $H_3PO_3 + 2KOH \longrightarrow K_2HPO_3 + 2H_2O$

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

$$\frac{0.1\times 20}{1} = \frac{0.1\times V_2}{2}$$

$$V_2 = 40\text{ mL}]$$

87. 10 cm^3 of 0.1 N monobasic acid requires 15 cm^3 of sodium hydroxide solution whose normality is :

(a) 0.066 N (b) 0.66 N (c) 1.5 N (d) 0.15 N

(KCET 2008)

[Hint : $$N_1V_1 = N_2V_2$$

$$0.1\times 10 = N_2\times 15$$

$$N_2 = 0.066]$$

88. Amount of oxalic acid present in solution can be oxidised by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl: (AIEEE 2008)

(a) oxidises oxalic acid to carbon dioxide and water

(b) gets oxidised by oxalic acid to chlorine

(c) Furnishes H^+ ions in addition to those from oxalic acid

(d) reduces permanganate to Mn^{2+}

89. How many moles of acidified $FeSO_4$ can be completely oxidised by one mole of $KMnO_4$? [BHU (Mains) 2008]

(a) 10 (b) 5 (c) 6 (d) 2

[Hint: $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

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

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

2 mole $KMnO_4 \equiv 10$ mole $FeSO_4$

1 mole $KMnO_4 \equiv 5$ mole $FeSO_4$]

90. In the titration of nitric acid against potassium carbonate, the indicator used is : [Comed (Karnataka) 2008]

(a) methyl orange (b) self indicator

(c) phenolphthalein (d) diphenylamine

91. In transforming 0.01 mole of PbS to $PbSO_4$, the volume of 10 volume H_2O_2 required will be : [JEE (WB) 2008]

(a) 11.2 mL (b) 22.4 mL (c) 33.6 mL (d) 44.8 mL

[Hint : $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

0.04 mole of H_2O_2 is required to react with 0.01 mole PbS.

Molarity of H_2O_2 may be calculated as,

$$\text{Volume strength} = \text{Molarity}\times 11.2$$

$$10 = M\times 11.2$$

$$M = 0.892$$

$$\text{Number of moles} = \frac{MV}{1000}$$

$$0.04 = \frac{0.892\times V}{1000}$$

$$V = 44.8\text{ mL}]$$

92. A solution containing Na_2CO_3 and NaOH requires 300 mL of 0.1 *N* HCl using phenolphthalein as an indicator. Methyl orange is then added to above titrated solution when a further 25 mL of 0.2 *N* HCl is required. The amount of NaOH present in the original solution is:

(a) 0.5 g (b) 1 g (c) 2 g (d) 4 g

[**Hint** : 300 mL HCl of 0.1 *N* neutralises entire amount of NaOH and 1/2 of Na_2CO_3. Remaining 1/2 of Na_2CO_3 is neutralised by 25 mL of 0.2 *N* HCl, *i.e.*, 50 mL of 0.1 *N* HCl.

Thus, 250 mL of 0.1 *N* HCl is required to neutralise NaOH completely.

$$N_1V_1(\text{NaOH}) = N_2V_2(\text{HCl})$$
$$= 0.1 \times 250$$
$$= 25$$
$$W_{\text{NaOH}} = \frac{ENV}{1000} = \frac{40 \times 25}{1000} = 1\text{ g}$$
]

93. Ceric ammonium sulphate and potassium permanganate are used as oxidising agents in acidic medium for oxidation of ferrous ammonium sulphate to ferric sulphate. The ratio of number of moles of ceric ammonium sulphate required per mole of ferrous ammonium sulphate to the number of moles of $KMnO_4$ required per mole of ferrous ammonium sulphate is:

(a) 5.0 (b) 0.2 (c) 0.6 (d) 2.0

[**Hint** : Oxidation of ferrous ammonium sulphate by $KMnO_4$ is :

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \longrightarrow$$
$$K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + 68H_2O$$

$\therefore$ 1 mole of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ consumes 1/5 mole of $KMnO_4$.

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

$$\text{Required ratio} = \frac{1}{1/5} = 5.0$$
]

94. One kilogram of sea water sample contains 6 mg of dissolved O_2. The concentration of O_2 in the sample in ppm is:

(a) 0.6 (b) 6.0 (c) 60.0 (d) 16.0
(e) 32.0

[**Hint** : 1 kg water ≡ 10^6 mg:

10^6 mg water contains 6 mg O_2

$\therefore$ Concentration of O_2 is 6 ppm.]

95. The estimation of available chlorine in bleaching powder is done by:

(a) Acid-base titration (b) Permanganometric titration
(c) Iodimetric titration (d) Iodometric titration

96. What volume of 0.1 M H_2SO_4 is required in litres to neutralize completely 1 litre of a solution containing 20 g of NaOH?

(a) 5.0 (b) 0.5 (c) 2.5 (d) 10.0

[**Hint** : $M_{\text{NaOH}} = \frac{w_B \times 1000}{m_B \times V} = \frac{20 \times 1000}{40 \times 1000} = 0.5$

Reaction : $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{2}$$
$$0.1 \times V_1 = \frac{0.5 \times 1}{2}$$
$$V_1 = 2.5\text{ L}$$
]

Assertion-Reason TYPE QUESTIONS

The questions given below consist of an **'Assertion' (A)** and **'Reason' (R).** Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If (A) is incorrect, but (R) is correct.

1. (A) H_3PO_3 is a dibasic acid.
   (R) Two H-atoms are directly attached to phosphorus '*P*'.
2. (A) Equivalent mass of $KMnO_4$ is equal to one-fifth of its molecular mass when it acts as an oxidising agent in acidic medium.
   (R) Oxidation number of Mn in $KMnO_4$ is +7.
3. (A) 5 *M* HCl solution is diluted 10 times, its molarity becomes 50.
   (R) On dilution, molarity of the solution decreases.
4. (A) In the reaction, $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$; I_2 is oxidised.
   (R) During oxidation, loss of electron takes place.
5. (A) In the titration of HCl against NaOH, phenolphthalein is used as suitable indicator.
   (R) Phenolphthalein is pink coloured in basic medium.
6. (A) Concentration of H_2O_2 is expressed in volume.
   (R) Volume strength of H_2O_2 = Normality × 5.6.
7. (A) Iodimetric titrations are redox titrations.
   (R) The iodine solution acts as an oxidising agent.
8. (A) Starch is used as absorption indicator in iodometric and iodimetric titrations.
   (R) Starch forms iodostarch complex with iodine, which is blue coloured.
9. (A) H_3BO_3 is monobasic Lewis acid but its salt Na_3BO_3 exists.
   (R) H_3BO_3 reacts with NaOH to give Na_3BO_3.
   [Hint $H_3BO_3 + NaOH \longrightarrow NaB(OH)_4$
   $3C_2H_5OH + H_3BO_3 \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$
   $(C_2H_5)_3BO_3 + 3NaOH \longrightarrow Na_3BO_3 + 3C_2H_5OH$]
10. (A) Equivalent weight of a base $= \dfrac{\text{Molecular weight}}{\text{Acidity}}$
    (R) Acidity is the number of replaceable hydrogen atoms in one molecule of the base.

Answers : OBJECTIVE QUESTIONS

1. (a) 2. (b) 3. (c) 4. (d) 5. (b) 6. (a) 7. (d) 8. (c)
9. (c) 10. (d) 11. (b) 12. (a) 13. (d) 14. (c) 15. (b) 16. (a)
17. (d) 18. (c) 19. (a) 20. (b) 21. (c) 22. (b) 23. (c) 24. (a)
25. (b) 26. (b) 27. (d) 28. (d) 29. (a) 30. (c) 31. (b) 32. (c)
33. (a) 34. (d) 35. (c) 36. (b) 37. (a) 38. (a) 39. (d) 40. (c)
41. (a) 42. (c) 43. (c) 44. (d) 45. (b) 46. (b) 47. (c) 48. (a)
49. (a) 50. (d) 51. (c) 52. (d) 53. (b) 54. (a) 55. (a) 56. (c)
57. (a) 58. (c) 59. (d) 60. (d) 61. (a) 62. (b) 63. (a) 64. (a, b, c)
65. (b) 66. (b, d) 67. (b, c) 68. (d) 69. (b) 70. (a) 71. (c) 72. (b)
73. (b) 74. (c) 75. (a) 76. (a) 77. (b) 78. (a) 79. (d) 80. (c)
81. (d) 82. (b) 83. (c) 84. (a) 85. (a) 86. (c) 87. (a) 88. (d)
89. (b) 90. (c) 91. (d) 92. (b) 93. (a) 94. (b) 95. (d) 96. (c)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (c) 2. (b) 3. (d) 4. (d) 5. (b) 6. (b) 7. (a) 8. (a)
9. (c) 10. (c)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

1. The value of n in the equation,

$$Cr_2O_7^{2-} + 14H^+ + ne^- \longrightarrow 2Cr^{3+} + 7H_2O$$

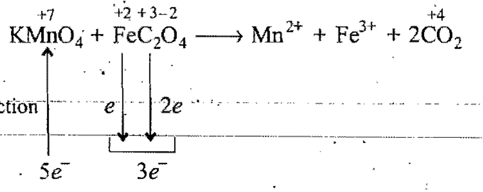
is:

(a) 2 (b) 3 (c) 4 (d) 6

2. The number of moles of acidified $KMnO_4$ required to oxidise one mole of ferrous oxalate (FeC_2O_4) is:

(a) 5 (b) 3 (c) 0.6 (d) 1.5

[Hint: $\overset{+7}{KMnO_4} + \overset{+2\ +3-2}{FeC_2O_4} \longrightarrow Mn^{2+} + Fe^{3+} + 2\overset{+4}{CO_2}$



$\therefore$ 5 mole $FeC_2O_4 \equiv$ 3 mole $KMnO_4$

1 mole $FeC_2O_4 \equiv$ 0.6 mole $KMnO_4$]

3. A solution contains Na_2CO_3 and $NaHCO_3$. 10 mL of the solution required 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 was required. Then the amount of Na_2CO_3 and $NaHCO_3$ in 1 litre of the solution is:

(a) 5.3 g and 4.2 g (b) 3.3 g and 6.2 g

(c) 4.2 g and 5.3 g (d) 6.2 g and 3.3 g

4. V_1 mL of NaOH of normality x and V_2 mL of $Ba(OH)_2$ of normality y are together sufficient to neutralize exactly 100 mL of 0.1 N HCl. If $V_1 : V_2 = 1:4$ and if $x : y = 4:1$, what fraction of the acid is neutralised by $Ba(OH)_2$?

(a) 0.5 (b) 0.33 (c) 0.67 (d) 0.25

5. A 0.518 g sample of limestone is dissolved in HCl and then the calcium is precipitated as CaC_2O_4. After filtering and washing the precipitate, it requires 40 mL of 0.25 N $KMnO_4$ solution acidified with H_2SO_4 to titrate it as,

$$MnO_4^- + H^+ + C_2O_4^{2-} \longrightarrow CO_2 + Mn^{2+} + 2H_2O$$

The percentage of CaO in the sample is:

(a) 54% (b) 27.1% (c) 42% (d) 84%

[Hint: Number of milliequivalents of CaC_2O_4, $KMnO_4$ and CaO will be same.

$$40 \times 0.25 = W / \frac{56}{2} \times 1000$$

$$W = 0.28 \text{ g (Mass of CaO)}$$

$$\% \text{ CaO} = \frac{0.28}{0.518} \times 100 = 54\%]$$

6. When 40 mL of 0.1 N HCl and 20 mL of 0.1 M H_2SO_4 are mixed together, the normality of the mixture will be:

(a) $\frac{1}{5} N$ (b) $\frac{2}{15} N$ (c) $\frac{15}{2} N$ (d) $\frac{5}{1} N$

[Hint: $N_1V_1 + N_2V_2 = N_R(V_1 + V_2)$

$$0.1 \times 40 + 0.2 \times 20 = N_R(60)$$

$$N_R = \frac{8}{60} = \frac{2}{15}\ ]$$

7. What is the normality of 0.3 M H_3PO_4 when it undergoes the reaction as?

$$H_3PO_4 + 2OH^- \longrightarrow HPO_3^{2-} + 2H_2O$$

(a) 0.3 N (b) 0.15 N (c) 0.60 N (d) 0.90 N

8. In the mixture of ($NaHCO_3 + Na_2CO_3$), volume of HCl required is x mL with phenolphthalein indicator and y mL with methyl orange indicator in same titration. Hence, volume of HCl for complete reaction of Na_2CO_3 is:

(a) $2x$ (b) y (c) $x/2$ (d) $(y - x)$

[Hint: In presence of phenolphthalein, 50% Na_2CO_3 is neutralised whereas $NaHCO_3$ remains unaffected. In presence of methyl orange, both Na_2CO_3 and $NaHCO_3$ will be 100% neutralised.

Let volume of HCl for complete reaction of $Na_2CO_3 = V_1$ mL and volume of HCl for complete reaction of $NaHCO_3 = V_2$ mL. With phenolphthalein, 50% Na_2CO_3 will be neutralized.

$$\therefore \quad \frac{V_1}{2} = x,\ V_1 = 2x]$$

9. 40 mL of 0.05 M $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (sesquicarbonate) is titrated against 0.05 M HCl. x mL of HCl is used when phenolphthalein is the indicator and y mL HCl is used when methyl orange is the indicator in two separate titrations; hence $(y - x)$ is:

(a) 80 mL (b) 30 mL

(c) 120 mL (d) none of these

10. Equivalent mass of H_3PO_2 when it disproportionates into PH_3 and H_3PO_3 is (Molecular mass = M):

(a) M (b) $\frac{M}{2}$ (c) $\frac{M}{4}$ (d) $\frac{3M}{4}$

[Hint: $H_3\overset{+1}{P}O_2 \longrightarrow H_3\overset{+3}{P}O_3$; Eq. wt. $= \frac{M}{2}$

(Change in oxidation number = 2)

$$H_3\overset{+1}{P}O_2 \longrightarrow \overset{-3}{P}H_3;\ \text{Eq. wt.} = \frac{M}{4}$$

(Change in oxidation number = 4)

The equivalent mass of H_3PO_2 in the process of disproportionation $= \frac{M}{2} + \frac{M}{4} = \frac{3M}{4}$]

11. The reagent commonly used to determine hardness of water titrimetrically is:

(a) oxalic acid (b) disodium salt of EDTA

(c) sodium citrate (d) sodium thiosulphate

12. The equivalent mass of sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) in the reaction,

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

is:

(a) 248 (b) 124 (c) 596 (d) 62

13. If 100 mL of the acid is neutralised by 100 mL of 4 M NaOH, the purity of concentrated HCl (sp. gravity = 1.2) is:

(a) 12% (b) 98% (c) 73% (d) 43%

14. 2 moles of $FeSO_4$ are oxidised by x moles of $KMnO_4$ in acid medium into ferric sulphate. 3 moles of ferric oxalate are oxidised by y moles of $K_2Cr_2O_7$ in acid medium. The value of (x/y) is:

(a) 6/5 (b) 2/15 (c) 18/5 (d) 3/5

15. What volume of 0.05 M $Cr_2O_7^{2-}$ in acid medium is needed for complete oxidation of 200 mL of 0.6 M FeC_2O_4 solution?

(a) 0.6 L (b) 1.2 L (c) 2.4 L (d) 3.6 L

16. $KMnO_4$ reacts with oxalic acid according to the reaction:

$$2KMnO_4 + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Then, 20 mL of 0.1 M $KMnO_4$ is equivalent to:

(a) 30 mL of 0.5 M $C_2H_2O_4$ (oxalic acid)
(b) 50 mL of 0.1 M $C_2H_2O_4$ (oxalic acid)
(c) 20 mL of 0.5 M $C_2H_2O_4$ (oxalic acid)
(d) 10 mL of 0.1 M $C_2H_2O_4$ (oxalic acid)

[**Hint:** $\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}(H_2C_2O_4)$

$$\frac{0.1\times 20}{2} = \frac{M_2V_2}{5}$$

$$M_2V_2 = 5$$

(It is possible in case of b.)]

17. Potassium permanganate is titrated against ferrous ammonium sulphate in acidic medium; the equivalent mass of potassium permanganate is:

(a) $\frac{\text{molecular mass}}{3}$ (b) $\frac{\text{molecular mass}}{5}$
(c) $\frac{\text{molecular mass}}{2}$ (d) $\frac{\text{molecular mass}}{10}$

[**Hint:** The ionic reaction involved in titration is:

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

Since, a molecule of $KMnO_4$ accepts 5 electrons in acid medium, its equivalent mass will be $\left(\frac{\text{molecular mass}}{5}\right)$.]

18. Number of moles of $K_2Cr_2O_7$ that can be reduced by 1 mole of Sn^{2+} ions is:

(a) 1/3 (b) 3/2 (c) 5/6 (d) 6/5

[**Hint:** The redox reaction is:

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}$$

$\therefore$ 1 mole of Sn^{2+} will reduce 1/3 mole of $K_2Cr_2O_7$]

19. Potassium permanganate acts as an oxidising agent in acidic, alkaline as well as neutral media. Which among the following statements is incorrect?

(a) $N = M/5$ (in acid medium)
(b) $N = M/3$ (in alkaline medium)
(c) $N = M/3$ (in neutral medium)
(d) $N = M$ (in alkaline medium)

20. The number of equivalents of $Na_2S_2O_3$ required for the volumetric estimation of one equivalent of Cu^{2+} is:

(a) 1/3 (b) 1 (c) 3/2 (d) 2/3

[**Hint:** Number of equivalents of reacting species in a chemical reaction are same.]

21. The equivalent mass of $MnSO_4$ becomes half of its molecular mass when it is converted into:

(a) MnO_4^- (b) MnO_2 or Mn_3O_4
(c) MnO_4^{2-} (d) $Mn_2O_4^{2-}$

[**Hint:** When $\overset{(+2)}{Mn}SO_4$ is converted to $\overset{(+4)}{Mn}O_2$, the oxidation number changes by 2, thus

$$\text{Equivalent mass of } MnSO_4 = \frac{\text{Molecular mass}}{2}]$$

22. A solution of 10 mL of $\frac{M}{10}$ $FeSO_4$ was titrated with $KMnO_4$ solution in acidic medium; the amount of $KMnO_4$ used will be:

(a) 10 mL of 0.5 M (b) 10 mL of 0.1 M
(c) 10 mL of 0.02 M (d) 5 mL of 0.1 M

[**Hint:** The involved reaction is:

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

$$\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}(FeSO_4)$$

$$\frac{M_1V_1}{2} = \frac{0.1\times 10}{10}$$

$M_1V_1 = 0.2$ which is possible in (c)]

23. Among the following reactions, used in titrations, select the reaction(s) in which the chlorine is oxidised:

1. $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
2. $2KI + Cl_2 \longrightarrow 2KCl + I_2$
3. $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$
4. $CrO_2Cl_2 + 2NaOH \longrightarrow Na_2CrO_4 + 2HCl$

(a) reactions 2, 3 and 4 (b) reaction 1 only
(c) reactions 1 and 3 (d) reaction 4 only
(e) reactions 2 and 4

24. Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O(s)$ is often used as a primary reagent to standardise sodium hydroxide solution. Which of these facts are reasons to choose this substance as a primary standard?

I. It is diprotic.
II. It is a stable compound that can be weighed directly in air.
III. It is available in pure form.

(a) III only (b) I and II only
(c) II and III only (d) I, II and III

25. A 20 mL sample of a $Ba(OH)_2$ solution is titrated with 0.245 M HCl. If 27.15 mL of HCl is required, what is the molarity of the $Ba(OH)_2$ solution?

(a) 0.166 M (b) 0.180 M (c) 0.333 M (d) 0.666 M

26. A solution of which substance can best be used as both titrant and its own indicator in an oxidation-reduction titration?

(a) I_2 (b) NaOCl (c) $K_2Cr_2O_7$ (d) $KMnO_4$

27. A 0.2 g sample of benzoic acid, C_6H_5COOH, is titrated with a 0.120 M $Ba(OH)_2$ solution. What volume of the $Ba(OH)_2$ solution is required to reach the equivalence point?

Substance	Molar mass
C_6H_5COOH	122.1 g mol^{-1}

(a) 6.82 mL (b) 13.6 mL (c) 17.6 mL (d) 35.2 mL

28. What mass of magnesium hydroxide is required to neutralise 125 mL of 0.136 *M* HCl solution?

Substance	Molar mass
$Mg(OH)_2$	58.33 g mol^{-1}

(a) 0.248 g (b) 0.496 g (c) 0.992 g (d) 1.98 g

29. In the titration of $K_2Cr_2O_7$ and $FeSO_4$, the following data is obtained: V_1 mL of $1M_1$ $K_2Cr_2O_7$ requires V_2 mL of $1M_2$ $FeSO_4$. Which of the following relations is true for the above titration?

(a) $6M_1V_1 = M_2V_2$ (b) $M_1V_1 = 6M_2V_2$
(c) $M_1V_1 = M_2V_2$ (d) $3M_1V_1 = 4M_2V_2$

[**Hint:**

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

$$\frac{M_1V_1}{n_1}(K_2Cr_2O_7) = \frac{M_2V_2}{n_2}(FeSO_4)$$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{6}$$

$$6M_1V_1 = M_2V_2]$$

30. When 20 mL of $\frac{M}{10}$ NaOH are added to 10 mL of $\frac{M}{10}$ HCl, the resulting solution will:

(a) turn blue litmus red
(b) turn phenolphthalein solution pink
(c) turn methyl orange red
(d) have no effect on either red or blue litmus

31. A sample of coconut oil weighing 1.5763 g is mixed with 25 mL of 0.4210 *M* KOH. Some KOH is used in saponification of coconut oil. After the saponification is complete, 8.46 mL of 0.2732 *M* H_2SO_4 is required to neutralize excess KOH. The saponification number of peanut oil is:

(a) 209.6 (b) 98.9 (c) 108.9 (d) 218.9

[**Hint:** Number of milliequivalent of KOH added

$$= 25 \times 0.421 = 10.525$$

Number of milliequivalents left unreacted

= Number of milliequivalents of H_2SO_4 used

$= 8.46 \times 0.2732 \times 2 = 4.623$ (Here, basicity of $H_2SO_4 = 2$)

Number of milliequivalents of KOH used by oil

$$= 10.525 - 4.623 = 5.902$$

$$\text{Mass of KOH used} = \frac{5.902 \times 56}{1000} = 0.3305 \text{ g} = 330.5 \text{ mg}$$

Saponification number = Mass of KOH in mg used by 1 g oil or fat

$$= \frac{0.3305 \times 1000}{1.5763} = 209.6]$$

32. 12.5 mL of a solution containing 6 g of a dibasic acid in one litre was found to be neutralized by 10 mL of a decinormal solution of NaOH. The molecular mass of the acid is:

(a) 110 (b) 75 (c) 120 (d) 150

[**Hint:** $N_1V_1 \text{ (acid)} = N_2V_2 \text{ (base)}$

$$N_1 \times 12.5 = \frac{1}{10} \times 10$$

$$N_1 = \frac{1}{12.5}$$

$$\text{Strength} = N \times Ew$$

$$6 = \frac{1}{12.5} \times Ew$$

$$Ew = 75$$

Molar mass = Equivalent mass × Basicity

$$= 75 \times 2 = 150]$$

33. 20 mL of 0.1 *M* H_3BO_3 solution on complete neutralisation requires *x* mL of 0.05 *M* NaOH solution. The value of *x* will be:

(a) 20 mL (b) 40 mL (c) 120 mL (d) 80 mL

[**Hint:** Boric acid is monobasic acid.

$$H_3BO_3 + NaOH \longrightarrow Na[B(OH)_4]$$

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

$$\frac{0.1 \times 20}{1} = \frac{0.05 \times x}{1}$$

$$x = 40 \text{ mL}]$$

34. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 *M* sulphuric acid. The excess of acid required 20 mL of 0.5 *M* sodium hydroxide solution for complete neutralization. The organic compound is:

(a) acetamide (b) benzamide (c) urea (d) thiourea

[**Hint:** $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$

$$\frac{M_1V_1}{1}(\text{excess } H_2SO_4) = \frac{M_2V_2}{2}(KOH)$$

$$\frac{0.1 \times V_1}{1} = \frac{0.5 \times 20}{2}$$

$$V_1 = 50 \text{ mL}$$

Volume of sulphuric acid used up to absorb $NH_3 = 50$ mL

$$\%N = \frac{2.8 \times MV}{W} = \frac{2.8 \times 0.1 \times 50}{0.3} = 46.6$$

Thus, the organic compound will be urea, which has 46.6% nitrogen.]

35. A solution contains Na_2CO_3 and $NaHCO_3$; 10 mL of this solution required 2.5 mL of 0.1 *M* H_2SO_4 for neutralisation using phenolphthalein indicator. Methyl orange is added after first end point, further titration required 2.5 mL of 0.2 *M* H_2SO_4. The amount of Na_2CO_3 and $NaHCO_3$ in 1 litre of the solution is:

(a) 5.3 g and 4.2 g (b) 3.3 g and 6.2 g
(c) 4.2 g and 5.3 g (d) 6.2 g and 3.3 g

36. MnO_4^- ions are reduced in acidic condition to Mn^{2+} ions whereas they are reduced in neutral condition to MnO_2. The oxidation of 25 mL of a solution *X* containing Fe^{2+} ions required in acidic condition, 20 mL of a solution *Y* containing MnO_4^- ions. What volume of solution *Y* would be required to oxidise 25 mL of solution *X* containing Fe^{2+} ions in neutral condition?

(a) 11.4 mL (b) 12 mL
(c) 33.3 mL (d) 35 mL
(e) 25 mL

[**Hint :**

Acid medium

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

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{5}$$

$$\frac{M_1 \times 20}{1} = \frac{M_2 \times 25}{5}$$

$$M_1 = \frac{M_2}{4} \qquad \text{...(i)}$$

Neutral medium

$$MnO_4^- + 3Fe^{2+} + 4H^+ \longrightarrow MnO_2 + 3Fe^{3+} + 2H_2O$$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{3}$$

$$\left(\frac{M_2}{4}\right) \times V_1 = \frac{M_2 \times 25}{3}$$

$$V_1 = 33.3 \text{ mL}]$$

Answers

1. (d) **2.** (c) **3.** (a) **4.** (a) **5.** (a) **6.** (b) **7.** (c) **8.** (a)
9. (a) **10.** (d) **11.** (b) **12.** (a) **13.** (a) **14.** (b) **15.** (b) **16.** (b)
17. (b) **18.** (a) **19.** (b) **20.** (b) **21.** (b) **22.** (c) **23.** (c) **24.** (c)
25. (a) **26.** (d) **27.** (a) **28.** (b) **29.** (a) **30.** (b) **31.** (a) **32.** (d)
33. (b) **34.** (c) **35.** (a) **36.** (c)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

Pyrolusite, MnO_2, is the main ore from which manganese is produced. The manganese content of the ore may be determined by reducing the MnO_2 under acetic conditions to Mn^{2+} with the oxalate ion, $C_2O_4^{2-}$, the oxalate ion being oxidised to carbon dioxide during the reaction. The analytical determination is carried out by adding a known excess volume of oxalate solution to a suspension of the pyrolusite and digesting the mixture on a hot water bath until all the MnO_2 has been reduced. The excess, unreacted oxalate solution is then titrated with standardised potassium permanganate, $KMnO_4$ solution after which the manganese content of the ore can be calculated.

A student prepared a standard solution of sodium oxalate by weighing 3.2 g of the dry anhydrous salt, dissolving it in distilled water and making the solution up to 500 mL. 25 mL of the oxalate solution required 24.76 mL of $KMnO_4$ solution.

Answer the following questions:

1. What is the equivalent mass of MnO_2 in the present titration?
   (a) $\frac{\text{M.w.}}{1}$ (b) $\frac{\text{M.w.}}{2}$ (c) $\frac{\text{M.w.}}{3}$ (d) $\frac{2\text{M.w.}}{3}$
2. How many moles of $C_2O_4^{2-}$ ions will be oxidised by 1 mole MnO_4^-?
   (a) 1/2 (b) 3/2 (c) 5/2 (d) 7/2
3. Molarity of the sodium oxalate solution is ....
   (a) 0.04776 (b) 0.07446 (c) 0.06447 (d) 0.07644
4. What is the molarity of $KMnO_4$ solution?
   (a) 0.04776 (b) 0.01929 (c) 0.038 (d) 0.028
5. Role of $KMnO_4$ in the given titration can be described as:
   (a) oxidising agent
   (b) reducing agent
   (c) indicator
   (d) oxidising agent and indicator

• Passage 2

For a series of indicators the following colours and pH range over which colour change takes place are as follows:

Indicator	Colour change over pH range	
U	*yellow to blue*	(pH 0 *to* 1.6)
V	*red to yellow*	(pH 2.8 *to* 4.1)
W	*red to yellow*	(pH 4.2 *to* 5.8)
X	*yellow to blue*	(pH 6.0 *to* 7.7)
Y	*colourless to red*	(pH 8.2 *to* 10)

Answer the following questions:

1. Indicator *V* could be used to find the equivalence point for 0.1 *M* acetic acid and 0.1 *M* ammonium hydroxide solution:
   (a) True (b) False
2. Indicator *Y* could be used to distinguish between the solutions of ammonium chloride and sodium acetate solution:
   (a) True (b) False
3. Indicator *X* could be used to distinguish between the solutions of ammonium chloride and sodium acetate solution:
   (a) True (b) False
4. Indicator *W* would be suitable for use in the determination of the concentration of acetic acid in white vinegar by base titration:
   (a) True (b) False
5. Indicator *U* could be used to distinguish between 0.1 *M* and 0.01 *M* solution of sulphuric acid:
   (a) True (b) False

• Passage 3

Chemists work with standardised solution, a solution whose concentration is known. The requirements to standardise the solution are:

1. *the volume of the solution.*
2. *the number of moles of solute in that volume.*

A primary standard solution is used in determining the molarity of a solution. To find the molarity of HCl, 0.317 g of Na_2CO_3, the primary standard dissolved in water, is used in titrating the solution of HCl. 22.9 mL of acid are required to neutralise the sodium carbonate. This is the needed volume (first requirement). The stoichiometric equation is used to know the second requirement.

$$2HCl(aq.) + Na_2CO_3(aq.) \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

Answer the following questions:

1. What is the molarity of HCl in the above case?
   (a) 0.261 *M* (b) 0.522 *M* (c) 0.1 *M* (d) 1 *M*
2. Equivalent mass of Na_2CO_3 in the above equation will be:
   (a) 106 (b) 53 (c) 26.5 (d) 13.25
3. The suitable indicator in the above titration will be:
   (a) phenolphthalein (b) methyl orange
   (c) litmus (d) bromothymol blue
4. Solution of Na_2CO_3 in water will be:
   (a) acidic (b) neutral
   (c) basic (d) cannot be predicted
5. What fraction of Na_2CO_3 will be neutralised by HCl in presence of phenolphthalein indicator?
   (a) 1/3 (b) 2/3 (c) 1/2 (d) 1/4

• Passage 4

0.5 g bleaching powder was suspended in water and excess KI is added. On acidifying with dil. H_2SO_4, I_2 was liberated which required 50 mL of N/10 hypo ($Na_2S_2O_3 \cdot 5H_2O$) in presence of starch. The reactions involved are:

I. $CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$
II. $2KI + Cl_2 \longrightarrow 2KCl + I_2$
III. $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Answer the following questions:

1. In the reaction (I), which one is reduced?
   (a) $CaOCl_2$ (b) H_2SO_4
   (c) Both (d) None of these

2. In the given titration, starch acts as:
   (a) oxidising agent (b) indicator
   (c) reducing agent (d) catalyst
3. In reaction (II), Cl_2 acts as:
   (a) reducing agent
   (b) oxidising agent
   (c) indicator
   (d) both oxidising agent and indicator
4. Percentage of available chlorine in bleaching powder is:
   (a) 35.5% (b) 71%
   (c) 17.25% (d) 50%
5. Starch forms iodo-starch complex in the given titration. The colour of the complex will be:
   (a) green (b) blue
   (c) pale yellow (d) milky white

• Passage 5

Hypo is the common name of sodium thiosulphate, with molecular formula $Na_2S_2O_3$. It is used as intermediate in iodometric as well as in iodimetric titrations.

Iodine and chlorine react with hypo in different ways as follows:

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

$$Cl_2(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + Cl^- + S$$

Suppose, 50 mL of 0.01 M $Na_2S_2O_3$ solution and 5×10^{-4} mol of Cl_2 are allowed to react according to the above equation. Hypo is also used in photography to dissolve AgBr, forming a complex compound.

$$2Na_2S_2O_3 + AgBr \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Answer the following questions:

1. The balanced chemical reaction with Cl_2 is:
   (a) $Cl_2 + 2Na_2S_2O_3 \longrightarrow 2NaCl + Na_2S_4O_6$
   (b) $Cl_2 + H_2O + Na_2S_2O_3 \longrightarrow Na_2SO_4 + 2HCl + S$
   (c) $Cl_2(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + S + Cl^-$
   (d) none of the above
2. Number of moles of $S_2O_3^{2-}$ present in the sample is:
   (a) 0.0005 (b) 0.01
   (c) 0.0025 (d) 0.02
3. What is the molarity of Na_2SO_4 formed in the reaction between $Na_2S_2O_3$ and Cl_2?
   (a) 0.08 M (b) 0.04 M
   (c) 0.02 M (d) 0.01 M
4. The process of photography, in which $Na_2S_2O_3$ is used, is called:
   (a) developing (b) image fixing
   (c) tonning (d) all of these
5. Oxidation state of silver in $Na_3[Ag(S_2O_3)_2]$ is:
   (a) 0 (b) +1
   (c) +2 (d) −1

• Passage 6

Equivalent mass of a substance may be calculated as,

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{n\text{-factor}} = \frac{\text{Atomic mass}}{n\text{-factor}}$$

n-factor = Basicity of acid or acidity of base
n-factor = Number of moles of electrons gained or lost per mole of oxidising or reducing agents
n-factor = Total positive or negative valency of a salt
n-factor = Valency of an ion.

Concept of n-factor is very important for redox as well as for non-redox reactions :

Answer the following questions:

1. When $KMnO_4$ is titrated against ferrous ammonium sulphate in acid medium then equivalent mass of $KMnO_4$ will be:
   (a) $\frac{\text{Molecular mass}}{10}$ (b) $\frac{\text{Molecular mass}}{5}$
   (c) $\frac{\text{Molecular mass}}{3}$ (d) $\frac{\text{Molecular mass}}{2}$
   [Hint:
   $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ n-factor = 5]
2. Equivalent mass of ferrous oxalate FeC_2O_4 in the following reaction is:
   $$FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2$$
   (a) $\frac{\text{Molecular mass}}{1}$ (b) $\frac{\text{Molecular mass}}{2}$
   (c) $\frac{\text{Molecular mass}}{3}$ (d) $\frac{\text{Molecular mass}}{4}$
   [Hint : $Fe^{2+} \longrightarrow Fe^{3+} + e^-$
   $$\begin{array}{l} C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \\ \hline FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2 + 3e^- \end{array} \quad n\text{-factor} = 3]$$
3. Equivalent mass of H_3PO_2 when it undergoes disproportionation to PH_3 and H_3PO_3 will be:
   (a) M.w./2 (b) M.w./4 (c) M.w./24 (d) 3M.w./4
   [Hint: $H_3PO_2 + 4H^+ + 4e^- \longrightarrow PH_3 + 2H_2O$ $n_1 = 4$
   $H_3PO_2 + H_2O \longrightarrow H_3PO_3 + 2H^+ + 2e^-$ $n_2 = 2$
   $$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2} = \frac{2 \times 4}{2 + 4} = \frac{8}{6} = \frac{4}{3}$$
   $$\text{E.w.} = \text{M.w.}/\frac{4}{3} = \frac{3\text{ M.w.}}{4}\ ]$$
4. BrO_3^- ion reacts with Br^- to form Br_2, in acid medium. The equivalent mass of Br_2 in this reaction is:
   (a) $\frac{4\text{M.w.}}{6}$ (b) $\frac{3\text{M.w.}}{5}$ (c) $\frac{5\text{M.w.}}{3}$ (d) $\frac{5\text{M.w.}}{8}$
   [Hint : $2BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O$ $n_1 = 10$
   $2Br^- \longrightarrow Br_2 + 6e^-$ $n_2 = 2$
   $$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2} = \frac{10 \times 2}{10 + 2} = \frac{20}{12} = \frac{5}{3}$$
   $$\text{E.w.} = \frac{\text{M.w.}}{5/3} = \frac{3\text{M.w.}}{5}\ ]$$

Answers

Passage 1.	1. (b)	2. (c)	3. (a)	4. (b)	5. (d)
Passage 2.	1. (b)	2. (b)	3. (a)	4. (b)	5. (b)
Passage 3.	1. (a)	2. (b)	3. (b)	4. (c)	5. (c)
Passage 4.	1. (d)	2. (b)	3. (b)	4. (a)	5. (b)
Passage 5.	1. (b)	2. (a)	3. (d)	4. (b)	5. (b)
Passage 6.	1. (b)	2. (c)	3. (d)	4. (b)	

SELF ASSESSMENT

ASSIGNMENT NO. 14

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. For decolorisation of 1 mole of $KMnO_4$, the moles of H_2O_2 required is: (AIEEE 2007)
(a) $\frac{1}{2}$ (b) $\frac{3}{2}$ (c) $\frac{5}{2}$ (d) $\frac{7}{2}$

2. If equal volume of 1 M $KMnO_4$ and 1 M $K_2Cr_2O_7$ solutions are allowed to oxidise Fe^{2+} to Fe^{3+} in acidic medium, then Fe^{2+} will be oxidised: [illegible]
(a) more by $KMnO_4$ (b) more by $K_2Cr_2O_7$
(c) equal in both cases (d) cannot be determined

3. MnO_2 on reaction with conc. HCl liberates chlorine; the liberated chlorine on treatment with aqueous KI gives iodine. The iodine is neutralized by 40 mL of 0.1 N hypo solution. The reaction is:
$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$
The amount of MnO_2 used in the reaction is:
(a) 10 g (b) 0.174 g (c) 1.74 g (d) 0.0174 g

4. 1.520 g of hydroxide of a metal on ignition gave 0.995 g of oxide. The equivalent mass of metal is:
(a) 1.52 (b) 0.995 (c) 190 (d) 9

5. Identify the incorrect statement regarding the volumetric estimation of $FeSO_4$:
(a) $KMnO_4$ can be used in aqueous HCl
(b) $K_2Cr_2O_7$ can be used in aqueous HCl
(c) $KMnO_4$ can be used in aqueous H_2SO_4
(d) $K_2Cr_2O_7$ can be used in aqueous H_2SO_4

6. When one gram mole of $KMnO_4$ is mixed with hydrochloric acid then, the volume of chlorine gas liberated at NTP will be:
(a) 11.2 litre (b) 22.4 litre (c) 56 litre (d) 44.8 litre
[**Hint:** The reaction between $KMnO_4$ and HCl may be given as:
$$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O]$$

7. 0.7 g of $Na_2CO_3.xH_2O$ was dissolved in water to make 100 mL solution, 20 mL of this solution required 19.8 mL of 0.1 N HCl for complete neutralisation. The value of x is:
(a) 5 (b) 2
(c) 3 (d) 4

8. 0.5 g of impure ammonium chloride was heated with caustic soda solution to evolve ammonia gas, the gas is absorbed in 150 mL of $N/5$ H_2SO_4 solution. Excess sulphuric acid required 20 mL of 1 N NaOH for complete neutralization. The percentage of NH_3 in the ammonium chloride is:
(a) 68% (b) 34% (c) 48% (d) 17%

9. One mole of a mixture of CO and CO_2 requires exactly 20 g of NaOH to convert all the CO_2 into Na_2CO_3. How many more grams of NaOH would it require for conversion into Na_2CO_3 if the mixture (one mole) is completely oxidised to CO_2?
(a) 60 g (b) 80 g (c) 40 g (d) 20 g

10. 0.1 litre of 0.01M $KMnO_4$ is used by 100 mL of H_2O_2 in acidic medium. Volume of same $KMnO_4$ required in alkaline medium to oxidise 0.1 litre of some H_2O_2 will be:
(a) $\frac{100}{3}$ mL (b) $\frac{500}{3}$ mL (c) $\frac{300}{5}$ mL (d) $\frac{400}{3}$ mL

SECTION-II

Multiple Answers Type Objective Questions

11. One mole of acidic $KMnO_4$ reacts with:
(a) $\frac{5}{3}$ mol of FeC_2O_4 (b) $\frac{5}{2}$ mol of SO_2
(c) 4 mol of FeS (d) 1 mol of H_2SO_4

12. Boric acid (H_3BO_3) is:
(a) tribasic (b) dibasic (c) monobasic (d) aprotic

13. 0.6 mol $K_2Cr_2O_7$, in acid medium can oxidise:
(a) 3.6 mol $FeSO_4$ to $Fe_2(SO_4)_3$
(b) 0.1 mol $FeSO_4$ to $Fe_2(SO_4)_3$
(c) 0.05 mol of Sn^{2+} to Sn^{4+}
(d) 1.8 mol of Sn^{2+} to Sn^{4+}

14. Which of the following statement(s) is/are correct?
(a) H_2SO_4 and H_3PO_3 both are dibasic
(b) H_3BO_3 and H_3PO_4 both are tribasic
(c) H_3BO_3 and H_3PO_2 both are monobasic
(d) HNO_3 and HCl both are monobasic

15. In the titration of CH_3COOH against NaOH, we cannot use the:
(a) methyl orange (b) methyl red
(c) phenolphthalein (d) bromothymol blue

SECTION-III

Assertion-Reason Type Questions

This section contains 3 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** Equivalent mass of H_3PO_2 is equal to its molecular mass.

Because

Statement-2: H_3PO_2 is a monobasic acid.

17. **Statement-1:** When Na_2CO_3 is titrated against HCl in presence of phenolphthalein indicator, it is converted to NaCl.

Because

Statement-2: Phenolphthalein shows colour change in the pH range of (3.5 — 4.6).

18. **Statement-1:** 1 mol of H_2SO_4 is neutralised by 2 mol of NaOH; however, 1 equivalent of H_2SO_4 is neutralised by 1 equivalent of NaOH.

Because

Statement-2: Equivalent mass of H_2SO_4 is half of its molecular mass, however, the equivalent mass of NaOH is equal to its molecular mass.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbles as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correctly bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

Match the Column-I with Column-II:

[EAMCET (Med.) 2007]

Column-I	Column-II
(a) 10 volume H_2O_2	(p) Perhydrol
(b) 20 volume H_2O_2	(q) 5.358 *N*
(c) 30 volume H_2O_2	(r) 1.785 *M*
(d) 100 volume H_2O_2	(s) 3.03%

20. Match the Column-I with Column-II:

Column-I (Acid)	Column-II (Information)
(a) CH_3COOH	(p) Tribasic (E_w = M.w./3)
(b) H_3PO_4	(q) Dibasic reducing
(c) H_2SO_4	(r) Dibasic (E_w = M.w./2)
(d) H_3PO_3	(s) Monobasic (E_w = M.w.)

21. Match the Column-I with Column-II:

Column-I (Reaction)	Column-II (Equivalent mass of reactant)
(a) $NH_3 \longrightarrow NO_3^-$	(p) M.w./20
(b) $Fe_2S_3 \longrightarrow FeSO_4 + SO_2$	(q) M.w./2
(c) $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$	(r) M.w./8
(d) $CuS \longrightarrow CuSO_4$	(s) 50

Answers

1. (c) **2.** (a) **3.** (b) **4.** (d) **5.** (a) **6.** (c) **7.** (b) **8.** (b)
9. (a) **10.** (b) **11.** (a, b) **12.** (c, d) **13.** (a, d) **14.** (a, c, d) **15.** (a, b, d)
16. (a) **17.** (c) **18.** (b) **19.** (a-s) (b-r) (c-q) (d-p) **20.** (a-s) (b-p) (c-r) (d-q,r)
21. (a-r) (b-p) (c-q,s) (d-r)