

converted to
 NaHCO_3

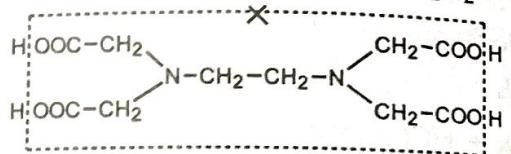
first end point is reached

The second step is the same as in the previous one.

Now using the above equations, one can calculate the amounts Na_2CO_3 , NaHCO_3 and NaOH , whatever is given in the sample, as illustrated by the following examples (Ex. 44 to Ex. 47).

EDTA Titrations

The estimation of many metal ions like Ca^{2+} , Mg^{2+} , Zn^{2+} , etc., may be carried out by complexometric titrations. These metallic ions form complexes with ethylenediaminetetraacetic acid (EDTA). EDTA is a tetrabasic acid, represented by H_4X and its disodium salt is represented by $\text{Na}_2\text{H}_2\text{X}$



EDTA has an advantage of forming very stable complexes so that small amounts of cations can be detected. Disodium salt affords the complex-forming ions, H_2X^{2-} in aqueous medium. These ions form a complex with dipositive metal ions on a one-to-one basis. In this titration the pH is controlled by using suitable buffers. The end point is detected by a suitable metal-ion indicator which forms a complex with specific metal ions having different colour from the free indicator. Ex 73 is just one of the vast number of applications of this type of titrations to analytical problems.

Useful Formulae for Volumetric Calculations

1. m.e. = normality \times volume in millilitres.

2. At the end point of titration, the two titrants, say 1 and 2, have the same number of milliequivalents, i.e., $N_1 V_1 = N_2 V_2$, volumes being in mL.

3. No. of equivalents = $\frac{\text{m.e.}}{1000}$.

4. (i) No. of equivalents = $\frac{\text{weight in grams}}{\text{equivalent weight}}$.

(ii) No. of equivalents for a gas

$$= \frac{\text{volume at NTP}}{\text{equivalent volume (vol. of 1 eq. at NTP)}}$$

5. Grams per litre = normality \times equivalent weight.

6. (i) Normality = molarity \times factor relating mol. wt. and eq. wt.

(ii) No. of equivalents = no. of moles \times factor relating mol. wt. and eq. wt.

The factors relating mol. wt. and eq. wt. in case of acids and bases are respectively the basicity and acidity; in oxidants and reductants, it is the change in oxidation number per mole, and so on.

7. (i) In a given reaction $a A + b B \rightarrow m M + n N$,
eq. of A = eq. of B = eq. of M = eq. of N
or m.e. of A = m.e. of B = m.e. of M = m.e. of N.

(ii) In a compound $M_x N_y$,
equivalents of $M_x N_y$ = equivalents of M = equivalents of N
or m.e. of $M_x N_y$ = m.e. of M = m.e. of N.

EXAMPLES

Ex. 1. Calculate the number of m.e. of H_2SO_4 present in 10 mL of N/2 H_2SO_4 solution.

Solution : Number of m.e. = normality \times volume in mL ... (Eqn. 1)
 $= \frac{1}{2} \times 10 = 5$.

Ex. 2. Calculate the number of m.e. and equivalents of NaOH present in 1 litre of N/10 NaOH solution.

Solution : Number of m.e. = normality \times volume in mL ... (Eqn. 1)
 $= \frac{1}{10} \times 1000 = 100$.

Number of equivalents = $\frac{\text{no. of m.e.}}{1000}$... (Eqn. 3)
 $= \frac{100}{1000} = 0.10$.

Ex. 3. Calculate the weight of NaOH in grams in Example 2.

Solution : Weight in g = equivalents \times eq. wt.
 $= 0.1 \times 40 = 4$ g. ... (Eqn. 4)

Ex. 4. Calculate number of m.e. of the acids present in

- (i) 100 mL of 0.5 M oxalic acid solution,
- (ii) 50 mL of 0.1 M sulphuric acid solution.

- Solution :* Normality = molarity × factor relating mol. wt. and eq. wt.
- Normality of oxalic acid = $0.5 \times 2 = 1$ N
m.e. of oxalic acid = normality × vol. in mL = $1 \times 100 = 100$... (Eqn. 2)
 - Normality of sulphuric acid = $0.1 \times 2 = 0.2$ N
m.e. of sulphuric acid = $0.2 \times 50 = 10$.

Ex. 5. A 100 mL solution of KOH contains 10 milliequivalents of KOH. Calculate its strength in normality and grams/litre.

Solution : Normality = $\frac{\text{no. of m.e.}}{\text{volume in mL}}$... (Eqn. 1)

$$= \frac{10}{100} = 0.1.$$

∴ strength of the solution = N/10. Again,

$$\text{strength in grams/litre} = \text{normality} \times \text{eq. wt.} = \frac{1}{10} \times 56 = 5.6 \text{ grams/litre}$$

$$\left(\text{eq. wt. of KOH} = \frac{\text{molecular wt.}}{\text{acidity}} = \frac{56}{1} = 56 \right)$$

Ex. 6. Calculate the normality of a solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ containing 2.4 g/100 mL (Fe = 56, S = 32, O = 16, H = 1) which converts to ferric form in a reaction.

Solution : Weight per 100 mL = 2.4 g.

$$\text{Equivalents/100 mL} = \frac{2.4}{278} = 0.0086. \quad (\text{eq. wt. of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278)$$

$$\left. \begin{array}{l} \text{As } \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \\ \text{eq. wt. of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{\text{molecular wt.}}{\text{change in ON}} = \frac{278}{1} \end{array} \right\}$$

$$\text{Thus m.e. per 100 mL} = 0.0086 \times 1000 = 8.6$$

$$\begin{aligned} \text{Normality of solution} &= \frac{\text{m.e.}}{\text{volume in mL}} \\ &= \frac{8.6}{100} \\ &= 0.086 \text{ N.} \end{aligned}$$

Ex. 7. Calculate the number of milliequivalents, gram eq., weight in grams and number of moles contained in 10 litres of 0.5 M Ba(OH)_2 solution. ($\text{Ba} = 137$)

Solution : Normality of Ba(OH)_2 solution = molarity × acidity
= 0.5×2

$$\begin{aligned} \text{m.e. of the solution} &= \text{normality} \times \text{vol. in mL} \\ &= 1 \times 10000 \\ &= 10000. \end{aligned}$$

$$\begin{aligned} \text{Equivalent of the solution} &= \frac{\text{m.e.}}{1000} \\ &= \frac{10000}{1000} \\ &= 10. \end{aligned}$$

$$\begin{aligned} \text{Weight of } \text{Ba(OH)}_2 \text{ in solution} &= \text{equivalents} \times \text{eq. wt.} \\ &= 10 \times 85.5 \\ &= 855 \text{ g.} \end{aligned}$$

$$\left\{ \text{equivalent wt. of } \text{Ba(OH)}_2 = \frac{\text{mol. wt.}}{\text{acidity}} = \frac{171}{2} = 85.5 \right\}$$

$$\begin{aligned} \text{Moles of } \text{Ba(OH)}_2 \text{ solution} &= \frac{\text{wt. in grams}}{\text{mol. wt.}} \\ &= \frac{855}{171} = 5.00 \text{ moles.} \end{aligned}$$

Ex. 8. What is the strength in grams/litre of a solution of H_2SO_4 , 12 cc of which neutralises 15 cc of $\frac{N}{10}$ NaOH solution?

$$\text{Solution : m.e. of NaOH solution} = \frac{1}{10} \times 15 = 1.5$$

$$\text{m.e. of 12 cc of } \text{H}_2\text{SO}_4 = 1.5$$

$$\therefore \text{normality of } \text{H}_2\text{SO}_4 = \frac{1.5}{12}$$

$$\begin{aligned} \text{Strength in grams/litre} &= \text{normality} \times \text{eq. wt.} \\ &= \frac{1.5}{12} \times 49 \text{ grams/litre} \end{aligned}$$

$$= 6.12 \text{ grams/litre.}$$

$$\left\{ \text{eq. wt. of } \text{H}_2\text{SO}_4 = \frac{\text{mol. wt.}}{\text{basicity}} = \frac{98}{2} = 49 \right\}$$

Ex. 9. What weight of KMnO_4 will be required to prepare 250 mL of its $\frac{N}{10}$ solution if eq. wt. of KMnO_4 is 31.6?

$$\text{Solution : m.e. of } \text{KMnO}_4 \text{ solution} = \frac{1}{10} \times 250 = 25$$

... (Eqn. 1)

Hence current =
the part going along



(ii) When Cu
As shown
Further simplification

$$\text{Equivalent of } \text{KMnO}_4 = \frac{25}{1000} = 0.025.$$

Wt. of KMnO_4 solution required to prepare

$$250 \text{ mL of } \frac{N}{10} \text{ solution} = \text{eq. wt.} \times \text{eq. wt.}$$

$$= 0.025 \times 31.6$$

$$= 0.79 \text{ g.}$$

Ex. 10. 100 mL of 0.6 N H_2SO_4 and 200 mL of 0.3 N HCl were mixed together. What will be the normality of the resulting solution?

$$\text{Solution : m.e. of } \text{H}_2\text{SO}_4 \text{ solution} = 0.6 \times 100 = 60$$

$$\text{m.e. of HCl solution} = 0.3 \times 200 = 60$$

$$\therefore \text{m.e. of } 300 \text{ mL (100 + 200)} \text{ of acid mixture} = 60 + 60 = 120.$$

$$\text{Normality of the resulting solution} = \frac{\text{m.e.}}{\text{total vol.}}$$

$$= \frac{120}{300} = \frac{2}{5} \text{ N.}$$

Ex. 11. What will be the normality of the resulting solution of Example 10 if it is diluted to 600 mL?

Solution : In this problem it should be remembered that the m.e. of a solution does not change on dilution.

Thus, m.e. of 600 mL of the resulting solution = 120 and therefore, normality of this diluted solution

$$= \frac{120}{600} = \frac{N}{5}$$

Ex. 12. A sample of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ weighing 0.62 g is added to 100 mL of 0.1 N H_2SO_4 . Will the resulting solution be acidic, basic or neutral?

$$\text{Solution : Equivalents of } \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = \frac{0.62}{62} = 0.01.$$

$$\left(\text{eq. wt. of } \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = \frac{124}{2} = 62 \right)$$

$$\text{m.e. of } \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = 0.01 \times 1000 = 10$$

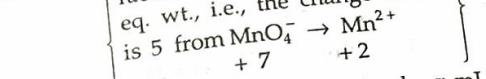
$$\text{m.e. of } \text{H}_2\text{SO}_4 = 0.1 \times 100 = 10.$$

Since the m.e. of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ is equal to that of H_2SO_4 , the resulting solution will be neutral.

Ex. 13. How many millilitres of a 0.05 M KMnO_4 solution are required to oxidise 2.0 g of FeSO_4 in a dilute acid solution? ($\text{Fe} = 56, \text{S} = 32, \text{O} = 16$)

$$\text{Normality of } \text{KMnO}_4 \text{ solution} = 0.05 \times 5 = 0.25 \text{ N} \quad \dots (\text{Eqn. 6})$$

Solution : Normality of KMnO_4 solution = factor relating mol. wt. and eq. wt., i.e., the change in ON is 5 from $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$



Let the volume of KMnO_4 solution be v mL.

$$\text{Thus m.e. of } \text{KMnO}_4 = 0.25 v.$$

$$\text{Equivalents of } \text{FeSO}_4 = \frac{2}{152}$$

$\left. \begin{array}{l} \text{In the above reaction,} \\ \text{eq. weight of } \text{FeSO}_4 = \frac{\text{molecular wt.}}{\text{change in ON}} = \frac{152}{1} = 152 \end{array} \right\}$

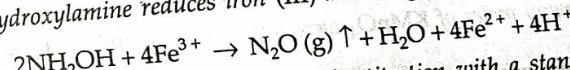
$$\text{m.e. of } \text{FeSO}_4 = \frac{2}{152} \times 1000$$

$$\text{Now, m.e. of } \text{KMnO}_4 = \text{m.e. of } \text{FeSO}_4$$

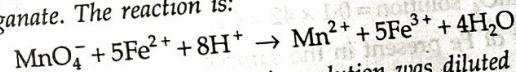
$$0.25 v = \frac{2}{152} \times 1000.$$

$$v = 52.63 \text{ mL.}$$

Ex. 14. Hydroxylamine reduces iron (III) according to the equation:



Iron (II) thus produced is estimated by titration with a standard solution of permanganate. The reaction is:



A 10 mL sample of hydroxylamine solution was diluted to 1 litre. 50 mL of this diluted solution was boiled with an 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 weight of hydroxylamine in one litre of the original solution.

Solution : m.e. of 50 mL of the diluted solution of NH_2OH

$$= \text{m.e. of } \text{Fe}^{3+}$$

$$= \text{m.e. of } \text{Fe}^{2+} \text{ produced}$$

$$= \text{m.e. of } \text{KMnO}_4 \text{ solution}$$

$$= 0.1 \times 12 = 1.2$$

... (Eqn. 1)

$$\left\{ \begin{array}{l} \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \text{ change in ON} = 5 \\ +7 \quad \quad \quad +2 \\ \therefore \text{normality} = 5 \times \text{molarity} = 5 \times 0.02 = 0.1 \end{array} \right\}$$

$\therefore \text{m.e. of 1000 mL of diluted solution of NH}_2\text{OH} = \frac{1.2}{50} \times 1000 = 24.$

$\therefore \text{m.e. of 10 mL of original solution of NH}_2\text{OH} = 24.$

$\therefore \text{m.e. of 1000 mL of original solution of NH}_2\text{OH} = 2400.$

$\therefore \text{number of equivalents per litre} = \frac{2400}{1000}. \quad \dots (\text{Eqn. 3})$

$\therefore \text{strength of NH}_2\text{OH in g/L} = \frac{2400}{1000} \times 16.5 = 39.6. \quad \dots (\text{Eqn. 4})$

$\left\{ \begin{array}{l} \text{eq. wt. of NH}_2\text{OH from the given reaction} = \frac{33}{2} = 16.5 \\ \text{eq. wt. of NH}_2\text{OH} \end{array} \right\}$

Ex. 15. In a quantitative determination of iron in an ore, an analyst converted 0.42 g of the ore into its ferrous form. This required 42.00 mL of 0.1 N solution of KMnO₄ for titration.

- How many milliequivalents of KMnO₄ does 42.00 mL of 0.1 N solution represent?
- How many equivalents of iron were present in the sample of the ore taken for analysis?
- How many grams of iron were present in the sample?
- What is the percentage of iron in the ore?
- What is the molarity of KMnO₄ solution used?
- How many moles of KMnO₄ were used for titration? (Fe = 56)

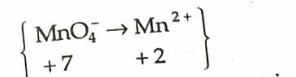
Solution : In this problem Fe²⁺ is oxidised to Fe³⁺ by KMnO₄.

- m.e. of KMnO₄ solution = $0.1 \times 42 = 4.2. \quad \dots (\text{Eqn. 1})$
- Equivalent of Fe present in the sample
 $= \text{equivalent of KMnO}_4 \text{ solution} \quad \dots (\text{Eqn. 2})$
 $= \frac{\text{m.e. of KMnO}_4 \text{ solution}}{1000} \quad \dots (\text{Eqn. 3})$
 $= \frac{4.2}{1000} = 0.0042.$
- Wt. of iron = equivalent \times eq. wt.
 $= 0.0042 \times 56 = 0.2352 \text{ g.} \quad \dots (\text{Eqn. 4})$

$$\left\{ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \therefore \text{eq. wt. of Fe} = \frac{\text{at. wt.}}{\text{change in ON}} = \frac{56}{1} = 56 \right\}$$

(iv) % of iron = $\frac{0.2352}{0.42} \times 100 = 56.00\%.$

(v) Molarity of KMnO₄ = $\frac{\text{normality}}{\text{factor relating mol. wt. and eq. wt.}}$
i.e., change in ON ... (Eqn. 6i)
 $= \frac{0.1}{5} = 0.02 \text{ M.}$



(vi) Moles of KMnO₄ = $\frac{\text{equivalents}}{\text{factor relating mol. wt. and eq. wt.}}$... (Eqn. 6ii)
 $= \frac{0.0042}{5} = 0.00084 \text{ mole.}$

[Note: Thus we see how the equations 1 to 7 have been put into use in the problems given above. However, application of these equations and the ability to use them come only from practice. The students are advised to apply the said rules in as many problems as possible.]

Ex. 16. A 0.5-g sample of an iron-containing mineral, mainly in the form of CuFeS₂, was reduced suitably to convert all the ferric iron into ferrous form and was obtained as a solution. In the absence of any interfering matter, the solution required 42 mL of 0.01 M K₂Cr₂O₇ solution for titration. Calculate the percentage of CuFeS₂ in the mineral. (Cu = 63.5, Fe = 55.8, S = 32, O = 16)

Solution : In this problem Fe²⁺ is oxidised by K₂Cr₂O₇ to Fe³⁺.

Normality of K₂Cr₂O₇ solution = molarity \times ON change per mole ... (Eqn. 6i)

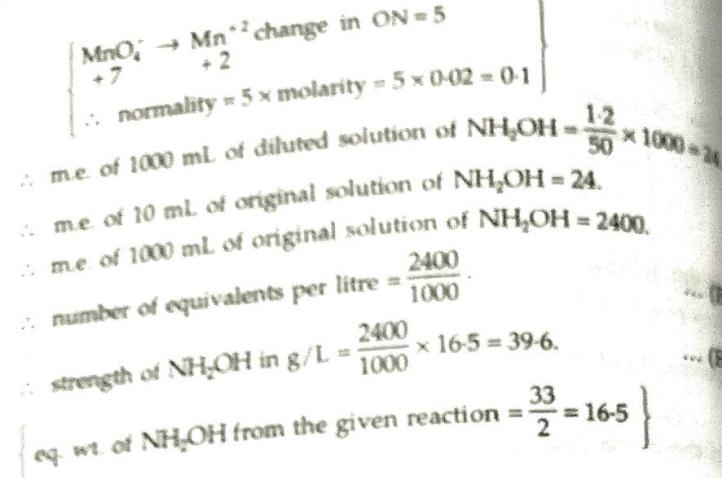
$= 0.01 \times 6 = 0.06$

$$\left\{ \begin{array}{l} \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}; \text{change in ON} = 6 \\ +12 \quad \quad \quad +6 \end{array} \right\}$$

$\text{m.e. of K}_2\text{Cr}_2\text{O}_7 = 0.06 \times 42 = 2.52. \quad \dots (\text{Eqn. 1})$

$$\therefore \text{m.e. of CuFeS}_2 = \text{m.e. of Fe}^{2+} \text{ salt} \\ = \text{m.e. of K}_2\text{Cr}_2\text{O}_7 \\ = 2.52. \quad \dots (\text{Eqn. 2})$$

$$\text{Equivalents of CuFeS}_2 = \frac{2.52}{1000}. \quad \dots (\text{Eqn. 3})$$



Ex. 15. In a quantitative determination of iron in an ore, an analyst converted 0.4 g of the ore into its ferrous form. This required 42.00 mL of 0.1 N solution of KMnO_4 for titration.

- How many milliequivalents of KMnO_4 does 42.00 mL of 0.1 N solution represent?
- How many equivalents of iron were present in the sample of the ore used for analysis?
- How many grams of iron were present in the sample?
- What is the percentage of iron in the ore?
- What is the molarity of KMnO_4 solution used?
- How many moles of KMnO_4 were used for titration? (Fe = 56)

Solution: In this problem Fe^{2+} is oxidised to Fe^{3+} by KMnO_4 .

$$(i) \text{m.e. of } \text{KMnO}_4 \text{ solution} = 0.1 \times 42 = 4.2. \quad \dots (\text{Eqn. 1})$$

$$(ii) \text{Equivalent of Fe present in the sample} \quad \dots (\text{Eqn. 2})$$

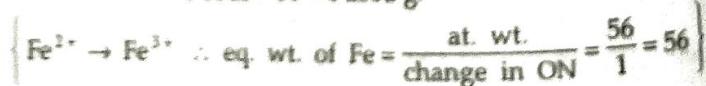
$$= \text{equivalent of } \text{KMnO}_4 \text{ solution} \quad \dots (\text{Eqn. 2})$$

$$= \frac{\text{m.e. of } \text{KMnO}_4 \text{ solution}}{1000} \quad \dots (\text{Eqn. 2})$$

$$= \frac{4.2}{1000} = 0.0042. \quad \dots (\text{Eqn. 2})$$

$$(iii) \text{Wt. of iron} = \text{equivalent} \times \text{eq. wt.} \quad \dots (\text{Eqn. 3})$$

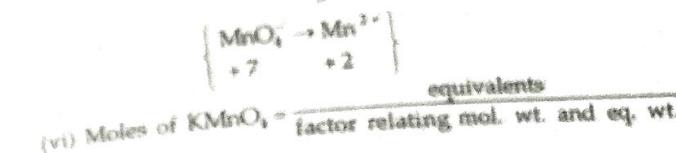
$$= 0.0042 \times 56 = 0.2352 \text{ g.}$$



$$(iv) \% \text{ of iron} = \frac{0.2352}{0.42} \times 100 = 56.00\%.$$

$$(v) \text{Molarity of } \text{KMnO}_4 = \frac{\text{factor relating mol. wt. and eq. wt.}}{\text{i.e., change in ON}} \quad \dots (\text{Eqn. 6})$$

$$= \frac{0.1}{5} = 0.02 \text{ M.}$$



$$= \frac{0.0042}{5} = 0.00084 \text{ mole.}$$

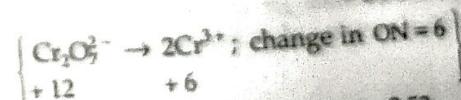
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Ex. 16. A 0.5-g sample of an iron-containing mineral, mainly in the form of CuFeS_2 , was reduced suitably to convert all the ferric iron into ferrous form and was obtained as a solution. In the absence of any interfering matter, the solution required 42 mL of 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution for titration. Calculate the percentage of CuFeS_2 in the mineral. (Cu = 63.5, Fe = 55.8, S = 32, O = 16)

Solution: In this problem Fe^{2+} is oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ to Fe^{3+} .

$$\text{Normality of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ solution} = \text{molarity} \times \text{ON change per mole} \quad \dots (\text{Eqn. 6})$$

$$= 0.01 \times 6 = 0.06$$



$$\text{m.e. of } \text{K}_2\text{Cr}_2\text{O}_7 = 0.06 \times 42 = 2.52. \quad \dots (\text{Eqn. 1})$$

$$\therefore \text{m.e. of } \text{CuFeS}_2 = \text{m.e. of } \text{Fe}^{2+} \text{ salt}$$

$$= \text{m.e. of } \text{K}_2\text{Cr}_2\text{O}_7$$

$$= 2.52 \quad \dots (\text{Eqn. 2})$$

$$\text{Equivalents of } \text{CuFeS}_2 = \frac{2.52}{1000}. \quad \dots (\text{Eqn. 3})$$

$$\text{Weight of } \text{CuFeS}_2 \text{ in the mineral} = \frac{2.52}{1000} \times 183.3 \\ = 0.4619 \text{ g}$$

... (Eqn. 4)

{ eq. weight of CuFeS_2 is equal to its molecular weight, i.e., 183.3
because the change in ON of Fe is one ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$) }

$$\text{Percentage of } \text{CuFeS}_2 \text{ in the mineral} = \frac{0.4619 \times 100}{0.5} = 92.83\%$$

Ex. 17. 25 grams of a sample of ferrous sulphate was dissolved in dilute sulphuric acid and water and its volume was made up to 1 litre. 25 mL of this solution required 20 mL of $\frac{N}{10}$ KMnO₄ solution for complete oxidation. Calculate the percentage of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the sample.

$$\text{Solution : m.e. of KMnO}_4 \text{ solution} = \frac{1}{10} \times 20 = 2. \quad \dots (\text{Eqn. 1})$$

$$\therefore \text{m.e. of 25 mL of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O solution} = 2.$$

$$\therefore \text{m.e. of 1000 mL of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O solution} = \frac{2}{25} \times 1000 = 80.$$

$$\text{Equivalents of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{80}{1000}. \quad \dots (\text{Eqn. 3})$$

$$\therefore \text{weight of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \text{equivalent} \times \text{eq. wt.} \\ = \frac{80}{1000} \times 278 = 22.24 \text{ g.}$$

$$\left\{ \text{As } \text{Fe}^{2+} \rightarrow \text{Fe}^{3+}, \text{ eq. wt. of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{\text{mol. wt.}}{\text{change in ON}} = \frac{278}{1}. \right\}$$

$$\text{Thus the percentage of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O in the sample} = \frac{22.24}{25} \times 100 \\ = 88.96\%.$$

Ex. 18. 5.39 g of a mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and anhydrous ferric sulphate requires 80 mL of 0.125 N permanganate solution for complete conversion to ferric sulphate. Calculate the individual weights of each component of the original mixture.

Solution : Ferrous sulphate present in the mixture is oxidised to ferric sulphate by permanganate solution. Let the weight of ferrous sulphate be x gram.

$$\text{m.e. of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \text{m.e. of permanganate solution} \\ = 0.125 \times 80 = 10.$$

$$\therefore \text{eq. of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{10}{1000}. \quad \dots (\text{Eqn. 3})$$

$$\therefore \text{wt. of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \text{eq.} \times \text{eq. wt.} \\ = \frac{10}{1000} \times 278 \\ = 2.78 \text{ g} \\ \text{and wt. of } \text{Fe}_2(\text{SO}_4)_3 = (5.39 - 2.78) \text{ g} \\ = 2.61 \text{ g.}$$

Ex. 19. 100 g of a sample of HCl solution of relative density 1.17 contains 33.4 g of HCl. What volume of this HCl solution will be required to neutralise exactly 5 litres of $\frac{N}{10}$ NaOH solution?

$$\text{Solution : Volume of HCl solution} = \frac{100}{1.17} \text{ mL.}$$

$$\left(\text{density} = \frac{\text{mass}}{\text{volume}} \right)$$

$$\text{Equivalents of HCl} = \frac{33.4}{36.5}$$

$$(\text{eq. wt. of HCl} = 36.5)$$

$$\text{m.e. of HCl} = \frac{33.4}{36.5} \times 1000. \quad \dots (\text{Eqn. 3})$$

$$\text{Normality of HCl} = \frac{\text{m.e.}}{\text{volume in mL}} \quad \dots (\text{Eqn. 1}) \\ = \frac{33.4}{36.5} \times 1000 \times \frac{1.17}{100} \\ = 10.7 \text{ N.}$$

Now let the volume of HCl, of normality calculated above, required to neutralise exactly the given NaOH solution be v mL.

$$\text{m.e. of HCl} = \text{m.e. of NaOH}$$

$$10.7 \times v = \frac{1}{10} \times 5000$$

$$10.7 \times v = 500.$$

$$\therefore v = 46.7 \text{ mL.}$$

Ex. 20. Derive a formula to calculate the normality of an acid of sp. gr. 'd' containing $x\%$ by weight. The eq. wt. of the acid is E.

Solution : 100 g of the acid solution contains x g of the acid or $\frac{100}{d}$ mL of the acid solution contains $\frac{x}{E}$ eq. of the acid ... (Eqn. 4i)

or $\frac{100}{d}$ mL solution contains $\frac{x}{E} \times 1000$ m.e. of the acid ... (Eqn. 3)

$$\text{Normality of acid} = \frac{\text{m.e.}}{\text{volume in mL}}$$

$$= \frac{x}{E} \times 1000 \times \frac{d}{100}$$

$$\therefore \text{normality} = \frac{10 \times x \times d}{E}$$

Ex. 21. A bottle of commercial sulphuric acid (density 1.787 g/mL) is labelled 86% by weight. What is the molarity of the acid? What volume of the acid to be used to make 1 litre of 0.2 M H_2SO_4 ?

Solution : 100 g of H_2SO_4 solution contains 86 g of H_2SO_4 .

$$\therefore \frac{100}{1.787} \text{ mL } \text{H}_2\text{SO}_4 \text{ solution contains } \frac{86}{98} \text{ mole.}$$

$$\therefore 1000 \text{ mL } \text{H}_2\text{SO}_4 \text{ solution contains } \frac{86}{98} \times \frac{1.787}{100} \times 1000.$$

$$= 15.68 \text{ M.}$$

$$\therefore \text{normality of } \text{H}_2\text{SO}_4 = (2 \times 15.68) \text{ N} = 31.36 \text{ N.}$$

(basicity of $\text{H}_2\text{SO}_4 = 2$)

Suppose that v mL of 31.36 N H_2SO_4 is to be used to make 1000 mL 0.2 M (i.e., 0.4 N) H_2SO_4 .

$$\therefore \text{m.e. of } v \text{ mL of } 31.36 \text{ N } \text{H}_2\text{SO}_4 = \text{m.e. of } 1000 \text{ mL of } 0.4 \text{ N } \text{H}_2\text{SO}_4$$

$$31.36 \times v = 0.4 \times 1000$$

$$v = \frac{0.4 \times 1000}{31.36} = 12.75 \text{ mL.}$$

Ex. 22. How many millilitres of concentrated sulphuric acid of sp. gr. 1.84 containing 98% H_2SO_4 by weight are required to prepare 200 mL of 0.50 N solution?

Solution : 98% of H_2SO_4 by weight means 100 g H_2SO_4 solution contains 98% of H_2SO_4 .

$$\text{Volume of } 100 \text{ g of } \text{H}_2\text{SO}_4 = \frac{100}{1.84} \text{ mL}$$

$$\text{i.e., } \frac{100}{1.84} \text{ mL of } \text{H}_2\text{SO}_4 \text{ solution contains } 98.00 \text{ g of } \text{H}_2\text{SO}_4.$$

$$\text{Equivalents of } \text{H}_2\text{SO}_4 = \frac{98}{49} = 2$$

$$(\text{eq. wt. of } \text{H}_2\text{SO}_4 = 49)$$

$$\text{m.e. of } \text{H}_2\text{SO}_4 = 2 \times 1000 = 2000.$$

$$\text{Normality of } \text{H}_2\text{SO}_4 \text{ solution} = \frac{\text{m.e.}}{\text{volume in mL}}$$

$$= \frac{2000}{100/1.84} = 36.8 \text{ N.}$$

Let the volume of H_2SO_4 of normality calculated above to prepare 200 mL of 0.5 N H_2SO_4 solution be v mL.

$$\therefore \text{m.e. of } v \text{ mL of } \text{H}_2\text{SO}_4 \text{ of normality } 36.8 \text{ N} = 36.8 \text{ v} \quad \dots (\text{Eqn. 1})$$

$$\text{and m.e. of } 200 \text{ mL of } \text{H}_2\text{SO}_4 \text{ of normality } 0.5 \text{ N} = 0.5 \times 200$$

$$= 100.$$

Since both the solutions of H_2SO_4 should have the same number of m.e. we have,

$$36.8 v = 100.$$

$$\therefore v = \frac{100}{36.8} = 2.72 \text{ mL.}$$

Ex. 23. A piece of aluminium weighing 2.7 g is heated with 75.0 mL of sulphuric acid (sp. gr. 1.18 containing 24.7% H_2SO_4 by weight). 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 : Normality of the given $\text{H}_2\text{SO}_4 = 5.95 \text{ N}$
(calculated as in Example 20 or 21)

$$\therefore \text{m.e. of } 75 \text{ mL of } \text{H}_2\text{SO}_4 = 5.95 \times 75$$

$$= 446.25. \quad \dots (\text{Eqn. 1})$$

$$\text{Equivalent of Al} = \frac{2.7}{9} = 0.3.$$

$$\left\{ \text{eq. wt. of Al} = \frac{\text{at. wt.}}{\text{valency}} = \frac{27}{3} = 9 \right\}$$

$$\therefore \text{m.e. of Al} = 0.3 \times 1000 = 300.$$

Since 300 m.e. of Al will react with 300 m.e. of H_2SO_4

$$\begin{aligned} \text{m.e. of free } \text{H}_2\text{SO}_4 &= \text{total m.e. of } \text{H}_2\text{SO}_4 - 300 \\ &= 446.25 - 300 \\ &= 146.25. \end{aligned}$$

Now the free H_2SO_4 is diluted to 400 mL and we know that the m.e. of H_2SO_4 does not change on dilution.

\therefore normality of the diluted free H_2SO_4 in the resulting solution

$$\begin{aligned} &= \frac{\text{m.e. of free } \text{H}_2\text{SO}_4}{\text{volume (mL)}} \\ &= \frac{146.25}{400} = 0.366 \text{ N.} \end{aligned}$$

$$\therefore \text{molarity} = \frac{0.366}{2} = 0.183 \text{ M}$$

(basicity of $\text{H}_2\text{SO}_4 = 2$)

Ex. 24. Two litres of ammonia at 30°C and 0.90 atmospheric pressure neutralise 134 mL of a solution of sulphuric acid. Calculate the normality of the acid.

Solution : Volume of NH_3 at NTP = $\frac{0.9 \times 2 \times 273}{303}$ lit. = 1.622 lit.

$$\left(\because \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \right)$$

$$\therefore \text{number of moles of } \text{NH}_3 = \frac{\text{volume at NTP (litres)}}{22.4}$$

$$= \frac{1.622}{22.4} = 0.0724.$$

Number of equivalents of NH_3

= number of moles \times factor relating mol. wt. and eq. wt.

$$= 0.0724.$$

... (Eqn. 6)

{ according to the reaction $2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$,
eq. wt. of NH_3 is equal to its mol. wt. }

\therefore m.e. of NH_3 = equivalent \times 1000

$$= 0.0724 \times 1000 = 72.4.$$

Let the normality of H_2SO_4 be N

\therefore m.e. of $\text{H}_2\text{SO}_4 = N \times 134$.

Now m.e. of H_2SO_4 = m.e. of NH_3

... (Eqn. 7)

$$134 \times N = 72.4$$

$$\therefore \text{normality of } \text{H}_2\text{SO}_4 = \frac{72.4}{134}$$

$$= 0.54 \text{ N.}$$

Ex. 25. (a) Calculate the strength of '20 V' of H_2O_2 in terms of:

- (i) normality (ii) grams per litre (iii) molarity and (iv) percentage.
- (b) Calculate the volume strength of 3.58 N H_2O_2 solution.

Solution : (a) The strength of H_2O_2 as '20 V' means 1 volume of H_2O_2 on decomposition gives 20 volumes of oxygen at NTP or 1 litre of H_2O_2 gives 20 litres of oxygen at NTP.



1 lit.

20 lit. at NTP

$$\frac{20}{5.6} \text{ eq.}$$

... (Eqn. 4ii)

\therefore 1 mole of oxygen (32 g) occupies a vol. of 22.4 lit. at NTP

\therefore 1 eq. of oxygen (8 g) shall occupy $\frac{22.4}{4}$ lit at NTP = 5.6 lit.

\therefore equivalent in 1 lit. of H_2O_2 = eq. of oxygen produced

$$= \frac{20}{5.6} = 3.58.$$

\therefore equivalent per litre represents normality.

\therefore normality of '20 V' H_2O_2 = 3.58 N

(ii) From the above reaction,

$$\text{eq. wt. of } \text{H}_2\text{O}_2 = \frac{\text{mol. wt.}}{2} = \frac{34}{2} = 17.$$

\therefore strength of '20 V' H_2O_2 = normality \times eq. wt.

$$= 3.58 \times 17$$

$$= 60.86 \text{ g/lit.}$$

normality

... (Eqn. 6i)

(iii) Molarity = $\frac{\text{factor relating mol. wt. and eq. wt.}}{\text{normality}}$

$$= \frac{3.58}{2} = 1.79 \text{ M.}$$

(iv) Strength in percentage is grams per 100 mL so from part (ii) of the solution,

strength in percentage of '20 V' H_2O_2 = 6.086 % (g/100 mL).

(b) The strength of H_2O_2 is 3.58 equivalents per litre.

\therefore the equivalent of oxygen = 3.58.

The volume of O_2 (lit.) at NTP = $3.58 \times 5.6 = 20$ litres. ... (Eqn. 4ii)

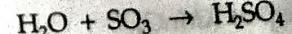
(1 eq. of oxygen occupies 5.6 litres.)

Thus 1 litre of H_2O_2 at NTP gives a volume of 20 litres

That is to say— strength of H_2O_2 is '20 V'.

Ex. 26. Calculate the percentage of free SO_3 in an oleum (considered as a solution of SO_3 in H_2SO_4) that is labelled '109% H_2SO_4 '.

Solution : '109% H_2SO_4 ' refers to the total mass of pure H_2SO_4 , i.e., 109 g that will be formed when 100 g of oleum is diluted by 9 g of H_2O which (H_2O) combines with all the free SO_3 present in oleum to form H_2SO_4 .



1 mole of H_2O combines with 1 mole of SO_3

Ex. 30. Calculate the percentage amount of oxalate in a given sample of salt when 0.3 g of salt was dissolved in 100 mL and 10 mL of which required $\frac{N}{20}$ KMnO₄ solution.

Solution : Let the amount of oxalate in the sample be x g.

Now,

$$\text{m.e. of KMnO}_4 = \frac{1}{20} \times 8 = 0.4.$$

$$\therefore \text{m.e. of 10 mL of oxalate salt solution} = 0.4.$$

$$\therefore \text{m.e. of 100 mL of oxalate solution} = 4.0$$

$$\text{but m.e. of oxalate} = \text{m.e. of oxalate salt} = 4.$$

$$\therefore \text{equivalent of oxalate} = \frac{4}{1000} = 0.004.$$

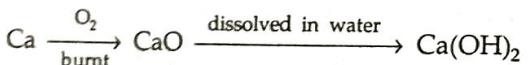
$$\begin{aligned}\text{Wt. of oxalate} &= (0.004 \times 44) \text{ g} \\ &= 0.176 \text{ g.}\end{aligned}$$

$$\left\{ \text{eq. wt. of C}_2\text{O}_4^{2-} = \frac{88}{2} = 44. \right\}$$

$$\text{Percentage amount of oxalate} = \frac{0.176}{0.3} \times 100 = 58.67\%.$$

Ex. 31. One gram-atom of Ca was burnt in excess of oxygen and the oxide dissolved in water to make up a 1-litre solution. Calculate the normality of the alkaline solution.

Solution : First Method



$$\text{m.e. of Ca} = \text{m.e. of CaO} = \text{m.e. of 1000 mL of Ca(OH)}_2 \text{ solution}$$

... (Eqn. 1)

$$\therefore \text{m.e. of 1000 mL of Ca(OH)}_2 \text{ solution} = \text{m.e. of Ca}$$

$$= \text{eq.} \times 1000$$

$$= (\text{gram-atom} \times \text{valency of Ca}) \times 1000$$

$$= 1 \times 2 \times 1000$$

$$= 2000.$$

$$\begin{aligned}\therefore \text{normality of Ca(OH)}_2 \text{ solution} &= \frac{\text{m.e.}}{\text{vol. in mL}} \\ &= \frac{2000}{1000} = 2 \text{ N.}\end{aligned}$$

Second Method See the first method in Example 13, Chapter 2.

Ex. 32. How much AgCl will be formed by adding 1.70 g of AgNO₃ in 200 mL of 5 N HCl solution? (Ag = 108, N = 14, O = 16)

$$\text{Solution : Equivalent of AgNO}_3 = \frac{1.70}{170} = 0.01.$$

... (Eqn. 4i)

$$(\text{eq. wt. of AgNO}_3 = 170)$$

$$\text{m.e. of HCl solution} = 5 \times 200 = 1000.$$

... (Eqn. 1)

$$\therefore \text{equivalent of HCl solution} = \frac{1000}{1000} = 1.$$

... (Eqn. 3)

Since equivalent of AgNO₃ is less than the eq. of HCl,
equivalent of AgCl = eq. of AgNO₃ = 0.01.

$$\therefore \text{wt. of AgCl} = 0.01 \times 143.5$$

... (Eqn. 4ii)

$$= 1.435 \text{ g.}$$

Ex. 33. A mixture of aluminium and zinc weighing 1.67 g was completely dissolved in acid and evolved 1.69 litres of hydrogen at NTP. What was the weight of aluminium in the original mixture? (Al = 27, Zn = 65.4)

Solution : Since H₂ is formed by both Al and Zn,
eq. of Al + eq. of Zn = eq. of H₂.

Let w be the mass in grams of Al in the mixture.

$$\therefore \frac{w}{\text{eq. wt. of Al}} + \frac{(1.67 - w)}{\text{eq. wt. of Zn}} = \frac{1.69}{\text{vol. of 1 eq. of H}_2 \text{ at NTP in lit.}}$$

$$\frac{w}{27/3} + \frac{1.67 - w}{65.4/2} = \frac{1.69}{11.2} \quad \left\{ \begin{array}{l} \text{eq. wt. of Al} = \frac{27}{3} \\ \text{eq. wt. of Zn} = \frac{65.4}{2} \end{array} \right\}$$

$$w = 1.24 \text{ g.}$$

Ex. 34. A metal weighing 0.43 g was dissolved in 50 mL of N H₂SO₄. The unreacted H₂SO₄ required 14.2 mL of N NaOH for neutralisation. Find out the equivalent weight of the metal.

$$\text{Solution : Eq. of metal} = \frac{0.43}{E} \cdot (\text{eq. wt. of metal} = E)$$

$$\therefore \text{m.e. of metal} = \frac{0.43}{E} \times 1000 = \frac{430}{E}$$

$$\text{m.e. of total H}_2\text{SO}_4 \text{ solution} = 1 \times 50 = 50$$

But m.e. of H₂SO₄ reacted with metal = m.e. of the metal

$$= \frac{430}{E}.$$

$$\therefore \text{m.e. of unreacted } \text{H}_2\text{SO}_4 = \left(50 - \frac{430}{E} \right).$$

Again m.e. of unreacted H_2SO_4 = m.e. of NaOH .

$$\therefore 50 - \frac{430}{E} = 1 \times 14.2 \quad \dots (\text{Eqn. 4i})$$

$$\therefore E = 12.01. \quad \dots (\text{Eqn. 4i})$$

Ex. 35. 7.35 g of a dibasic acid was dissolved in water and diluted to 250 mL of this solution was neutralised by 15 mL of N NaOH solution. Calculate eq. wt. and mol. wt. of the acid.

Solution : Let the equivalent weight of the acid be E .

$$\text{Equivalent of acid} = \frac{7.35}{E}.$$

$$\text{m.e. of the acid} = \frac{7.35}{E} \times 1000 = \frac{7350}{E}. \quad \dots (\text{Eqn. 4i})$$

Now,

$$250 \text{ mL of the acid contains} \frac{7350}{E} \text{ m.e.}$$

$$\therefore 25 \text{ mL of the acid contains} \frac{735}{E} \text{ m.e.}$$

Again, m.e. of 25 mL of the acid = m.e. of NaOH ... (Eqn. 2)

$$\frac{735}{E} = 1 \times 15$$

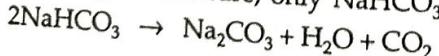
$$E = \frac{735}{15} = 49.$$

$$\therefore \text{eq. wt. of acid} = 49.$$

$$\begin{aligned} \therefore \text{molecular weight of the acid} &= \text{eq. wt.} \times \text{basicity} \\ &= 49 \times 2 \\ &= 98. \end{aligned}$$

Ex. 36. 2.0 g of a mixture of carbonate, bicarbonate and chloride of sodium, on heating, produced 56 mL of CO_2 at NTP. 1.6 g of the same mixture required 25 mL of N HCl solution for neutralisation. Calculate the percentage of Na_2CO_3 , NaHCO_3 and NaCl in the mixture from the given data.

Solution : On heating the given mixture, only NaHCO_3 decomposes as



$$\therefore \text{eq. of NaHCO}_3 = \text{eq. of CO}_2 = \frac{56}{11200}.$$

(1 eq. of CO_2 occupies 11200 mL at NTP)

$$\therefore \text{wt. of NaHCO}_3 = \frac{56}{11200} \times 84 = 0.42 \text{ g.} \quad \dots (\text{Eqn. 4i})$$

$$(\text{eq. wt. of NaHCO}_3 = 84)$$

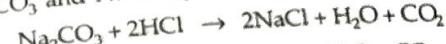
$$\therefore \% \text{ of NaHCO}_3 = \frac{0.42}{2} \times 100 = 21\%.$$

Now, if x is the weight of NaCl in 1.6 g of the mixture

$$\text{then wt. of NaHCO}_3 = 0.336 \text{ g (i.e., 21% of 1.6 g)}$$

$$\text{and wt. of Na}_2\text{CO}_3 = 1.6 - 0.336 - x = (1.264 - x) \text{ g.}$$

Since Na_2CO_3 and NaHCO_3 are neutralised by HCl solution as:



$$\text{m.e. of Na}_2\text{CO}_3 + \text{m.e. of NaHCO}_3 = \text{m.e. of HCl}$$

$$\text{or eq. of Na}_2\text{CO}_3 \times 1000 + \text{eq. of NaHCO}_3 \times 1000 = \text{m.e. of HCl} \quad \dots (\text{Eqn. 3})$$

$$\frac{1.264 - x}{53} \times 1000 + \frac{0.336}{84} \times 1000 = 1 \times 25$$

$$x = 0.151 \text{ g.}$$

$$\therefore \% \text{ of NaCl} = \frac{0.151}{1.6} \times 100 = 9.42\%$$

$$\text{and \% of Na}_2\text{CO}_3 = 100 - (21 + 9.42) = 69.58\%.$$

$$\begin{cases} \text{Na}_2\text{CO}_3 = 69.58\% \\ \text{NaHCO}_3 = 21.00\% \\ \text{NaCl} = 9.42\% \end{cases}$$

Ex. 37. Find out the volume in mL of 0.1 N HCl solution required to react completely with 1.0 g of a mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of the two compounds.

Solution : Let the amount of Na_2CO_3 in 1 g of mixture be x g and since the Na_2CO_3 and NaHCO_3 are in equimolar amounts,

$$\frac{x}{106} = \frac{1-x}{84} \text{ where } \begin{cases} \text{mol. wt. of Na}_2\text{CO}_3 = 106 \\ \text{mol. wt. of NaHCO}_3 = 84 \end{cases}$$

$$\therefore x = 0.558 \text{ g.}$$

$$\text{Thus wt. of Na}_2\text{CO}_3 = 0.558 \text{ g}$$

$$\text{and wt. of NaHCO}_3 = 1 - 0.558 = 0.442 \text{ g.}$$

Now,

$$\text{m.e. of HCl} = \text{m.e. of Na}_2\text{CO}_3 + \text{m.e. of NaHCO}_3$$

m.e. of HCl = eq. of $\text{Na}_2\text{CO}_3 \times 1000 + \text{eq. of } \text{NaHCO}_3 \times 1000$

If v is the volume of HCl in mL

$$\text{then } 0.1 \times v = \frac{0.558}{53} \times 1000 + \frac{0.442}{84} \times 1000.$$

$$\therefore v = 157.9 \text{ mL.}$$

Ex. 38. 5 mL of 8 N nitric acid, 4.8 mL of 5 N HCl and a certain volume of sulphuric acid are mixed together and made up to 2 litres. 30 mL of this mixture exactly neutralises 42.9 mL of sodium carbonate solution containing $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in 100 mL of water. Calculate the amount in grams of sulphate ions in the solution.

Solution : Let the volume of 17 M (i.e., 34 N) H_2SO_4 solution be v mL

$$\therefore \text{total m.e. of the acid mixture} = 8 \times 5 + 5 \times 4.8 + 34v \quad \dots (\text{Eqn. 1})$$

$$= (64 + 34v).$$

$$\therefore \text{normality of the mixture} = \frac{\text{m.e.}}{\text{total volume (mL)}} \quad \dots (\text{Eqn. 2})$$

$$= \frac{64 + 34v}{2000}.$$

$$\text{m.e. of 30 mL of this acid mixture} = \frac{64 + 34v}{2000} \times 30. \quad \dots (\text{Eqn. 3})$$

$$\text{Now, normality of } \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ solution} = \frac{\text{g/litre}}{\text{eq. wt.}}$$

$$= \frac{10}{143}.$$

$$\left. \begin{array}{l} \therefore \text{grams/litre of } \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} = 10 \\ \text{and eq. wt.} = \frac{\text{mol. wt.}}{2} = \frac{286}{2} = 143 \end{array} \right\}$$

$$\therefore \text{m.e. of 42.9 mL of } \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ solution} = \frac{10}{143} \times 42.9.$$

Thus, m.e. of 30 mL of acid mixture

$$= \text{m.e. of 42.9 mL of } \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \text{ solution} \quad \dots (\text{Eqn. 1})$$

$$\therefore \frac{64 + 34v}{2000} \times 30 = \frac{10}{143} \times 42.9$$

$$v = \frac{68}{17}.$$

$$\therefore \text{m.e. of 34 N (i.e., 17 M) } \text{H}_2\text{SO}_4 = 34 \times \frac{68}{17} \quad \dots (\text{Eqn. 1})$$

$$= 136.$$

$$\text{equivalent of } \text{H}_2\text{SO}_4 = \frac{136}{1000} = 0.136. \quad \dots (\text{Eqn. 3})$$

$$\text{equivalent of } \text{SO}_4^{2-} = 0.136 \quad \dots (\text{Eqn. 7ii})$$

$$\text{weight of } \text{SO}_4^{2-} = \text{eq.} \times \text{eq. wt. of } \text{SO}_4^{2-} \quad \dots (\text{Eqn. 4i})$$

$$= 0.136 \times 48$$

$$= 6.528 \text{ g.}$$

$$\left(\text{eq. wt. of } \text{SO}_4^{2-} = \frac{\text{ionic wt.}}{\text{valency}} = \frac{96}{2} = 48 \right)$$

Ex. 39. 1.42 g of a mixture of CaCO_3 and MgCO_3 was dissolved in 200 mL of 0.2 N HCl solution which was then diluted to 250 mL. 10 mL of this solution was neutralised by 12 mL of (N/30) Na_2CO_3 . Find out the percentage of each in the mixture. (Ca = 40, Mg = 24, C = 12, O = 16)

Solution : Let the wt. of CaCO_3 be x g.

$$\therefore \text{wt. of } \text{MgCO}_3 = (1.42 - x) \text{ g.} \quad \dots (\text{Eqn. 4})$$

$$\therefore \text{eq. of } \text{CaCO}_3 = \frac{x}{50} \text{ and eq. of } \text{MgCO}_3 = \frac{1.42 - x}{42}.$$

$$\left(\text{eq. wt. of } \text{CaCO}_3 = \frac{100}{2} = 50; \text{eq. wt. of } \text{MgCO}_3 = \frac{84}{2} = 42 \right)$$

$$\text{Total m.e. of } \text{CaCO}_3 \text{ and } \text{MgCO}_3 = \frac{x}{50} \times 1000 + \frac{1.42 - x}{42} \times 1000 \quad \dots (\text{Eqn. 3})$$

$$\text{m.e. of HCl} = 0.2 \times 200 = 40. \quad \dots (\text{Eqn. 1})$$

From the given question it is clear that m.e. of HCl is greater than those of CaCO_3 and MgCO_3 .

$$\therefore \text{m.e. of excess HCl} = \text{m.e. of HCl} - \text{m.e. of } \text{CaCO}_3 \text{ and } \text{MgCO}_3$$

$$= 40 - \left\{ 1000 \left(\frac{x}{50} + \frac{1.42 - x}{42} \right) \right\}.$$

\therefore the m.e. of the resulting solution does not change on dilution.

\therefore normality of excess HCl in the diluted resulting solution

$$= \frac{\text{m.e.}}{250} = \frac{40 - \left\{ 1000 \left(\frac{x}{50} + \frac{1.42 - x}{42} \right) \right\}}{250}.$$

$$\therefore \text{m.e. of 10 mL of the resulting solution}$$

$$= \frac{40 - \left\{ 1000 \left(\frac{x}{50} + \frac{1.42 - x}{42} \right) \right\}}{250} \times 10. \quad \dots (\text{Eqn. 1})$$

$$\text{m.e. of } \text{Na}_2\text{CO}_3 \text{ solution} = \frac{1}{30} \times 12. \quad \dots (\text{Eqn. 1})$$

$$\therefore \frac{40 - \left\{ 1000 \left(\frac{x}{50} + \frac{1.42 - x}{42} \right) \right\}}{250} \times 10 = \frac{1}{30} \times 12.$$

$$\therefore x = 1.$$

$$\therefore \% \text{ of } \text{CaCO}_3 = \frac{1}{1.42} \times 100 = 70.4\%,$$

$$\% \text{ of } \text{MgCO}_3 = 100 - 70.4 = 29.6\%.$$

Ex. 40. 3.68 g of a mixture of CaCO_3 and MgCO_3 , on reaction with 1000 mL of HCl solution produced 1.76 g of CO_2 . Calculate the percentage of each in mixture.



From the equation, 2 eq. of HCl produces 1 mole of CO_2 .

\therefore 1 eq. of HCl produces 1/2 mole of CO_2 .

$$\therefore \text{eq. wt. of } \text{CO}_2 = \frac{44}{2} = 22.$$

$$\therefore \text{eq. of } \text{CO}_2 = \frac{1.76}{22} = 0.08. \quad \dots (\text{Eqn. 1})$$

From the given problem it is clear that the number of equivalents of the mixture of CaCO_3 and MgCO_3 is lesser than that of HCl solution. And so the CO_2 is produced by the complete consumption of CaCO_3 and MgCO_3 .

$$\therefore \text{eq. of } \text{CaCO}_3 + \text{eq. of } \text{MgCO}_3 = \text{eq. of } \text{CO}_2$$

$$\frac{x}{50} + \frac{3.68 - x}{42} = 0.08 \quad (x = \text{amount of } \text{CaCO}_3)$$

$$x = 2.0 \text{ g.}$$

$$\therefore \% \text{ of } \text{CaCO}_3 = \frac{2}{3.68} \times 100 = 54.34\%,$$

$$\% \text{ of } \text{MgCO}_3 = 100 - 54.34 = 45.66\%.$$

Ex. 41. 1.25 g of a mixture of Na_2CO_3 and Na_2SO_4 was dissolved in 250 mL of water. 25 mL of this solution required 20 mL of 0.1 N H_2SO_4 solution for exact neutralisation. Calculate the percentage of Na_2CO_3 in the mixture.

Solution : In this problem only Na_2CO_3 is neutralised by H_2SO_4 . Let the amount of Na_2CO_3 be x g.

$$\therefore \text{equivalent of } \text{Na}_2\text{CO}_3 = \frac{x}{53} \quad \dots (\text{Eqn. 4})$$

$$\text{m.e. of } \text{Na}_2\text{CO}_3 = \frac{x}{53} \times 1000 \quad \dots (\text{Eqn. 3})$$

$$\therefore \text{m.e. of } \text{Na}_2\text{CO}_3 \text{ in } 250 \text{ mL of the mixture solution} = \frac{1000x}{53}.$$

$$\therefore \text{m.e. of } \text{Na}_2\text{CO}_3 \text{ in } 25 \text{ mL of the mixture solution} = \frac{100x}{53}.$$

$$\begin{aligned} \text{Now m.e. of } 25 \text{ mL of mixture solution} \\ = \text{m.e. of } 20 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4 \end{aligned} \quad \dots (\text{Eqn. 2})$$

$$\frac{100x}{53} = 0.1 \times 20$$

$$x = 1.06 \text{ g.}$$

$$\therefore \% \text{ of } \text{Na}_2\text{CO}_3 = \frac{1.06}{1.25} \times 100 = 84.8\%.$$

Ex. 42. 4.35 g of a mixture of NaCl and Na_2CO_3 was dissolved in 100 mL of water, 20 mL of which was exactly neutralised by 75.5 mL of N/10 solution of H_2SO_4 . Calculate the percentage of NaCl and Na_2CO_3 in the mixture.

Solution : In this problem, Na_2CO_3 is neutralised by H_2SO_4 solution. Let the amount of Na_2CO_3 be x g.

$$\therefore \text{equivalent of } \text{Na}_2\text{CO}_3 \text{ in } 100 \text{ mL of solution} = \frac{x}{53}. \quad \dots (\text{Eqn. 4})$$

$$\therefore \text{m.e. of } \text{Na}_2\text{CO}_3 \text{ in } 100 \text{ mL of solution} = \frac{x}{53} \times 1000. \quad \dots (\text{Eqn. 3})$$

$$\therefore \text{m.e. of } \text{Na}_2\text{CO}_3 \text{ in } 20 \text{ mL of solution} = \frac{1000x}{53} \times \frac{20}{100} = \frac{200x}{53}.$$

$$\therefore \text{m.e. of } \text{Na}_2\text{CO}_3 = \frac{1}{10} \times 75.50. \quad \dots (\text{Eqn. 1})$$

$$\text{Now, m.e. of } \text{H}_2\text{SO}_4 \text{ solution} = \frac{1}{10} \times 75.50. \quad \dots (\text{Eqn. 2})$$

$$\therefore \text{m.e. of } \text{Na}_2\text{CO}_3 = \text{m.e. of } \text{H}_2\text{SO}_4 \quad \dots (\text{Eqn. 3})$$

$$\frac{200x}{53} = 7.55$$

$$x = 2.$$

$$\therefore \% \text{ of } \text{Na}_2\text{CO}_3 = \frac{2}{4.35} \times 100 = 45.99\%,$$

$$\% \text{ of } \text{NaCl} = 100 - 45.99 = 54.01\%.$$

Ex. 43. 1.216 g of a sample of $(\text{NH}_4)_2\text{SO}_4$ was boiled with excess of NaOH and the ammonia gas so produced was absorbed in 100 mL of N H_2SO_4 solution. The unreacted H_2SO_4 required 81.6 mL of normal solution of a base for neutralisation. Calculate percentage amount of ammonia in ammonium sulphate.

Solution : m.e. of unreacted H_2SO_4 = m.e. of the base
 $= 1 \times 81.6 = 81.6$.

$$\begin{aligned} \text{m.e. of } \text{NH}_3 &= \text{m.e. of } \text{H}_2\text{SO}_4 \text{ reacted with ammonia} \\ &= \text{m.e. of total } \text{H}_2\text{SO}_4 - \text{m.e. of unreacted } \text{H}_2\text{SO}_4 \\ &= 1 \times 100 - 81.6 = 18.4. \end{aligned}$$

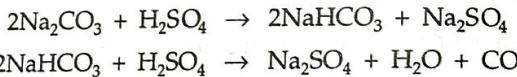
$$\therefore \text{equivalent of } \text{NH}_3 = \frac{18.4}{1000}$$

$$\begin{aligned} \text{Wt. of } \text{NH}_3 &= \frac{18.4}{1000} \times 17 \\ &= 0.3128 \text{ g.} \end{aligned}$$

$$\therefore \% \text{ of } \text{NH}_3 \text{ in } (\text{NH}_4)_2\text{SO}_4 = \frac{0.3128}{1.216} \times 100 = 25.72\%.$$

Ex. 44. 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 an indicator. Methyl orange is 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 : The neutralisation reactions are



The volume of H_2SO_4 (2.5 mL), used while using phenolphthalein corresponds to the volume required for conversion of Na_2CO_3 to NaHCO_3 while volume of H_2SO_4 (2.5 mL) further added corresponds to the volume required for conversion of NaHCO_3 to Na_2SO_4 . Thus at the end point with phenolphthalein, we have,

m.e. of 2.5 mL of 0.1 M (i.e., 0.2 N) H_2SO_4 = m.e. of Na_2CO_3

or $2.5 \times 0.2 = \text{m.e. of } \text{Na}_2\text{CO}_3$

or m.e. of $\text{Na}_2\text{CO}_3 = 0.5$.

Equivalent of $\text{Na}_2\text{CO}_3 = \frac{0.5}{1000}$.

$$\text{Wt. of } \text{Na}_2\text{CO}_3 / 10 \text{ mL} = \frac{0.5}{1000} \times 106 = 0.053 \text{ g.}$$

*(equivalent wt. of Na_2CO_3 is 106 according to given reaction)

$$\therefore \text{wt. of } \text{Na}_2\text{CO}_3 \text{ per litre} = 5.3 \text{ g.}$$

Again with methyl orange, we have,

m.e. of 2.5 mL of 0.2 M (i.e., 0.4 N) H_2SO_4 solution

* Read page 89, Chapter 6.

$$\begin{aligned} &= \text{m.e. of } \text{NaHCO}_3 \text{ produced from } \text{Na}_2\text{CO}_3 \\ &\quad + \text{m.e. of } \text{NaHCO}_3 \text{ originally present.} \end{aligned}$$

Since m.e. of NaHCO_3 (produced) = m.e. of Na_2CO_3 ,

$$\therefore 2.5 \times 4 = \text{m.e. of } \text{Na}_2\text{CO}_3 + \text{m.e. of } \text{NaHCO}_3 \text{ originally present.}$$

$$\therefore 1 = 0.5 + \text{m.e. of } \text{NaHCO}_3 \text{ originally present.}$$

$$\therefore \text{m.e. of } \text{NaHCO}_3 \text{ originally present} = 1 - 0.5 = 0.5.$$

$$\text{equivalent of } \text{NaHCO}_3 = \frac{0.5}{1000}.$$

$$\therefore \text{wt. of } \text{NaHCO}_3 \text{ per 10 mL} = \frac{0.5}{1000} \times 84 = 0.042 \text{ g.}$$

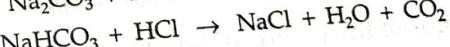
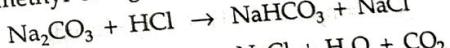
(eq. wt. of NaHCO_3 = 84 according to given reaction)

$$\text{Wt. of } \text{NaHCO}_3 \text{ per litre} = 4.2 \text{ g.}$$

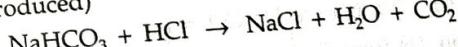
Ex. 45. A solution contained Na_2CO_3 and NaHCO_3 . 25 mL of this solution required 5 mL of 0.1 N HCl for titration with phenolphthalein as an indicator. The titration was repeated with the same volume of the solution but with methyl orange. 12.5 mL of 0.1 N HCl was required this time. Calculate the amount of Na_2CO_3 and NaHCO_3 in the solution.

Solution : Neutralisation reaction with phenolphthalein is
 $\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl}$

while with methyl orange, the reactions are,



(produced)



and (originally present)

Thus,

we have with phenolphthalein,

$$\begin{aligned} \text{m.e. of } \text{Na}_2\text{CO}_3 &= \text{m.e. of 5 mL of 0.1 N HCl} \\ &= 0.1 \times 5 = 0.5. \end{aligned}$$

$$\therefore \text{eq. of } \text{Na}_2\text{CO}_3 = \frac{0.5}{1000} = 0.0005$$

$$\therefore \text{wt. of } \text{Na}_2\text{CO}_3 = (0.0005 \times 106) \text{ g}$$

$$= 0.053 \text{ g.}$$

(Eq. wt. of Na_2CO_3 in the given reaction is 106)

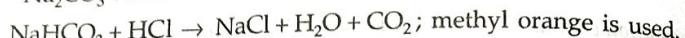
And with methyl orange,

$$\begin{aligned} \text{m.e. of } \text{Na}_2\text{CO}_3 + \text{m.e. of } \text{NaHCO}_3 &= \text{m.e. of } \text{NaHCO}_3 \text{ (produced)} + \text{m.e. of } \text{NaHCO}_3 \text{ (originally present)} \\ &= \text{m.e. of 12.5 mL of 0.1 N HCl} \end{aligned}$$

$$\begin{aligned} \text{or } 0.5 + 0.5 + \text{m.e. of NaHCO}_3 &= 0.1 \times 12.5 = 1.25 \\ \text{or } \text{m.e. of NaHCO}_3 &= 0.25 \\ \therefore \text{wt. of NaHCO}_3 &= \frac{0.25}{1000} \times 84 = 0.021 \text{ g.} \\ (\text{eq. wt. of NaHCO}_3 &= 84) \end{aligned}$$

Ex. 46. A mixed solution of KOH and Na_2CO_3 required 20 mL of N/20 HCl solution when titrated with phenolphthalein as indicator. But the same amount of solution when titrated with methyl orange as indicator required 30 mL of the same acid. Calculate the amount of KOH and Na_2CO_3 .

Solution : Neutralisation reactions are



As discussed in the previous example we have with phenolphthalein
m.e. of 20 mL of N/20 HCl = m.e. of KOH + m.e. of Na_2CO_3

$$\text{or m.e. of KOH} + \text{m.e. of Na}_2\text{CO}_3 = 20 \times \frac{1}{20} = 1.$$

Now, with methyl orange,

$$\text{m.e. of 30 mL of N/20 HCl}$$

$$= \text{m.e. of KOH} + \text{m.e. of Na}_2\text{CO}_3 + \text{m.e. of NaHCO}_3 \text{ produced.}$$

Since m.e. of Na_2CO_3 = m.e. of NaHCO_3 produced.

$$\therefore 30 \times \frac{1}{20} = \text{m.e. of KOH} + \text{m.e. of Na}_2\text{CO}_3 + \text{m.e. of NaHCO}_3$$

$$\text{or m.e. of KOH} + 2 \times \text{m.e. of Na}_2\text{CO}_3 = 1.5.$$

Subtracting Eqn. (1) from Eqn. (2), we get,

$$\text{m.e. of Na}_2\text{CO}_3 = 1.5 - 1 = 0.5$$

$$\therefore \text{equivalent of Na}_2\text{CO}_3 = \frac{0.5}{1000}.$$

$$\therefore \text{wt. of Na}_2\text{CO}_3 = \frac{0.5}{1000} \times 106 = 0.053 \text{ g.}$$

$$(\text{eq. wt. of Na}_2\text{CO}_3 = 106)$$

From eqns. (3) and (1),

$$\text{m.e. of KOH} = 1 - 0.5 = 0.5.$$

$$\text{Equivalent of KOH} = \frac{0.5}{1000}.$$

$$\text{Weight of KOH} = \frac{0.5}{1000} \times 56 = 0.028 \text{ g. (eq. wt. of KOH = 56.)}$$

Ex. 47. 50 mL of a solution, containing 1 g each of Na_2CO_3 , NaHCO_3 and NaOH, was titrated with N HCl. What will be the titre readings if

- (a) only phenolphthalein is used as indicator?
- (b) only methyl orange is used as indicator from the very beginning?
- (c) methyl orange is added after the first end point with phenolphthalein?

Solution : (a) The titration reactions in this case are



and

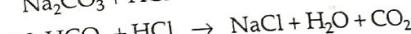
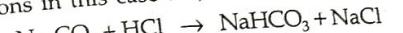


Thus, we have,

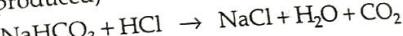
$$\text{m.e. of Na}_2\text{CO}_3 + \text{m.e. of NaOH} = \text{m.e. of } v_1 \text{ mL (say) of N HCl}$$

$$\frac{1}{106} \times 1000 + \frac{1}{40} \times 1000 = 1 \times v_1; \quad \therefore v_1 = 34.4 \text{ mL.}$$

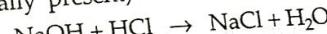
(b) The reactions in this case are,



(produced)



(originally present)



and

$$\text{Thus, we have,}$$

$$\text{m.e. of Na}_2\text{CO}_3 + \text{m.e. of NaHCO}_3 + \text{m.e. of NaHCO}_3 + \text{m.e. of NaOH}$$

$$\text{(produced)} \quad \text{(originally present)}$$

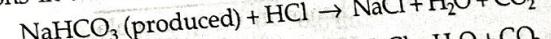
$$= \text{m.e. of } v_2 \text{ mL (say) of N HCl}$$

$$\frac{1}{106} \times 1000 + \frac{1}{106} \times 1000 + \frac{1}{84} \times 1000 + \frac{1}{40} \times 1000 = 1 \times v_2$$

$$v_2 = 55.8 \text{ mL.}$$

∴

(c) The reactions in this case are,



and NaHCO_3 (originally present) + HCl $\rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$

Thus we have,

$$\text{m.e. of NaHCO}_3 + \text{m.e. of NaHCO}_3 = \text{m.e. of } v_3 \text{ mL (say) of N HCl}$$

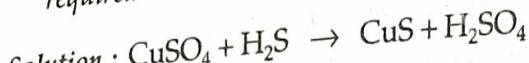
$$\text{(produced)} \quad \text{(originally present)}$$

$$\text{or m.e. of Na}_2\text{CO}_3 + \text{m.e. of NaHCO}_3 = \text{m.e. of } v_3 \text{ mL (say) of N HCl}$$

$$\frac{1}{106} \times 1000 + \frac{1}{84} \times 1000 = 1 \times v_3.$$

$$\therefore v_3 = 21.3 \text{ mL.}$$

Ex. 48. 1.245 g of $\text{CuSO}_4 \cdot x \text{H}_2\text{O}$ was dissolved in water and H_2S was passed into it till CuS was completely precipitated. The H_2SO_4 produced in the filtrate required 10 mL of N NaOH solution. Calculate x .



$$\text{m.e. of CuSO}_4 \cdot x \text{H}_2\text{O solution} = \text{m.e. of H}_2\text{SO}_4$$

$$= \text{m.e. of 10 mL of N NaOH}$$

$$= 1 \times 10 = 10.$$

$$\therefore \text{number of equivalent of CuSO}_4 \cdot x \text{H}_2\text{O solution} = \frac{10}{1000}.$$

$$\text{Weight of CuSO}_4 \cdot x \text{H}_2\text{O} = \text{equivalent} \times \text{eq. wt.}$$

$$= \frac{10}{1000} \times \frac{159.5 + 18x}{2}.$$

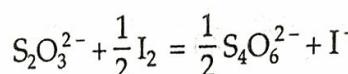
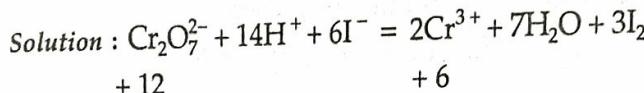
$$\left\{ \text{eq. wt. of CuSO}_4 \cdot x \text{H}_2\text{O} = \frac{159.5 + 18x}{2} \right\}$$

$$\text{Thus, } \frac{10}{1000} \times \frac{159.5 + 18x}{2} = 1.245 \quad (\text{given})$$

$$18x = 89.5$$

$$x \approx 5.$$

Ex. 49. A 10 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ solution liberated iodine from KI solution. The liberated iodine was titrated by 16 mL of M/25 sodium thiosulphate solution. Calculate the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ solution in grams per litre.



mol. wt.

$$\text{Eq. wt. of K}_2\text{Cr}_2\text{O}_7 = \frac{\text{change in ON per mole}}{\text{change in ON per mole}}$$

$$= \frac{29418}{6}$$

$$= 49.03.$$

$$\text{m.e. of 10 mL of K}_2\text{Cr}_2\text{O}_7 \text{ solution} = \text{m.e. of iodine}$$

$$= \text{m.e. of sodium thiosulphate}$$

$$= \frac{1}{25} \times 16 = 0.64.$$

$$\therefore \text{equivalent of 10 mL of K}_2\text{Cr}_2\text{O}_7 \text{ solution} = \frac{0.64}{1000} = 0.00064.$$

$$= \frac{248.2}{1}$$

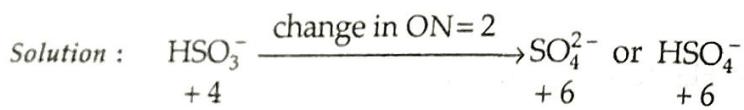
m.e. of 10 mL of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution = m.e. of iodine solution
 $= \frac{1}{20} \times 15 = 0.75$.

Equivalent of 10 mL of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = \frac{0.75}{1000}$.

Weight per 10 mL = $\frac{0.75}{1000} \times 248 = 0.186$ g.

Concentration of hypo in grams per litre = $0.186 \times \frac{1000}{10}$
 $= 18.6$ g/L.

Ex. 52. 25 mL of 0.017 M HSO_3^- , in strongly acidic solution required the addition of 16.9 mL of 0.01 M MnO_4^- for its complete oxidation to SO_4^{2-} or HSO_4^- . In neutral solution it required 28.6 mL. Assign oxidation numbers to Mn in each case.



$$\therefore 0.017 \text{ M } \text{HSO}_3^- \equiv 2 \times 0.017 \text{ N}$$

$$= 0.034 \text{ N.}$$

In the first case suppose the ON of Mn in the product is X

$$\therefore 0.01 \text{ M } \text{MnO}_4^- = 0.01(7 - X) \text{ N } \text{MnO}_4^-$$

$$\text{m.e. of } \text{HSO}_3^- = \text{m.e. of } \text{MnO}_4^-$$

$$+ 7$$

$$0.034 \times 25 = 0.01(7 - X) 16.9$$

$$\therefore 7 - X = \frac{0.034 \times 25}{16.9 \times 0.01} = 5.00$$

$$\text{or } X = 2.$$

Now in the second titration, suppose the ON of Mn in the product is Y.

$$\therefore 0.01 \text{ M } \text{MnO}_4^- = 0.01(7 - Y) \text{ N } \text{MnO}_4^-$$

$$0.034 \times 25 = 0.01(7 - Y) \times 28.6$$

$$7 - Y = \frac{0.034 \times 25}{0.01 \times 28.6} = 3$$

$$\therefore Y = 4.$$

Applying POAC for M and C atoms, we get,

$$\frac{x}{y+60} = \frac{(x-0.44)}{y+16}$$

and

$$\frac{x}{y+60} = \frac{0.44}{44} = 0.01$$

From eqns. (1) and (2), we have,

$$\frac{x-0.44}{y+16} = 0.01.$$

Now, m.e. of NaOH = $2.5 \times 16 = 40$.

∴ m.e. of excess acid = 40.

∴ m.e. of the acid used to neutralise BaO and MO

$$\begin{aligned} &= \text{m.e. of total acid} - \text{m.e. of excess acid} \\ &= 1 \times 100 - 40 = 60. \end{aligned}$$

∴ eq. of the acid = $\frac{60}{1000} = 0.06$ = eq. of BaO + eq. of MO

$$\text{or } \frac{4.08-x}{154/2} + \frac{(x-0.44)}{(y+16)/2} = 0.06.$$

$$\left(\text{eq. wt. of BaO} = \frac{154}{2}; \text{eq. wt. of MO} = \frac{y+16}{2} \right)$$

Substituting the value of $\frac{x-0.44}{y+16}$ from Eqn. (3) in Eqn. (4),

we get, $x = 1$ and $y = 40$.

Hence, the metal M must be Ca.

Ex. 55. (a) (i) A sample of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ is strongly heated in air. The residue

Mn_3O_4 .

(ii) The residue is dissolved in 100 mL of 0.1 N FeSO_4 containing dilute H_2SO_4 .

(iii) The solution reacts completely with 50 mL of KMnO_4 solution.

(iv) 25 mL of the KMnO_4 solution used in step (ii) requires 30 mL of 0.1 N FeSO_4 solution for complete reaction.

Find the amount of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ present in the sample.

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

Solution : (a) m.e. of 25 mL of KMnO_4 solution

$$= \text{m.e. of 30 mL of 0.1 N } \text{FeSO}_4 \text{ solution}$$

$$= 0.1 \times 30 = 3$$

$$\therefore \text{m.e. of 50 mL of } \text{KMnO}_4 \text{ solution} = 2 \times 3 = 6.$$

(p. 4, Chapter 1)

∴ m.e. of FeSO_4 (remained which did not react with Mn_3O_4) = 6.

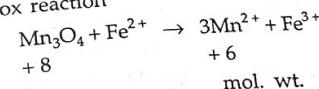
Now, m.e. of total FeSO_4 solution = $0.1 \times 100 = 10$.

m.e. of FeSO_4 oxidised by $\text{Mn}_3\text{O}_4 = 10 - 6 = 4$

∴ m.e. of $\text{Mn}_3\text{O}_4 = 4$

$$\therefore \text{eq. of } \text{Mn}_3\text{O}_4 = \frac{4}{1000}$$

From the redox reaction

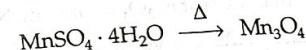


$$\begin{aligned} \text{Equivalent wt. of } \text{Mn}_3\text{O}_4 &= \frac{\text{change in ON per mole}}{\text{wt. of Mn}_3\text{O}_4} \\ &= \frac{229}{2} = 114.50 \end{aligned}$$

wt. of $\text{Mn}_3\text{O}_4 = \text{equivalent} \times \text{eq. wt.}$

$$= \frac{4}{1000} \times 114.5 = 0.458 \text{ g.}$$

As given in the problem, Mn_3O_4 is obtained by heating $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.



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Applying POAC for Mn atoms, we get,

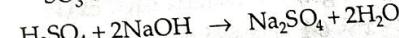
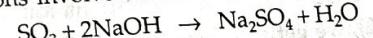
1 × moles of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O} = 3 \times \text{moles of } \text{Mn}_3\text{O}_4$

$$\text{or } \frac{\text{wt. of } \text{MnSO}_4 \cdot 4\text{H}_2\text{O}}{\text{mol. wt. of } \text{MnSO}_4 \cdot 4\text{H}_2\text{O}} = \frac{3 \times 0.458}{229}$$

$$\therefore \text{wt. of } \text{MnSO}_4 \cdot 4\text{H}_2\text{O} = \frac{3 \times 0.458}{229} \times 223$$

$$= 1.338 \text{ g.}$$

(b) Reactions involved are



$$\text{Eq. wt. of } \text{SO}_3 = \frac{80}{2} = 40.$$

$$\text{Eq. wt. of } \text{H}_2\text{SO}_4 = \frac{98}{2} = 49.$$

Now, m.e. of $\text{SO}_3 + \text{m.e. of } \text{H}_2\text{SO}_4 = \text{m.e. of NaOH}$.

$$\therefore \text{eq. of } \text{SO}_3 \times 1000 + \text{eq. of } \text{H}_2\text{SO}_4 \times 1000 = 0.4 \times 26.7.$$

Suppose the wt. of SO_3 is x g.

$$\therefore \text{wt. of } \text{H}_2\text{SO}_4 = (0.5 - x) \text{ g.}$$

$$\therefore \frac{x}{40} + \frac{(0.5-x)}{49} = 0.4 \times 26.7; x = 0.1036 \text{ g.}$$

$$\therefore \% \text{ of SO}_3 = \frac{0.1036}{0.5} \times 100 = 20.67\%.$$

Ex. 56. A mixture of $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) and NaHC_2O_4 weighing 2.02 g dissolved in water and the solution made up to one litre. 10 mL of the solution required 3 mL of 0.1 N NaOH solution for complete neutralisation. In a first experiment, 10 mL of the same solution, in hot dilute H_2SO_4 medium, required 4 mL of 0.1 N KMnO₄ solution for complete reaction. Calculate the amounts of $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 in the mixture. (IIT 1991)

Solution : Let the wt. of $\text{H}_2\text{C}_2\text{O}_4$ in 10 mL of the solution be x g. The wt. of NaHC_2O_4 in 10 mL will be $(0.0202 - x)$ g.

In the first experiment, $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 are neutralised by changing into $\text{Na}_2\text{C}_2\text{O}_4$. The eq. wt. of $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 therefore, be 90/2 and 112 respectively.

Thus,

$$\begin{aligned} \text{m.e. of } \text{H}_2\text{C}_2\text{O}_4 + \text{m.e. of } \text{NaHC}_2\text{O}_4 &= \text{m.e. of NaOH} \\ \frac{x}{90/2} \times 1000 + \frac{(0.0202 - x)}{112} \times 1000 &= 0.1 \times 3. \end{aligned}$$

In the second experiment, both $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 are oxidised to CO_2 by KMnO₄. The equivalent weight of $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 therefore, be 90/2 and 112/2 respectively $\left(\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 \right)$

Thus,

$$\begin{aligned} \text{m.e. of } \text{H}_2\text{C}_2\text{O}_4 + \text{m.e. of } \text{NaHC}_2\text{O}_4 &= \text{m.e. of KMnO}_4 \\ \frac{x}{90/2} \times 1000 + \frac{(0.0202 - x)}{112/2} \times 1000 &= 0.1 \times 4. \end{aligned}$$

Subtracting (1) from (2), we get,

$$\frac{0.0202 - x}{112} = \frac{0.1}{1000}.$$

$\therefore x = 0.009 \text{ g}/10 \text{ mL of solution.}$

The 1000 mL of solution contains

$$\text{H}_2\text{C}_2\text{O}_4 = 0.9 \text{ g}$$

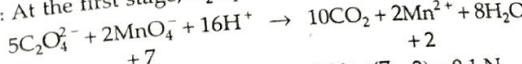
$$\text{and } \text{NaHC}_2\text{O}_4 = 2.02 - 0.9 = 1.12 \text{ g.}$$

[Note: This question may be solved by the data of the first experiment only.]

Ex. 57. A solution of 0.2 g of a compound containing Cu^{2+} and $\text{C}_2\text{O}_4^{2-}$ ions on titration with 0.02 M KMnO₄ in presence of H_2SO_4 consumes 22.6 mL of the

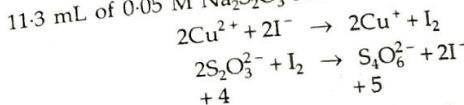
oxidant. The resultant solution is neutralised with Na_2CO_3 , acidified with dilute acetic acid and treated with excess KI. The liberated I_2 required 11.3 mL of 0.05 M $\text{Na}_2\text{S}_2\text{O}_3$ solution for complete reduction. Find out the mole ratio of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ in the compound. Write down the balanced redox reactions involved in the above titrations. (IIT 1991)

Solution : At the first stage, $\text{C}_2\text{O}_4^{2-}$ is oxidised to CO_2 by the oxidant KMnO₄.



\therefore normality of KMnO₄ solution = $0.02 \times (7 - 2) = 0.1 \text{ N.}$

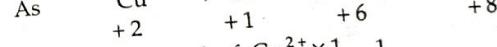
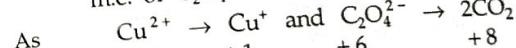
At the second stage, Cu^{2+} liberates I_2 from KI and this liberated I_2 requires



$$+ 4 \quad + 5$$

Normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution = $0.05(5 - 4) = 0.05 \text{ N.}$

$$\text{Now, } \frac{\text{m.e. of Cu}^{2+}}{\text{m.e. of C}_2\text{O}_4^{2-}} = \frac{\text{m.e. of Na}_2\text{S}_2\text{O}_3}{\text{m.e. of KMnO}_4} = \frac{0.05 \times 11.3}{0.1 \times 22.3} = \frac{1}{4}.$$



$$\therefore \frac{\text{mmol of Cu}^{2+} \times 1}{\text{mmol of C}_2\text{O}_4^{2-} \times 2} = \frac{1}{4}$$

$$\text{or } \frac{\text{mole of Cu}^{2+}}{\text{mole of C}_2\text{O}_4^{2-}} = \frac{1}{2}.$$

Ex. 58. 1.25 g of a sample of bleaching powder is dissolved in 100 mL of water and 25 mL of which are treated with KI solution. The iodine so liberated required 12.5 mL of N/25 hypo solution in titration. Find the percentage of chlorine available from the sample of bleaching powder.

Solution : m.e. of available chlorine in 25 mL of bleaching powder solution

$$= \text{m.e. of iodine liberated}$$

$$= \text{m.e. of hypo solution}$$

$$= \frac{1}{25} \times 12.5 = 0.5.$$

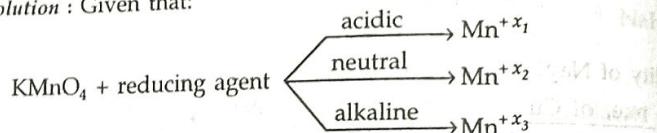
$$\therefore \text{m.e. of available chlorine in 100 mL} = \frac{0.5 \times 100}{25} = 2.$$

$$\therefore \text{eq. of available chlorine} = \frac{2}{1000}.$$

wt. of available chlorine in 1.25 grams of bleaching powder
 $= \frac{0.2}{1000} \times 35.5 = 0.071 \text{ g.}$ (eq. wt. of chlorine = 35.5)
 $\therefore \text{percentage of available chlorine} = \frac{0.071}{1.25} \times 100$
 $= 5.68\%.$

Ex. 59. An equal volume of a reducing agent is titrated separately with KMnO₄ in acid, neutral and alkaline media. The volumes of KMnO₄ required to reduce the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half reactions. Find out the volume of 1 M K₂Cr₂O₇ consumed, if the same volume of the reducing agent is titrated in acid medium. (IIT 1991)

Solution : Given that:



where x_1 , x_2 and x_3 are the oxidation states of Mn in the product in acidic, neutral and alkaline media respectively. Since equal volumes of the reducing agent is used in each titration,

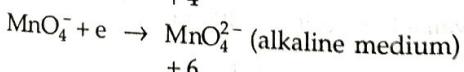
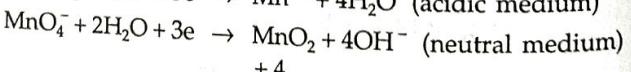
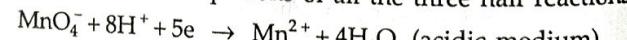
$$\begin{aligned} \therefore \text{m.e. of reducing agent} &= \text{m.e. of KMnO}_4 \text{ in acidic medium} \\ &= \text{m.e. of KMnO}_4 \text{ in neutral medium} \\ &= \text{m.e. of KMnO}_4 \text{ in alkaline medium} \\ \text{or } 1 \times (7 - x_1) \times 20 &= 1 \times (7 - x_2) \times 33.4 \\ &= 1 \times (7 - x_3) \times 100 \end{aligned}$$

[m.e. = $N \times V$ (mL); $N = M \times \text{change in ON}$]

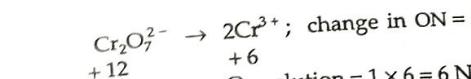
$$\text{or } \frac{7 - x_1}{5} = \frac{7 - x_2}{3} = \frac{7 - x_3}{1}$$

On inspection, we see that the equality exists for

$x_1 = +2$, $x_2 = +4$ and $x_3 = +6$ as x_1 , x_2 and x_3 can never be greater than 7. The balanced chemical equations of all the three half reactions are



Further, in acidic medium,

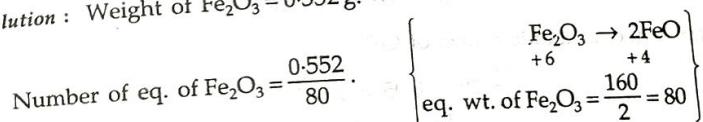


∴ normality of K₂Cr₂O₇ solution = $1 \times 6 = 6 \text{ N}$.

Let the volume of K₂Cr₂O₇ solution be $v \text{ mL}$.
 $\therefore \text{m.e. of K}_2\text{Cr}_2\text{O}_7 = \text{m.e. of KMnO}_4 \text{ in acidic medium}$
 $6 \times v = 5 \times 20$ (normality of KMnO₄ = 5 N)
 $v = 16.67 \text{ mL}$.

Ex. 60. A 1.0-g sample of Fe₂O₃ solid of 55.2 per cent purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100 mL. An aliquot of 25 mL of this solution requires 17 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. (IIT 1991)

Solution : Weight of Fe₂O₃ = 0.552 g.



Let the number of electrons taken up by the oxidant in the reaction be n (i.e., the change in oxidation number).

∴ normality of the oxidant = 0.0167 $n \text{ N}$.

∴ m.e. of the oxidant = 0.0167 $n \times 17$.

∴ m.e. of 25 mL of Fe²⁺ solution = 0.0167 $n \times 17$

∴ m.e. of 100 mL of Fe²⁺ solution = $4 \times 0.0167 n \times 17$

∴ eq. of 100 mL of Fe²⁺ solution = $\frac{68 \times 0.0167 n}{1000}$.

eq. of Fe₂O₃ = eq. of FeO

$$\frac{0.552}{80} = \frac{68 \times 0.0167 n}{1000}; n = 6.$$

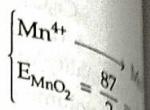
Ex. 61. 1.6 g of pyrolusite ore was treated with 50 cc of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 cc in a flask. 25 cc of this solution when titrated with 0.1 N KMnO₄ required 32 cc of the solution. Find out the percentage of pure MnO₂ in the sample and also the percentage of available oxygen.

Solution : m.e. of the remaining 25 mL of oxalic acid = m.e. of KMnO₄
 $= 0.1 \times 32 = 3.2$

m.e. of 250 mL of oxalic acid = 32.

∴ m.e. of MnO₂ = m.e. of oxalic acid reacted = $1 \times 50 - 32 = 18$.

$$\begin{aligned}\text{wt. of MnO}_2 &= \frac{18}{1000} \times 43.5 \\ &= 0.783 \text{ g.}\end{aligned}$$



$$\% \text{ MnO}_2 = \frac{0.783}{1.6} \times 100 = 48.9 \%$$

$$\text{Mole of O in MnO}_2 = 2 \times \text{mole of MnO}_2 = 2 \times \frac{0.783}{87} = 0.018$$

$$\text{Wt. of O} = 0.018 \times 16 = 0.288 \text{ g.}$$

$$\% \text{ of available oxygen} = \frac{0.288}{1.6} \times 100 = 18 \%$$

Ex. 62. The iodide content of a solution was determined by titration with cerium sulphate in the presence of HCl, in which I^- is converted to ICl . A 25 ml sample of the solution required 20 mL of 0.05 N Ce^{4+} solution. What is the iodide concentration in the original solution in g/L?

Solution : m.e. of iodide = m.e. of Ce^{4+}

$$= 20 \times 0.05 = 1.$$

$$\therefore \text{normality of iodide} = \frac{1}{250} \text{ N}$$



change in ON of I^- = 2.

$$\text{Eq. wt. of I}^- = \frac{127}{2}.$$

$$\begin{aligned}\therefore \text{iodide concentration} &= \frac{1}{250} \times \frac{127}{2} \text{ g/L} \\ &= 0.254 \text{ g/L.}\end{aligned}$$

Ex. 63. To a 25 mL H_2O_2 solution, excess of acidified solution of KI was added. The iodine liberated required 20 mL of 0.3 N $\text{Na}_2\text{S}_2\text{O}_3$ solution. Calculate volume strength of H_2O_2 solution.

Solution : m.e. of 25 mL of H_2O_2 = m.e. of I_2 = m.e. of $\text{Na}_2\text{S}_2\text{O}_3$

$$= 20 \times 0.3 = 6.$$

$$\therefore \text{normality of H}_2\text{O}_2 = \frac{6}{25} \text{ eq/L}$$

Let the volume strength of H_2O_2 be ' xV '. Thus, 1 litre of H_2O_2 produces x litres of O_2 at NTP.

$$\therefore \text{equivalent of H}_2\text{O}_2/\text{L} = \text{eq. of O}_2 = \frac{V \text{ (NTP)}}{\text{eq. vol. of O}_2} = \frac{x}{5.6}.$$

$$\therefore \frac{x}{5.6} = \frac{6}{25}$$

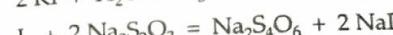
$$x = 1.344.$$

The volume strength of H_2O_2 is '1.344V'.

Ex. 64. 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?

(IIT 1997)

Solution : The reactions involved are



From the stoichiometry of the equations, we get,

$$\text{mole of O}_3 = \text{mole of I}_2 = \frac{1}{2} \text{ mole of Na}_2\text{S}_2\text{O}_3$$

$$= \frac{1}{2} \times \frac{40}{1000} \times \frac{1}{10} = \frac{1}{500}.$$

$$\text{Wt. of O}_3 = \frac{48}{500} = 0.096 \text{ g.}$$

$$\text{Volume of O}_3 \text{ at NTP} = \frac{22.4}{500} = 0.0448 \text{ litre.}$$

$$\text{Volume of O}_2 = 1 - 0.0448 = 0.9552 \text{ litre.}$$

$$\text{Wt. of O}_2 = \frac{0.9552}{22.4} \times 32 = 1.3654 \text{ g.}$$

$$\text{Wt. \% of O}_3 = \frac{0.096}{0.096 + 1.3654} \times 100 = 6.57 \text{ \%}.$$

Further,

$$\begin{aligned}\text{number of photons} &= \text{no. of O}_3 \text{ molecules} = \frac{6.022 \times 10^{23}}{500} \\ &= 1.2 \times 10^{21}.\end{aligned}$$

Ex. 65. A 3-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 into Fe^{2+} alongwith the liberation of iodine. The resulting solution is diluted to 100 mL. 20 mL of the diluted solution requires 11 mL of 0.5 N

$\text{Na}_2\text{S}_2\text{O}_3$ solution to reduce the iodine present. 50 mL of the diluted solution after complete extraction of the iodine requires 12.8 mL of 0.25 M KMnO_4 solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+} . Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample. (IIT 1978)

Solution: Let the amount of Fe_3O_4 and Fe_2O_3 in the sample be x and y respectively. Thus the mixture contains x moles of FeO and $(x+y)$ moles of Fe_2O_3 .

In the first titration KI is oxidised to I_2 and so Fe_2O_3 is reduced ($\text{Fe}_2\text{O}_3 \rightarrow 2\text{FeO}$; change in ON = 2).

$$\text{m.e. of } \text{Fe}_2\text{O}_3 = \text{m.e. of } \text{I}_2 = \text{m.e. of } \text{Na}_2\text{S}_2\text{O}_3$$

$$(x+y) \times 2 \times 1000 = 5 \times 11 \times 0.5 = 27.5.$$

After the first titration, all the iron is in Fe^{2+} state, i.e., FeO , which is titrated with KMnO_4 to oxidise Fe^{2+} to Fe^{3+} .

$$\begin{aligned} \text{Total moles of FeO} &= \text{moles of FeO (originally present)} + \text{moles of FeO (produced by red. of } \text{Fe}_2\text{O}_3) \\ &= [x + 2(x+y)] \end{aligned}$$

Thus,

$$\text{m.e. of FeO} = \text{m.e. of } \text{KMnO}_4$$

$$(x + 2(x+y)) \times 1000 = 2 \times 12.8 \times 0.25 \times 5 = 32.$$

Solving (1) and (2), we get

$$x = 0.0045.$$

$$\therefore \text{wt. of } \text{Fe}_2\text{O}_3 = 0.0045 \times 232 = 1.044 \text{ g.}$$

$$\text{Percentage of } \text{Fe}_3\text{O}_4 = \frac{1.044}{3} \times 100 = 34.8 \text{ %}.$$

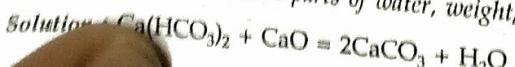
Substituting the value of x in equation (1), we get,

$$y = 0.00925.$$

$$\therefore \text{wt. of } \text{Fe}_2\text{O}_3 = 0.00925 \times 160 = 1.49 \text{ g.}$$

$$\text{Percentage of } \text{Fe}_2\text{O}_3 = \frac{1.49}{3} \times 100 = 49.66 \text{ %}.$$

Ex. 66. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm HCO_3^- , with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions? (Assume CaCO_3 to be completely insoluble with hydrogen ions, what will be its pH? (One ppm means one part of the substance in one million parts of water, weight/weight.) (IIT 1978)



Mole of CaO = mole of $\text{Ca}(\text{HCO}_3)_2$ in 10^6 g of solution

$$\begin{aligned} &= \frac{1}{2} \times \text{mole of } \text{HCO}_3^- \\ &= \frac{1}{2} \times \frac{183}{61} = 1.5. \end{aligned}$$

As CaCO_3 is assumed to be completely insoluble in water, Ca^{2+} ions left are, therefore, those associated only with SO_4^{2-} ion (96 ppm).

For CaSO_4 , we have,

$$\begin{aligned} \text{mole of } \text{Ca}^{2+}/10^6 \text{ g} &= \text{mole of } \text{SO}_4^{2-}/10^6 \text{ g} = \frac{96}{96} \text{ mole}/10^6 \text{ g} \\ &= 1 \text{ mole}/10^6 \text{ g.} \end{aligned}$$

$$\text{Wt. of } \text{Ca}^{2+} \text{ in } \text{g}/10^6 \text{ g} = 40 \text{ g}/10^6 \text{ g} = 40 \text{ ppm.}$$

Now, assuming density of solution to be 1 g/mL,

mole of Ca^{2+} per litre = mole of SO_4^{2-} per litre

$$= \frac{96}{10^6} \times \frac{10^3}{96} = 10^{-3} \text{ M.}$$

If Ca^{2+} is replaced by H^+ ,

$$[\text{H}^+] = 2 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(2 \times 10^{-3}) = 2.7.$$

Ex. 67. A sample of Mg was burnt in air to give a mixture of MgO and Mg_3N_2 . The ash was dissolved in 60 m.e. of HCl and the resulting solution back titrated with NaOH. 12 m.e. of NaOH were required to reach the end point. An excess of NaOH was then added and the solution distilled. The ammonia released was then trapped in 10 m.e. of second acid solution. Back titration of this solution required 6 m.e. of the base. Calculate the percentage of Mg burnt to nitride.

Solution :

First Method : m.e. method

$$\begin{aligned} \text{m.e. of } \text{MgO} + \text{m.e. of } \text{Mg}_3\text{N}_2 &= \text{m.e. of HCl reacted} \\ &= \text{m.e. of total HCl} - \text{m.e. of NaOH} \\ &= 60 - 12 = 48. \end{aligned}$$

In the dissolution of ash, HCl reacts with total Mg in Mg_3N_2 and in MgO and also with N in Mg_3N_2 .

$$\therefore \text{m.e. of total Mg} + \text{m.e. of N} = 48$$

$$\text{or m.e. of total Mg} + \text{m.e. of } \text{NH}_3 = 48$$

$$\text{m.e. of total Mg} = 48 - 4 = 44.$$

Further, Mg converted to Mg_3N_2 whose N converts to NH_4Cl (or NH_3),

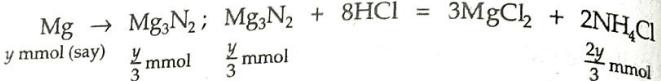
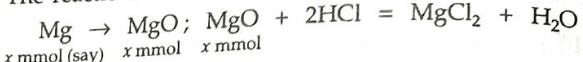
$$\therefore \text{m.e. of Mg converted to } \text{Mg}_3\text{N}_2 = 3 \times \text{m.e. of } \text{NH}_3$$

Hence
the part go

$$\begin{aligned}
 &= 3 \times (10 - 6) \\
 &= 12. \\
 \therefore \text{percentage of Mg converted to Mg}_3\text{N}_2 &= \frac{12}{44} \times 100 \\
 &= 27.27\%.
 \end{aligned}$$

Second Method : Mole Method

The reactions involved are



$$\begin{aligned}
 \therefore 2x \text{ mmol of HCl} + \frac{8y}{3} \text{ mmol of HCl} \\
 &= \text{total mmol of HCl} - \text{mmol of NaOH} \\
 &= 60 - 12 = 48
 \end{aligned}$$

$$2x + \frac{8y}{3} = 48 \quad \dots (1)$$

Further, mmol of NH₄Cl = mmol of NH₃ = (10 - 6)

$$\text{or } \frac{2y}{3} = 4.$$

From eqns. (1) and (2), one can calculate: $x = 16$ and $y = 6$.

$$\therefore \text{percentage of Mg converted to Mg}_3\text{N}_2 = \frac{y}{x+y} = \frac{6}{16+6} = 27.27\%$$

(Note: Mole method is more convenient to equivalent method.)

Ex. 68. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of KMnO₄ (20 mL) acidified with dilute H₂SO₄. The same volume of KMnO₄ solution is just decolourised by 10 mL of MnSO₄ in neutral medium forming a dark brown precipitate of hydrated MnO₂. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H₂SO₄. Write the balanced equations involved in the reactions and calculate the molarity of H₂O₂. (IIT 2001)

Solution : m.e. of H₂O₂ in 20 mL solution

$$\begin{aligned}
 &= \text{m.e. of 20 mL of KMnO}_4 \\
 &= \text{m.e. of 20 mL of MnSO}_4 \\
 &= \text{m.e. of MnO}_2 \\
 &= \text{m.e. of Na}_2\text{C}_2\text{O}_4
 \end{aligned}$$

Volumetric Calculations

$$\begin{aligned}
 &= 0.4 \times 10 \quad (\text{normality} = \text{molarity} \times \text{change in ON}) \\
 &= 4.
 \end{aligned}$$

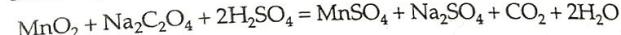
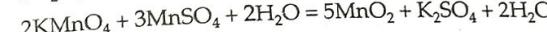
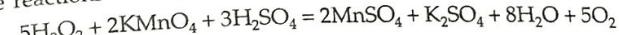
Eq. of H₂O₂ in 20 mL solution

$$= \frac{4}{1000}.$$

$$\text{Mole of H}_2\text{O}_2/20 \text{ mL} = \frac{4}{1000} \times \frac{1}{2}.$$

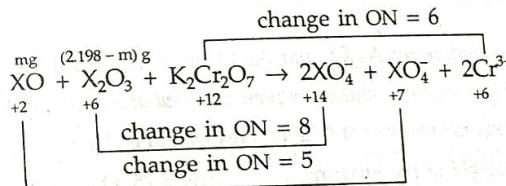
$$\begin{aligned}
 \text{Molarity (mole/L)} &= \frac{4}{2000} \times \frac{1000}{20} \\
 &= 0.1 \text{ M}.
 \end{aligned}$$

The reactions involved are,



Ex. 69. You are given a 2.198-g sample containing a mixture of XO and X₂O₃. It requires 0.015 mol of K₂Cr₂O₇ to oxidise the sample completely to form XO₄⁻ and Cr³⁺. If 0.0187 mole of XO₄⁻ is formed, what is the atomic mass of X?

Solution :



Applying POAC for X atoms of atomic mass, say x,
mole of XO + 2 × mole of X₂O₃ = mole of XO₄⁻

$$\frac{m}{x+16} + \frac{2(2.198-m)}{2x+48} = 0.0187. \quad \dots (1)$$

Applying law of equivalence,

$$\text{eq. of XO} + \text{eq. of X}_2\text{O}_3 = \text{eq. of K}_2\text{Cr}_2\text{O}_7$$

$$\frac{m}{x+16} \times 5 + \frac{(2.198-m)}{2x+48} \times 8 = 0.015 \times 6 \quad \dots (2)$$

Solving equations (1) and (2),

$$x = 100.04.$$

Ex. 70. The arsenic in a 1.22-g sample of a pesticide was converted to AsO₄³⁻ by suitable chemical treatment. It was then titrated using Ag⁺ to form Ag₃AsO₄

Hence
the part go

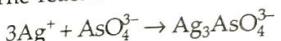
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as a precipitate. If it took 25 mL of 0.102 M Ag^+ to reach to equivalence in this titration, what is the percentage of arsenic in the pesticide?

Solution : The reaction



is not a redox reaction but a precipitation reaction. The equivalent weight of AsO_4^{3-} and Ag^+ are given by $E_{\text{AsO}_4^{3-}} = \frac{139}{3}$ and $E_{\text{Ag}^+} = \frac{108}{1}$

$$\text{Now, m.e. of AsO}_4^{3-} = \text{m.e. of Ag}^+ = \text{mmol of Ag}^+ \\ = 0.102 \times 25 = 2.55.$$

$$\text{Eq. of AsO}_4^{3-} = \frac{2.55}{1000} = 0.00255.$$

$$\text{Mole of AsO}_4^{3-} = \frac{0.00255}{3} = 0.00085.$$

$$\text{Mole of As} = 0.00085.$$

$$\text{Wt. of As} = 0.00085 \times 75 = 0.06375 \text{ g.}$$

Percentage of arsenic in the pesticide

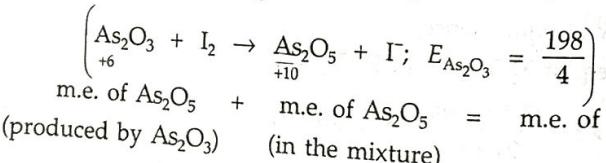
$$= \frac{0.06375}{1.22} \times 100 \\ = 5.22\%.$$

Ex. 71. A mixture containing As_2O_3 and As_2O_5 required 20 mL of 0.05 N iodine for titration. The resulting solution is then acidified and excess of KI was added. The liberated iodine required 1.0 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ for complete reaction. Calculate the weight of the mixture. (As = 75, O = 16, S = 32, Na = 23)

Solution : m.e. of As_2O_3 = m.e. of iodine

$$= 20 \times 0.05 = 1.0.$$

$$\text{Wt. of As}_2\text{O}_3 = \frac{1.0}{1000} \times \frac{198}{4} \text{ g} = 0.0495 \text{ g}$$



$$\text{or m.e. of As}_2\text{O}_3 + \text{m.e. of As}_2\text{O}_5 = \text{m.e. of Na}_2\text{S}_2\text{O}_3$$

$$1.0 + \text{m.e. of As}_2\text{O}_5 = \frac{1}{248/1} \times 1000$$

$$\text{m.e. of As}_2\text{O}_5 = 4.032.$$

Volumetric Calculations

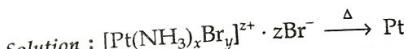
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$$\text{Wt. of As}_2\text{O}_5 \text{ in the mixture} = \frac{4.032}{1000} \times \frac{230}{4} \text{ g} \\ = 0.232 \text{ g.}$$

$$\left(\text{As}_2\text{O}_5 + \text{I}^- \xrightarrow{\Delta} \text{As}_2\text{O}_3 + \text{I}_2; E_{\text{As}_2\text{O}_5} = \frac{230}{4} \right)$$

$$\therefore \text{wt. of } (\text{As}_2\text{O}_3 + \text{As}_2\text{O}_5) = 0.0495 + 0.232 \text{ g} \\ = 0.2815 \text{ g.}$$

Ex. 72. A sample of 0.15 g of the compound $[\text{Pt}(\text{NH}_3)_x\text{Br}_y]^{z+} \cdot z\text{Br}^-$, ignited and dissolved in water and titrated rapidly with 0.01 M AgNO_3 solution. 51.50 mL was required to precipitate all the ionic bromide. A third 0.15-g sample was heated for two hours on a steam bath in a solution to which 0.2 mole of AgNO_3 has been added. This precipitated all the bromide (not just the free ionic Br^-) as AgBr . The weight of the precipitate thus produced was 0.20 g. Find x , y and z . ($\text{Pt} = 195$, $\text{Ag} = 108$, $\text{Br} = 80$, $\text{N} = 14$ and $\text{H} = 1$)



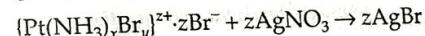
Applying POAC for Pt atoms,

$$1 \times \text{mole of the compound} = 1 \times \text{mole of Pt}$$

$$\frac{0.15}{M} = \frac{0.0502}{195} \quad \dots (1)$$

$$\text{where, } M = 195 + 17x + 80y + 80z. \quad \dots (2)$$

For 0.15 g of the second sample containing z Br atoms per molecule (only the ionic bromide), one molecule of the compound shall combine with z molecules of AgNO_3 to give z molecules of AgBr .

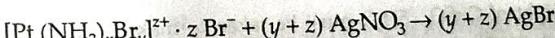


Applying mole ratio method to reactants

$$z \times \text{mole of the compound} = 1 \times \text{mole of AgNO}_3$$

$$z \times \frac{0.15}{M} = \frac{0.01 \times 51.5}{1000}. \quad \dots (3)$$

For the 0.15 g of the third sample, all bromine atoms ($y+z$) in the compound combine with AgNO_3 to give $(y+z)$ molecules of AgBr ,



Applying mole ratio method,

$$(y+z) \times \text{mole of the compound} = 1 \times \text{mole of AgBr}$$

$$(y+z) \times \frac{0.15}{M} = 1 \times \frac{0.20}{188}. \quad \dots (4)$$

Solving equations (1), (2), (3) and (4), we get,

$$x = 4, \quad y = 2 \quad \text{and} \quad z = 2.$$

Ex. 73. 10 mL of tap water containing Ca^{2+} and Mg^{2+} in the presence of was properly buffered and the indicator murexide added. The sample was heated to 60°C. Titration with 0.01 M EDTA solution changed the colour at 7.50 mL. This complexed Ca^{2+} only.

A second 10-mL sample was made basic and Eriochrome Black T indicator. Titration with 0.01 M EDTA solution changed the indicator colour at 13.0 mL. Under these conditions both Ca^{2+} and Mg^{2+} are complexed.

If the 10 mL of water sample were to be evaporated to dryness, what of $\text{CaCO}_3 + \text{MgCO}_3$ would be formed?

Solution : All EDTA complexes are formed on a one-to-one basis dispositive ions.

$$\text{Mole of } \text{Ca}^{2+} + \text{Mg}^{2+} = \text{mole of } \text{CaCO}_3 + \text{mole of } \text{MgCO}_3$$

$$= \frac{0.01 \times 13.02}{1000} = 13 \times 10^{-5}$$

$$\text{Mole of } \text{Ca}^{2+} = \text{mole of } \text{CaCO}_3$$

$$= \frac{0.01 \times 7.50}{1000} = 7.50 \times 10^{-5}$$

$$\therefore \text{mole of } \text{MgCO}_3 = 13 \times 10^{-5} - 7.50 \times 10^{-5} = 5.5 \times 10^{-5}$$

$$\therefore \text{weight of } \text{CaCO}_3 + \text{MgCO}_3 = 7.50 \times 10^{-5} \times 100 + 5.5 \times 10^{-5} \times 84 \\ = 1.21 \times 10^{-2} \text{ g.}$$

$$(\text{CaCO}_3 = 100, \text{MgCO}_3 = 84)$$

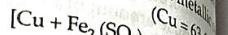
PROBLEMS

(Answers bracketed with questions)

- Calculate the strength in g/L of 3 N HCl and $\frac{N}{2} \text{H}_2\text{SO}_4$ solutions. (1095, 134)
- How many mL of 1 M sulphuric acid is required to neutralise 10 mL of sodium hydroxide solution? (5)
- 2 litres of ammonia at 13°C and 0.90 atmospheric pressure is neutralised by 134 mL of H_2SO_4 solution. Find the normality of the acid. (134)
- What weight of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ must be taken to make 0.5 litre of 0.01 M copper (II) ion solution? (124)
- (a) Calculate the molarity of hydrogen chloride in a solution when 0.365 g of has been dissolved in 100 mL of the solution.
(b) 3 g of a salt of molecular weight 30 is dissolved in 250 g of water. The molarity of the solution is
[(a) 0.1 M (b) 0.04]

After all copper is precipitated it was found that not all the zinc had dissolved. After filtration the total solid at the end of the reaction was 9.810 g. Calculate (i) the weight of copper deposited and (ii) molarity of copper sulphate in the original solution. ($\text{Cu} = 63.5$, $\text{Zn} = 65.4$)

19. 0.108 g of finely-divided copper was treated with an excess of ferric sulphate solution until copper was completely dissolved. The solution after the addition of excess dilute sulphuric acid required 33.7 mL of 0.1 N KMnO_4 for complete oxidation. Find the equation which represents the reaction between metallic copper and ferric sulphate solution.



20. A commercial sample (2.013 g) of NaOH containing Na_2CO_3 as an impurity was dissolved to give 250 mL of solution. A 10 mL portion of the solution required 20 mL of 0.1 N H_2SO_4 solution for complete neutralisation. Calculate the percentage by weight of Na_2CO_3 in the sample.

21. (i) A solution of a mixture of KCl and KOH was neutralised with 120 mL of 0.1 N HCl. Calculate the amount of KOH in the mixture.
(ii) After titration, the resultant solution was made acidic with HNO_3 . Then 10 mL of AgNO_3 solution was added to precipitate the AgCl which weighed 3.7 g. On drying, Calculate percentage of KOH in the original mixture. (0.806 g)

22. 10.03 g of vinegar was diluted to 100 mL and a 25 mL sample was titrated with the 0.0176 M $\text{Ba}(\text{OH})_2$ solution. 34.30 mL was required for equivalence. What is the percent of acetic acid in the vinegar?

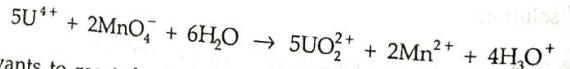
23. Zinc can be determined volumetrically by the precipitation reaction



- A sample of zinc ore weighing 1.5432 g was prepared for reaction and required 34.68 mL of 0.1043 M $\text{K}_4\text{Fe}(\text{CN})_6$ for titration. What is the percentage of zinc in the ore?

24. 5.5 g of a mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ requires 54 mL of 0.1 N KMnO_4 solution for complete oxidation. Calculate the number of moles of hydrated ferric sulphate in the mixture. (0.007 mole)

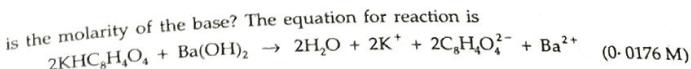
25. A chemist is preparing to analyse samples that will contain no more than 0.5% uranium. His procedure calls for preparing the uranium as U^{4+} ion and oxidising it by MnO_4^- in acid solution.



- If he wants to react the total U^{4+} sample with a maximum of 50 mL of KMnO_4 solution, what concentration should he choose? (0.016 M)

26. For the standardisation of a $\text{Ba}(\text{OH})_2$ solution, 0.2 g of potassium acid phthalate (wt. of one mole = 204.2 g) was weighed which was then titrated with $\text{Ba}(\text{OH})_2$ solution. The titration indicated equivalence at 27.80 mL of $\text{Ba}(\text{OH})_2$ solution. What is the molarity of the base? The equation for reaction is

Volumetric Calculations



27. A sample of magnesium metal containing some magnesium oxide as impurity was dissolved in 125 mL of 0.1 N H_2SO_4 . The volume of hydrogen evolved at 27.3°C and 1 atm was 120.1 mL. The resulting solution was found to be 0.02 N with respect to H_2SO_4 . Calculate (i) the weight of the sample dissolved and (ii) the percentage by weight of magnesium in the sample. Neglect any change in the volume of the solution. (0.1235 g ; 95.95%)

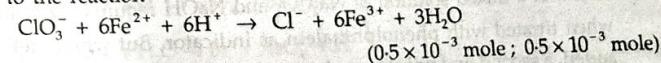
28. A piece of aluminium weighing 2.7 g is treated with 75 mL of H_2SO_4 (sp. gr. 1.18 containing 24.7% H_2SO_4 by weight). After the metal is completely dissolved, the solution is diluted to 400 mL. Calculate the molarity of free sulphuric acid in the resulting solution. (0.177 M)

29. 4.00 g of mixture of NaCl and Na_2CO_3 was dissolved in water and the volume made up to 250 mL; 25 mL of this solution required 50 mL of N/10 HCl for complete neutralisation. Calculate percentage composition of the original mixture. (33.75% ; 66.25%)

30. 1.00 g of a mixture consisting of equal number of moles of carbonates of the two univalent metals, required 44.4 mL of 0.5 N HCl for complete reaction. If the atomic weight of one of the metals is 7, find the atomic weight of the other metal. What will be the total amount of sulphate formed on gravimetric conversion of 1 g of the mixture of sulphates? (23.1 ; 1.4 g)

31. A mixture containing only Na_2CO_3 and K_2CO_3 weighing 1.22 g was dissolved in water to form 100 mL of a solution. 20 mL of this solution required 40 mL of 0.1 N HCl for neutralisation. Calculate the weight of Na_2CO_3 in the mixture. If another 20 mL portion of the solution is heated with excess of BaCl_2 , what will be the weight of the precipitate obtained? (0.53 g ; 0.3946 g)

32. 1.00 g of a moist sample of a mixture of KCl and KClO_3 was dissolved in water and made up to 250 mL. 25 mL of this solution was treated with SO_2 to reduce the chlorate to chloride and excess SO_2 was removed by boiling. The total chloride was precipitated as silver chloride. The weight of the precipitate was 0.1435 g. In another experiment, 25 mL of the original solution was heated with 30 mL of 0.2 N solution of ferrous sulphate and unreacted ferrous sulphate required 37.5 mL of 0.08 N solution of an oxidising agent for complete oxidation. Calculate the molar ratio of chlorate to chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to the reaction



33. 0.6 g of a sample of pyrolusite was boiled with 200 mL of N/10 oxalic acid and excess of dilute H_2SO_4 . The liquid was filtered and the residue washed. The filtrate and washings were mixed and made up to 500 mL. 100 mL of this solution required 50 mL of N/30 KMnO_4 solution. Calculate the percentage of MnO_2 in the given sample of pyrolusite. (84.58%)

34. 25 mL of a 0.107 M H_3PO_4 was titrated with a 0.115 M solution of a $NaOH$, to the end point identified by the colour change of the indicator, bromophenol green. This required 23.1 mL. The titration was repeated using phenolphthalein as the indicator. This time 25 mL of 0.107 M H_3PO_4 required 46.8 mL of the $NaOH$. What is the coefficient n in the equation,
 $H_3PO_4 + nOH^- \rightarrow nH_2O + [H_{(3-n)}PO_4]^{n-}$ for each reaction?

35. 9.8 g of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot xH_2O$ was dissolved in 250 mL of its solution. 10 mL of this solution required 20 mL of $KMnO_4$ solution containing 3.53 g of $KMnO_4$ dissolved per litre. Calculate x .

36. 10 mL of H_2O_2 weighs 10.205 g. The solution was diluted to 250 mL, which required 35.8 mL of a decinormal solution of $KMnO_4$. Calculate the strength of H_2O_2 in 100 mL and also the volume strength of the solution.

37. 50 mL of H_2O_2 was treated with excess of KI in presence of dilute sulphuric acid. I_2 so liberated was titrated with 20 mL of 0.1 N hypo solution. Calculate the strength of H_2O_2 in grams per litre. (6.086 g)

38. Calculate the percentage of available chlorine in a sample of 3.546 g of bleaching powder which was dissolved in 100 mL of water; 25 mL of this solution, after treatment with KI and dilute acid, required 20 mL of 0.125 N sodium thiosulphate solution.

39. (a) A zinc rod weighing 25.00 g was kept in 100 mL of 1 M $CuSO_4$ solution for a certain time. Molarity of Cu^{2+} in solution was 0.8 M. What was the molarity of the sulphate ion (SO_4^{2-})? What was the weight of the zinc rod after cleaning? (b) If the above experiment was done with a copper rod of weight 25 g and 25 mL of 2 M zinc sulphate ($ZnSO_4$) solution, what would be the molarity of Zn^{2+} at the end of the same interval?

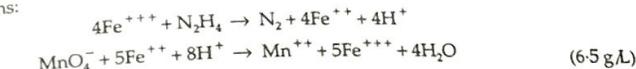
40. 25 mL of a mixed solution of Na_2CO_3 and $NaHCO_3$ required 12 mL of N/20 HCl when titrated using phenolphthalein as an indicator. But 25 mL of the same solution titrated separately with methyl orange required 30 mL of N/20 HCl. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in grams per litre. (2.544 g)

41. 20 mL of a mixed solution of Na_2CO_3 and $NaOH$ required 17.5 mL of N/10 HCl when titrated with phenolphthalein as indicator. But when methyl orange was added, a second end point was observed on the further addition of 2.5 mL of HCl. Calculate the amount of Na_2CO_3 and $NaOH$ in the solution. (0.02648 g)

42. 0.2 g of a chloride of an element was dissolved in water and then treated with excess of silver nitrate solution resulting in the formation of 0.47 g of silver chloride. Find the equivalent weight of the element. (25)

43. A sample of hydrazine sulphate ($N_2H_4SO_4$) was dissolved in 100 mL of water. 10 mL of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 mL of M/50 potassium permanganate solution. Estimate the amount of hydrazine sulphate in one litre of the solution. (IIT 1988)

Reactions:



Hint: Eq. wt. of $N_2H_4 = \frac{\text{mol. wt.}}{4}$

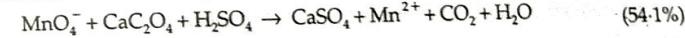
44. 5 g of bleaching powder was suspended in water and volume made up to half a litre. 20 mL of this suspension when acidified with acetic acid and treated with excess of KI solution, liberated I_2 which required 20 mL of a N/10 hypo solution for titration. Calculate the percentage of available chlorine in bleaching powder.

[Hint: See Example 58.]

45. A 10-g mixture of Cu_2S and CuS was treated with 200 mL of 0.75 M MnO_4^- in acid solution producing SO_2 , Cu^{2+} and Mn^{2+} . The SO_2 was boiled off and the excess MnO_4^- was titrated with 175 mL of 1 M Fe^{2+} solution. Calculate the percentage of CuS in the original mixture. (57.4%)

Hint: $Cu_2S \xrightarrow{\substack{+2 \\ -2}} 2Cu^{2+} + SO_2$; eq. wt. of $Cu_2S = \frac{\text{mol. wt.}}{8}$

46. A 0.518-g sample of limestone is dissolved and then Ca 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. What is the percentage of CaO in limestone?



47. 20 mL of M/60 solution of $KBrO_3$ was added to a certain volume of SeO_3^{2-} solution. Br_2 evolved was removed by boiling and the excess of $KBrO_3$ was back titrated with 5.1 mL of $\frac{M}{25}$ solution of $NaAsO_2$. Calculate the weight of SeO_3^{2-} in the solution. (0.084 g)

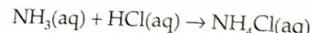
Hint: $SeO_3^{2-} + BrO_3^- + H^+ \rightarrow SeO_4^{2-} + Br_2 + H_2O$
 $BrO_3^- + AsO_3^{3-} + H_2O \rightarrow Br^- + AsO_4^{3-} + H^+$

48. Concentrated HCl solution is 37.0% HCl and has a density of 1.19 g/mL. A dilute solution of HCl is prepared by diluting 4.50 mL of this concentrated HCl solution to 100 mL with water. Then 10 mL of this dilute HCl solution reacts with an $AgNO_3$ solution. Calculate the volume of 0.108 M $AgNO_3$ solution required to precipitate all the chloride as $AgCl(s)$.

49. 0.9546 g of a Rochelle salt, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, on ignition, gave NaKCO_3 . It was treated with 41.72 mL of 0.1307 N H_2SO_4 . The unreacted H_2SO_4 was neutralised by 1.91 mL of 0.1297 N NaOH. Find the percentage purity of Rochelle salt in the sample.

50. A mixture of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ weighing 0.24 g on being treated with acid solution liberates just sufficient I_2 to react with 60 mL of 0.1 N solution. Calculate percentage of Cr and Mn in the mixture. (20.83%)

[Hint: $\text{KMnO}_4 \rightarrow \text{Mn}^{2+}$ and $\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow 2\text{Cr}^{3+}$]

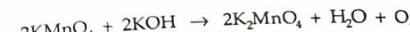


After drawing air through the acid solution for 10 minutes at a rate of 10 litres/min, the acid was titrated. The remaining acid required 13.1 mL of 0.0588 M NaOH to reach the equivalence point.

- (a) How many grams of NH_3 were drawn into the acid solution?
 - (b) How many ppm of NH_3 were in the air?
 - (c) Is this manufacturer in compliance with regulations?

(a) 0.00475 g (b) 61.6 ppm

Objective Problems



- (a) 52% of an acid requires 20 mL of 0.1 N NaOH for complete neutralisation.

9. H_3PO_4 is a tribasic acid and one of its salt is NaH_2PO_4 . What volume of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4 ?
 (a) 100 mL (b) 200 mL (c) 80 mL (d) 300 mL

11. In a reaction 4 moles of electrons are transferred to one mole of HNO_3 when acted as an oxidant. The possible reduction product is

- (a) $\frac{1}{2}$ mole of N_2 (b) $\frac{1}{2}$ mole of N_2O
 (c) 1 mole of NO_2 (d) 1 mole of NH_3

13. What volume of 0.1N HNO_3 solution can be prepared from 6.3 g of HNO_3 ?
(a) 20 ml (b) 2 litres (c) 0.5 litre (d) 5 litres

- (a) 1 litre (b) 2 litres (c) 3 litres (d) 4 litres

14. The volume of water to be added to 200 mL of semiconcentrated HCl solution to dilute it to 2000 mL is
(a) 400 mL (b) 600 mL (c) 800 mL (d) 1000 mL

15. 0.2 g of a sample of H_2O_2 required 10 mL of N KMnO_4 in a titration in the presence of H_2SO_4 . Purity of H_2O_2 is
 (a) 55% (b) 85% (c) 65% (d) 95%

16. 100 mL of 0.5 N NaOH solution is added to 10 mL of 3 N H_2SO_4 solution and 20 mL of 1 N HCl solution. The mixture is
 (a) acidic (b) alkaline (c) neutral (d) none of these

17. Which of the following has the highest normality?

18. Eq. wt. of a metal, x g of which reacts with 1 eq. of an acid, is

20. 0.7 g of $\text{Na}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$ is dissolved in 100 mL of water, 20 mL of which required 19.8 mL of 0.1 N HCl. The value of x is

21. The normality of 10 mL of a '20 V' H_2O_2 is
 (a) 1.79 (b) 3.58 (c) 60.86 (d) 6.086