# 8 Redox Titrations

**1.** The most important fact for solving the problems of redox changes is to evaluate equivalent mass of redox correctly using the formula:

Eq. mass of reductant or oxidant

$$= \frac{\text{Molar mass of reductant or oxidant}}{\begin{array}{c}\text{No. of electrons lost or gained by one molecule}\\ \text{of reductant or oxidant respectively}\end{array}}$$

**2.** Valence factor $= \dfrac{\text{Molar mass}}{\text{Equivalent mass}}$

or No. of electrons lost or gained by one molecule of reductant or oxidant.

**3.** Calculate the Meq. of desired substance and then calculate its mass by:

$$\text{Meq.} = N \times V_{\text{in mL}}$$
$$= M \times \text{Valence factor} \times V_{\text{in mL}}$$
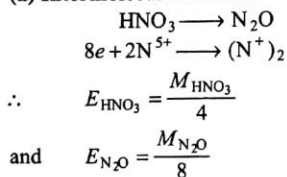$$\text{Meq.} = \frac{\text{Mass}}{\text{Eq. mass}} \times 1000$$

This equation gives mass of substance whose Eq. mass is substituted.

**4.** Be careful in deciding equivalent mass. First write redox change for each and then derive no. of electron lost or gained by one molecule of reductant or oxidant.
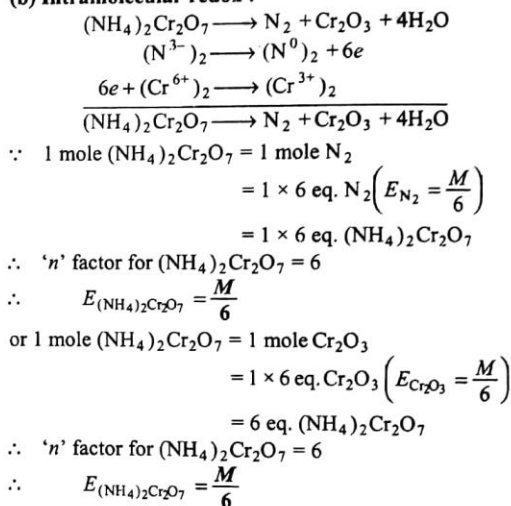
**5.** In case balanced equation is given, it is always advised to proceed with mole concept to avoid complications in equivalent mass determination.

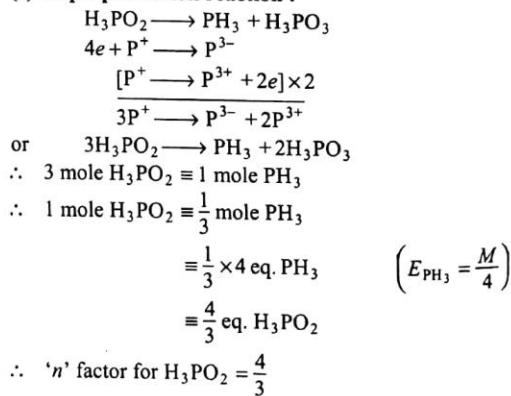**6.** Method to calculate equivalent mass of an oxidant/reductant in :

**(a) Intermolecular redox :**
$$HNO_3 \longrightarrow N_2O$$
$$8e + 2N^{5+} \longrightarrow (N^+)_2$$
$$\therefore \qquad E_{HNO_3} = \frac{M_{HNO_3}}{4}$$
$$\text{and} \qquad E_{N_2O} = \frac{M_{N_2O}}{8}$$

**(b) Intramolecular redox :**
$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$
$$(N^{3-})_2 \longrightarrow (N^0)_2 + 6e$$
$$\underline{6e + (Cr^{6+})_2 \longrightarrow (Cr^{3+})_2}$$
$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

$\because$ 1 mole $(NH_4)_2Cr_2O_7 = 1$ mole $N_2$
$$= 1 \times 6 \text{ eq. } N_2 \left(E_{N_2} = \frac{M}{6}\right)$$
$$= 1 \times 6 \text{ eq. } (NH_4)_2Cr_2O_7$$

$\therefore$ '$n$' factor for $(NH_4)_2Cr_2O_7 = 6$

$\therefore \qquad E_{(NH_4)_2Cr_2O_7} = \frac{M}{6}$

or 1 mole $(NH_4)_2Cr_2O_7 = 1$ mole $Cr_2O_3$
$$= 1 \times 6 \text{ eq. } Cr_2O_3 \left(E_{Cr_2O_3} = \frac{M}{6}\right)$$
$$= 6 \text{ eq. } (NH_4)_2Cr_2O_7$$

$\therefore$ '$n$' factor for $(NH_4)_2Cr_2O_7 = 6$

$\therefore \qquad E_{(NH_4)_2Cr_2O_7} = \frac{M}{6}$

**(c) Disproprionation reaction :**
$$H_3PO_2 \longrightarrow PH_3 + H_3PO_3$$
$$4e + P^+ \longrightarrow P^{3-}$$
$$\underline{[P^+ \longrightarrow P^{3+} + 2e] \times 2}$$
$$3P^+ \longrightarrow P^{3-} + 2P^{3+}$$

or $\qquad 3H_3PO_2 \longrightarrow PH_3 + 2H_3PO_3$

$\therefore$ 3 mole $H_3PO_2 \equiv 1$ mole $PH_3$

$\therefore$ 1 mole $H_3PO_2 \equiv \dfrac{1}{3}$ mole $PH_3$
$$\equiv \frac{1}{3} \times 4 \text{ eq. } PH_3 \qquad \left(E_{PH_3} = \frac{M}{4}\right)$$
$$\equiv \frac{4}{3} \text{ eq. } H_3PO_2$$

$\therefore$ '$n$' factor for $H_3PO_2 = \dfrac{4}{3}$

$$\therefore \quad E_{H_3PO_2} = \frac{M}{4/3} = \frac{3M}{4}$$

or 3 mole $H_3PO_2 \equiv 2$ mole $H_3PO_3$

or 1 mole $H_3PO_2 \equiv \frac{2}{3}$ mole $H_3PO_3$

$$\equiv \frac{2}{3} \times 2 \text{ eq. } H_3PO_3 \quad \left(E_{H_3PO_3} = \frac{M}{2}\right)$$

$$\equiv \frac{4}{3} \text{ eq. } H_3PO_2$$

$\therefore$ '$n$' factor for $H_3PO_2 = \frac{4}{3}$

$$\therefore \quad E_{H_3PO_2} = \frac{M}{4/3} = \frac{3M}{4}$$

## ● NUMERICAL PROBLEMS ●

1. Calculate the equivalent mass of each oxidant and reductant in:
   (a) $FeSO_4 + KClO_3 \longrightarrow KCl + Fe_2(SO_4)_3$
   (b) $Na_2SO_3 + Na_2CrO_4 \longrightarrow Na_2SO_4 + Cr(OH)_3$
   (c) $Fe_3O_4 + KMnO_4 \longrightarrow Fe_2O_3 + MnO_2$
   (d) $KI + K_2Cr_2O_7 \longrightarrow Cr^{3+} + 3I_2$
   (e) $Mn^{4+} \longrightarrow Mn^{2+}$
   (f) $NO_3^- \longrightarrow N_2$
   (g) $N_2 \longrightarrow NH_3$
   (h) $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$
   (i) $FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$

2. Calculate the equivalent mass of potassium permanganate ($KMnO_4$) in (i) neutral medium (ii) acidic medium (iii) alkaline medium, by oxidation number method. **(MLNR 1997)**

3. What is the mass of sodium bromate and molarity of solution to prepare 85.5 mL of 0.672$N$ solution when half cell reactions are?
   (i) $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$.
   (ii) $2BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O$
   **(IIT 1987)**

4. How many mL of 0.05$M$ $KMnO_4$ (acidic) are required to oxidize 2.0 g of $FeSO_4$ in dilute solution?

5. Dichromate ion in acid solution oxidizes stannous ion as
   $$3Sn^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$$
   (a) If $SnCl_2$ is the source of $Sn^{2+}$, how many gram of $SnCl_2$ would be contained in 2 litre of 0.1$N$ solution?
   (b) If $K_2Cr_2O_7$ is the source of $Cr_2O_7^{2-}$, what is the normality of solution containing 4.9 g $K_2Cr_2O_7$ in 0.1 litre of solution? **(IIT 1987)**

6. 20 mL of 0.2$M$ $MnSO_4$ are completely oxidized by 16 mL of $KMnO_4$ of unknown normality, each forming $Mn^{4+}$ oxidation state. Find out the normality and molarity of $KMnO_4$ solution.

7. Metallic tin in the presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic chloride. What volume of decinormal dichromate solution would be reduced by 1 g of tin? **(MLNR 1994)**

8. 5.5g of a mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ required 5.4 mL of 0.1$N$ $KMnO_4$ solution for complete oxidation. Calculate mole of hydrated ferric sulphate in mixture. **(IIT 1989)**

9. 0.5 g sample containing $MnO_2$ is treated with HCl, liberating $Cl_2$. The $Cl_2$ is passed into a solution of KI and 30.0 $cm^3$ of 0.1$M$ $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of $MnO_2$ in sample. (Atomic mass of Mn $= 55$) **(Roorkee 1994)**

10. The equivalent mass of an element is 13.16. It forms an acidic oxide which with KOH forms a salt, isomorphous with $K_2SO_4$. Deduce Atomic mass of element.

11. In an ore, the only oxidizable material is $Sn^{2+}$. This ore is titrated with a dichromate solution containing 2.5 g of $K_2Cr_2O_7$ in 0.5 litre. A 0.40g sample of the ore required 10.0 $cm^3$ of titrant to reach equivalence point. Calculate the percentage of tin in ore. **(Roorkee 1993)**

12. 1g of $H_2O_2$ solution containing $X$% $H_2O_2$ by mass requires $X$ mL of $KMnO_4$ for complete oxidation in acid medium. Calculate normality of $KMnO_4$ solution.

13. An element $A$ in a compound $ABD$ has an oxidation No. $A^{n-}$. It is oxidized by $Cr_2O_7^{2-}$ in acid medium. In an experiment $1.68 \times 10^{-3}$ mole of $K_2Cr_2O_7$ was required for $3.26 \times 10^{-3}$ mole of the compound $ABD$. Calculate new oxidation state of $A$.

14. 20 mL of a solution containing 0.2 g of impure sample of $H_2O_2$ reacts with 0.316 g of $KMnO_4$ (acidic). Calculate:
    (a) Purity of $H_2O_2$
    (b) Volume of dry $O_2$ evolved at 27°C and 750 mm P.
    **(IIT 1985)**

15. Find out the % of oxalate ion in given sample of oxalate salt of which 0.3 g dissolved in 100 mL of water required 90 mL of $N/20$ $KMnO_4$ for complete oxidation.

16. 50 mL of an aqueous solution of $H_2O_2$ was treated with an excess of KI solution in dil. $H_2SO_4$, the liberated iodine required 20 mL of 0.1 $N$ $Na_2S_2O_3$ solution for complete reaction. Calculate concentration of $H_2O_2$ in g/litre.

17. 1.2 g of a commercial sample of oxalic acid was dissolved in 200 mL of water. 10 mL of this sample required 8.5 mL of $N/10$ $KMnO_4$. Calculate % of purity of sample.

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

    (b) To a 25 mL $H_2O_2$ solution, excess of acidified solution of KI was added. The iodine liberated required 20 mL of $0.3$ $N$ sodium thiosulphate solution. Calculate the volume strength of $H_2O_2$ solution. **(IIT July 1997)**

19. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute $H_2SO_4$. The same volume of the $KMnO_4$ solution is just decolourized by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated $MnO_2$. The brown precipitate is dissolved in 10 mL of 0.2 $M$ sodium oxalate under boiling condition in the presence of dilute $H_2SO_4$. Write the balanced equations involved in the reactions and calculate the molarity of $H_2O_2$. **(IIT 2001)**

20. 0.56 g of limestone was treated with oxalic acid to give $CaC_2O_4$. The precipitate decolorized 45 mL of $0.2N$ $KMnO_4$ in acid medium. Calculate % of CaO in limestone. **(IIT 1988)**

21. 25 g of a sample of $FeSO_4$ was dissolved in water containing dil. $H_2SO_4$ and the volume made upto 1 litre. 25 mL of this solution required 20 mL of $N/10$ $KMnO_4$ for complete oxidation. Calculate % of $FeSO_4 \cdot 7H_2O$ in given sample.

22. $KMnO_4$ oxidizes $X^{n+}$ ion to $XO_3^-$, itself changing to $Mn^{2+}$ in acid solution. $2.68 \times 10^{-3}$ mole of $X^{n+}$ requires $1.61 \times 10^{-3}$ mole of $MnO_4^-$. What is the value of $n$? Also calculate the atomic mass of $X$, if the mass of 1g-equivalent of $XCl_n$ is 56.

23. 5.7 g of bleaching powder was suspended in 500 mL of water. 25 mL of this suspension on treatment with KI and HCl liberated iodine which reacted with 24.35 mL of $N/10$ $Na_2S_2O_3$. Calculate % of available $Cl_2$ in bleaching powder. **(Roorkee 1990)**

24. A solution of $0.1M$ $KMnO_4$ is used for the reaction:
$$S_2O_3^{2-} + 2MnO_4^- + H_2O \longrightarrow MnO_2 + SO_4^{2-} + OH^-$$
What volume of solution in mL will be required to react with 0.158 g of $Na_2S_2O_3$? **(MLNR 1991)**

25. A sample of $Fe_2(SO_4)_3$ and $FeC_2O_4$ was dissolved in dil. $H_2SO_4$. The complete oxidation of reaction mixture required 40 mL of $N/16$ $KMnO_4$. After the oxidation, the reaction mixture was reduced by Zn and dil. $H_2SO_4$. On again oxidation by same $KMnO_4$, 60 mL were required. Calculate the ratio of Meq. of $Fe_2(SO_4)_3$ and $FeC_2O_4$ in mixture.

26. A solution of 0.2 g of a compound containing $Cu^{2+}$ and $C_2O_4^{2-}$ ions on titration with $0.02M$ $KMnO_4$ in presence of $H_2SO_4$ consumes 22.6 mL oxidant. The resulting solution is neutralized by $Na_2CO_3$, acidified with dilute $CH_3COOH$ and titrated with excess of KI. The liberated $I_2$ required 11.3 mL of $0.05M$ $Na_2S_2O_3$ for complete reduction. Find out mole ratio of $Cu^{2+}$ and $C_2O_4^{2-}$ in compound. **(IIT 1991)**

27. 1 g sample of $AgNO_3$ is dissolved in 50 mL of water. It is titrated with 50 mL of KI solution. The AgI precipitated is filtered off. Excess of KI in filtrate is titrated with $M/10$ $KIO_3$ in presence of $6M$ HCl till all $I^-$ converted into ICl. It requires 50 mL of $M/10$ $KIO_3$ solution. 20 mL of the same stock solution of KI requires 30 mL of $M/10$ $KIO_3$ under similar conditions. Calculate % of $AgNO_3$ in sample. The reaction is:
$$KIO_3 + 2KI + 6HCl \longrightarrow 3ICl + 3KCl + 3H_2O$$
**(IIT 1992)**

28. 1.6 g of pyrolusite ore was treated with $50\,cm^3$ of $1.0\,N$ oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to $250\,cm^3$ in a flask. $25\,cm^3$ of this solution when titrated with 0.1 $N$ $KMnO_4$ required $32\,cm^3$ of the solution. Find out the percentage of pure $MnO_2$ in the sample and also the percentage of available oxygen. **(Roorkee 1996)**

29. An aqueous solution containing 0.10 g $KIO_3$ (formula mass = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated $I_2$ consumed 45 mL of thiosulphate solution to decolourize the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution. **(IIT 1998)**

30. 2.6 g sample of pyrolusite was boiled with 65 mL of $N$ oxalic acid and excess of dil. $H_2SO_4$. The liquid was then filtered and the residue washed. The filtrate and the washing were mixed and made upto 500 mL. 100 mL of this solution required 50 mL of $N/10$ $KMnO_4$. Calculate % of $MnO_2$ in sample.

31. 25 mL of a solution containing $Fe^{2+}$ and $Fe^{3+}$ sulphate acidified with $H_2SO_4$ is reduced by 3 g of metallic zinc. The solution required 34.25 mL of $N/10$ solution of $K_2Cr_2O_7$ for oxidation. Before reduction with zinc, 25 mL of the same solution required 22.45 mL of same $K_2Cr_2O_7$ solution. Calculate the strength of $FeSO_4$ and $Fe_2(SO_4)_3$ in solution.

32. A sample of $MnSO_4 \cdot 4H_2O$ is strongly heated in air. The residue ($Mn_3O_4$) left was dissolved in 100 mL of

$0.1N$ $FeSO_4$ containing dil. $H_2SO_4$. This solution was completely reacted with 50 mL of $KMnO_4$ solution. 25 mL of this $KMnO_4$ solution was completely reduced by 30 mL of 0.1 $N$ $FeSO_4$ solution. Calculate the amount of $MnSO_4 \cdot 4H_2O$ in sample. **(Roorkee 2001)**

33. A solution contains mixture of $H_2SO_4$ and $H_2C_2O_4$. 25 mL of this solution requires 35.5 mL of $N/10$ NaOH for neutralization and 23.45 mL of $N/10$ $KMnO_4$ for oxidation. Calculate:
    (a) Normality of $H_2C_2O_4$ and $H_2SO_4$.
    (b) Strength of $H_2C_2O_4$ and $H_2SO_4$.
    Assume molar mass of $H_2C_2O_4 = 126$

34. Calculate the mass of $MnO_2$ and the volume of HCl of specific gravity 1.2 g $mL^{-1}$ and 4% nature by mass, needed to produce 1.78 litre of $Cl_2$ at STP by the reaction:
    $$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

35. A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 mL water. 10 mL of this solution was reacted with excess of $FeCl_3$ solution and warmed to complete the reaction. Ferrous ions formed were estimated and it required 20 mL of $M/50$ $KMnO_4$ solution. Estimate the mass of hydrazine sulphate in one litre of solution:
    Given, $4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$
    $$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$
    **(IIT 1988; MLNR 1993, 96)**

36. A 1 g sample of $Fe_2O_3$ solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100 mL. An aliquot of 25 mL of this solution requires 17 mL of 0.0167$M$ solution of an oxidant for titration. Calculate no. of electrons taken up by oxidant in the above titration. **(IIT 1991)**

37. 0.5 g sample of iron containing mineral mainly in the form of $CuFeS_2$ was reduced suitably to convert all the ferric ions into ferrous ions ($Fe^{3+} \to Fe^{2+}$) and was obtained as solution. In the absence of any interferring radical, the solution required 42 mL of 0.01 $M$ $K_2Cr_2O_7$ for titration. Calculate % of $CuFeS_2$ in sample.

38. A mixture of $H_2C_2O_4$ and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and the solution made upto one litre. 10 mL of this solution required 3.0 mL of $0.1N$ NaOH solution for complete neutralization. In another experiment 10 mL of same solution in hot dilute $H_2SO_4$ medium required 4 mL of $0.1N$ $KMnO_4$ for complete neutralization. Calculate the mass of $H_2C_2O_4$ and $NaHC_2O_4$ in mixture. **(IIT 1990)**

39. An equal volume of reducing agent is titrated separately with 1$M$ $KMnO_4$ in acid, neutral and alkaline medium. The volumes of $KMnO_4$ required are 20 mL, 33.3 mL

and 100 mL in acid, neutral and alkaline medium respectively. Find out oxidation state of Mn in each reaction product. Give balance equation. Find the volume of 1 $M$ $K_2Cr_2O_7$ consumed if same volume of reductant is titrated in acid medium. **(IIT 1989)**

40. 0.2828 g of iron wire was dissolved in excess dilute $H_2SO_4$ and the solution was made upto 100 mL. 20 mL of this solution required 30 mL of $N/30$ $K_2Cr_2O_7$ solution for exact oxidation. Calculate % purity of Fe in wire.

41. The reaction $Cl_2(g) + S_2O_3^{2-} \to SO_4^{2-} + Cl^-$ is to be carried out in basic medium. Starting with 0.15 mole of $Cl_2$, 0.010 mole $S_2O_3^{2-}$ and 0.30 mole of $OH^-$, how many mole of $OH^-$ will be left in solution after the reaction is complete? Assume no other reaction occurs.

42. Mg can reduce $NO_3^-$ to $NH_3$ in basic solution:
    $$NO_3^- + Mg(s) + H_2O \longrightarrow Mg(OH)_2(s) +$$
    $$OH^-(aq.) + NH_3(g)$$
    A 25.0 mL sample of $NO_3^-$ solution was treated with Mg. The $NH_3(g)$ was passed into 50 mL of 0.15 $N$ HCl. The excess HCl required 32.10 mL of 0.10 $M$ NaOH for its neutralization. What was the molarity of $NO_3^-$ ions in the original sample?

43. A new developed method for water treatment uses chlorine dioxide, $ClO_2$ rather than $Cl_2$ itself. $ClO_2$ can be obtained by passing $Cl_2(g)$ into concentrated solution of sodium chlorite $NaClO_2 \cdot NaCl(aq.)$ is the other product. If this reaction has a 97% yield, how many mole of $ClO_2$ are produced per gallon of 2.0 $M$ $NaClO_2(aq.)$? (1 gallon = 3.78 litre)

44. A sample of ferrous sulphate and ferrous oxalate was dissolved in dil. $H_2SO_4$. The complete oxidation of reaction mixture required 40 mL of $N/15$ $KMnO_4$. After the oxidation, the reaction mixture was reduced by Zn and $H_2SO_4$. On again oxidation by same $KMnO_4$, 25 mL were required. Calculate the ratio of Fe in ferrous sulphate and oxalate.

45. Calculate the % of Cr in a sample of dichromate ore if 0.5 g of the sample after fusion in regular way is treated with 50 mL of 0.12 $N$ ferrous ammonium sulphate and the excess of $Fe^{2+}$ requires 15.05 mL of $K_2Cr_2O_7$. (1 mL of $K_2Cr_2O_7 = 0.006$ g Fe). Also find % of $Cr_2O_3$ in sample.

46. Hydroxylamine reduces iron III according to the equation
    $$4Fe^{3+} + 2NH_2OH \to N_2O + H_2O + 4Fe^{2+} + 4H^+.$$ Iron II thus produced is estimated by titration with standard $KMnO_4$ solution. The reaction is
    $$MnO_4^- + 5Fe^{2+} + 8H^+ \to Mn^{2+} + 5Fe^{3+} + 4H_2O.$$
    *A* 10 mL of hydroxylamine solution was diluted to one litre. 50 mL of this diluted solution was boiled with an

excess of $Fe^{3+}$ solution. The resulting solution required 12 mL of $0.02M$ $KMnO_4$ solution for complete oxidation of $Fe^{2+}$. Calculate the mass of $NH_2OH$ in one litre of original solution.

**47.** Chile salt peter, a source of $NaNO_3$ also contains $NaIO_3$. The $NaIO_3$ can be used as a source of iodine, produced in the following reactions.

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3H^+ + 3SO_4^{2-} \quad ...(1)$$

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2(s) + 3H_2O \quad ...(2)$$
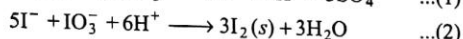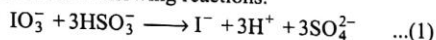
One litre of chile salt peter solution containing 5.80g $NaIO_3$ is treated with stoichiometric quantity of $NaHSO_3$. Now an additional amount of same solution is added to reaction mixture to bring about the second reaction. How many grams of $NaHSO_3$ are required in step I and what additional volume of chile salt peter must be added in step II to bring in complete conversion of $I^-$ to $I_2$ ?

**48.** 30 mL of a solution containing 9.15 g/litre of an oxalate $K_xH_y(C_2O_4)_z \cdot nH_2O$ are required for titrating 27 mL of $0.12N$ NaOH and 36 mL of $0.12$ $N$ $KMnO_4$ separately. Calculate $X, Y, Z$ and $n$. Assume all H-atoms are replaceable and $X, Y, Z$ are in the simple ratio of g-atoms.

**49.** A polyvalent metal weighing 0.1 g and having atomic mass 51.0 reacted with dil. $H_2SO_4$ to give 43.9 mL of $H_2$ at STP. The solution containing the metal in the lower oxidation state was found to require 58.8 mL of $0.1N$ $KMnO_4$ for complete oxidation. What are valencies of metal?

**50.** 25 mL of a solution of ferric alum $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ containing 1.25 g of the salt was boiled with iron when the reaction $Fe + Fe_2(SO_4)_3 \to 3FeSO_4$ occurred. The unreacted iron was filtered off and solution treated with $0.107N$ $KMnO_4$ in acid medium. What is titre value? If Cu had been used in place of Fe, what would have been titre value?

**51.** A 3.0 g sample containing $Fe_3O_4$, $Fe_2O_3$ and an inert impure substance is treated with excess of KI solution in presence of dilute $H_2SO_4$. The entire iron is converted to $Fe^{2+}$ along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of dilute solution requires 11.0 mL of 0.5 $M$ $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the diluted solution, after complete extraction of iodine requires 12.80 mL of $0.25$ $M$ $KMnO_4$ solution in dilute $H_2SO_4$ medium for the oxidation of $Fe^{2+}$. Calculate the percentage of $Fe_2O_3$ and $Fe_3O_4$ in the original sample.

**(IIT 1996)**

**52.** The calcium contained in a solution of 1.048 g of a substance being analysed was precipitated with 25 mL $H_2C_2O_4$. The excess of $C_2O_4^{2-}$ in one fourth of filtrate

was back titrated with 5 mL of 0.1025 $N$ $KMnO_4$. To determine the conc. of $H_2C_2O_4$ solution, it was diluted four folds and titration of 25 mL of dilute solution used up 24.1 mL of same $KMnO_4$ solution. Calculate % of Ca in substance.

**53.** 0.804 g sample of iron ore was dissolved in acid. Iron was oxidized to +2 state and it required 47.2 mL of $0.112$ $N$ $KMnO_4$ solution for titration. Calculate % of Fe and $Fe_3O_4$ in ore. **(Roorkee 1988)**

**54.** A solution is containing $2.52$ g litre$^{-1}$ of a reductant. 25 mL of this solution required 20 mL of $0.01M$ $KMnO_4$ in acid medium for oxidation. Find the molar mass of reductant. Given that each of the two atoms which undergo oxidation per molecule of reductant, suffer an increase in oxidation state by one unit.

**55.** On ignition, Rochelle salt $NaKC_4H_4O_6 \cdot 4H_2O$ (molar mass 282) is converted into $NaKCO_3$ (molar mass 122). 0.9546 g sample of the Rochelle salt on ignition gives $NaKCO_3$ which is titrated with 41.72 mL $H_2SO_4$. From the following data, find the percentage purity of the Rochelle salt. The solution after neutralization requires 1.91 mL of 0.1297 $N$ NaOH. The $H_2SO_4$ used for the neutralization requires its 10.27 mL against 10.35 mL of 0.1297 $N$ NaOH.

**56.** A mixture of $KMnO_4$ and $K_2Cr_2O_7$ weighing 0.24 g on being treated with KI in acid solution liberates just sufficient $I_2$ to react with 60 mL of $0.1N$ hypo. Find out % of Cr and Mn in mixture.

**57.** 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. Iodine liberated required $100 \, cm^3$ of $0.15N$ sodium thiosulphate solution for titration. Find the mass per cent of each in the mixture.

**(Roorkee 1995)**

**58.** A $5.0 \, cm^3$ solution of $H_2O_2$ liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of $H_2O_2$ solution in terms of volume strength at STP.

**(IIT 1995)**

**59.** A sample weighing 2.198 g containing a mixture of $AO$ and $A_2O_3$ takes 0.015 mole of $K_2Cr_2O_7$ to oxidize the sample completely to form $AO_4^-$ and $Cr^{3+}$. If 0.0187 mole of $AO_4^-$ is formed, what is atomic mass of $A$?

**(Roorkee 2001)**

**60.** Calculate the mass of $SeO_3^{2-}$ in solution on the basis of following data. 20 mL of $M / 60$ solution of $KBrO_3$ was added to a definite volume of $SeO_3^{2-}$ solution. The bromine evolved was removed by boiling and excess of $KBrO_3$ was back titrated with 5.1 mL of $M / 25$ solution of $NaAsO_2$. The reactions are given below:

(a) $SeO_3^{2-} + BrO_3^- + H^+ \longrightarrow SeO_4^{2-} + Br_2 + H_2O$

(b) $BrO_3^- + AsO_2^- + H_2O \longrightarrow Br^- + AsO_4^{3-} + H^+$

**61.** A mixture containing $As_2O_3$ and $As_2O_5$ required 20.10 mL of 0.05 $N$ iodine for titration. The resulting solution is then acidified and excess of KI was added. The liberated iodine required 1.1113 g hypo $(Na_2S_2O_3 \cdot 5H_2O)$ for complete reaction. Calculate mass of mixture. The reactions are:
$$As_2O_3 + 2I_2 + 2H_2O \longrightarrow As_2O_5 + 4H^+ + 4I^-$$
$$As_2O_5 + 4H^+ + 4I^- \longrightarrow As_2O_3 + 2I_2 + 2H_2O$$

**62.** 1.5 g of brass containing Cu and Zn reacts with $3M$ $HNO_3$ solution, the following reactions take place.
$$Cu + HNO_3 \longrightarrow Cu^{2+} + NO_2(g) + H_2O$$
$$Zn + H^+ + NO_3^- \longrightarrow NH_4^+ + Zn^{2+} + H_2O$$
The liberated $NO_2(g)$ was found to be 1.04 litre at $25°C$ and one atm.
(a) Calculate the percentage composition of brass.
(b) How many mL of $3M$ $HNO_3$ will be required for completely reacting 1 g of brass?

**63.** In a quality control analysis for sulphur impurity 5.6 g steel sample was burnt in a stream of oxygen and sulphur was converted into $SO_2$ gas. The $SO_2$ was then oxidized to sulphate by using $H_2O_2$ solution to which had been added 30 mL of $0.04M$ NaOH. The equation for reaction is:
$$SO_2(g) + H_2O_2(aq.) + 2OH^-(aq.) \longrightarrow SO_4^{2-}(aq.) + 2H_2O(l)$$
22.48 mL of $0.024M$ HCl was required to neutralize the base remaining after oxidation reaction. Calculate % of sulphur in given sample.

**64.** 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 $0.1N$ $KMnO_4$ for complete oxidation. Find the equation which represents the reaction between metallic copper and ferric sulphate solution. Atomic mass of $Cu = 63.6$; $Fe = 56$.

**65.** For estimating ozone in the air, a certain volume of air is passed through an acidified or neutral KI solution when oxygen is evolved and iodide is oxidized to give iodine. When such a solution is acidified, free iodine is evolved which can be titrated with standard $Na_2S_2O_3$ solution. In an experiment 10 litre of air at 1 atm and $27°C$ were passed through an alkaline KI solution, at the end, the iodine entrapped in a solution on titration as above required 1.5 mL of $0.01N$ $Na_2S_2O_3$ solution. Calculate volume % of $O_3$ in sample.

**66.** 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 mass 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?

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

**68.** One $g$ sample of NaCN was dissolved in 50 mL of $0.33M$ alkaline $KMnO_4$ and heated strongly to convert all the $CN^-$ to $OCN^-$. No other species in NaCN sample undergoes oxidation. Now acidifying the resulting mixture with $H_2SO_4$, the resulting solution requires 0.5 litre of 0.06 $M$ $FeSO_4$. Calculate the % purity of NaCN in sample.

**69.** 1.249 g of a sample of pure $BaCO_3$ and impure $CaCO_3$ containing some CaO was treated with dil. HCl and it evolved 168 mL of $CO_2$ at NTP. From this solution $BaCrO_4$ was precipitated, filtered and washed. The dry precipitate was dissolved in dilute $H_2SO_4$ and diluted to 100 mL. 10 mL of this solution when treated with KI solution liberated iodine which required exactly 20 mL of 0.05 $N$ $Na_2S_2O_3$. Calculate percentage of CaO in the sample.

**70.** Determine which reagent is in excess and by how much if 100.0 g $P_4O_6$ is treated with 100 g $KMnO_4$ in HCl solution to form $H_3PO_4$ and $MnCl_2$?

**71.** 12 g of an impure sample of arsenious oxide was dissolved in water containing 7.5 g of sodium bicarbonate and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidized by 22.4 mL of a solution of iodine. 25 mL of this iodine solution reacted with same volume of a solution containing 24.8g of sodium thiosulphate $(Na_2S_2O_3 \cdot 5H_2O)$ in one litre. Calculate the percentage of arsenious oxide in the sample. (Atomic mass of As = 75)

**72.** $H_2O_2$ is reduced rapidly by $Sn^{2+}$, the products being $Sn^{4+}$ and water. $H_2O_2$ decomposes slowly at room temperature to yield $O_2$ and water. Calculate the volume of $O_2$ produced at $20°C$ and 1.0 atm when 200 g of 10% by mass $H_2O_2$ in water is treated with 100 millilitre of 2.0 $M$ $Sn^{2+}$ and then the mixture is allowed to stand until no further reaction occurs.

**73.** A 1.7225 g of metal (bivalent) salt $A_x(CO_3)_y(OH)_z$ was dissolved to prepare 100 mL solution. 50 mL of this solution required 10 mL 1.0 $N$ $H_2SO_4$ solution to reach the equivalence point using phenolphthalein as indicator. Another 50 mL solution using methyl orange

as indicator required 15 mL of same acid. Deduce the formula of salt.

74. A 3.0 g sample of $Cu_2O$ is dissolved in dil. $H_2SO_4$ where it undergoes disproportionation quantitatively. The solution is filtered off and 8.3 g pure KI crystals are added to clear filtrate in order to precipitate CuI with evolution of $I_2$. The solution is again filtered and boiled till all the $I_2$ is expelled. Now excess of an oxidizing agent is added to filtrate which liberates $I_2$ again. The liberated $I_2$ this time requires 10 mL of 1.0 $N$ $Na_2S_2O_3$ solution. Calculate % by mass of $Cu_2O$ in sample.

75. 10 mL of 1.0 $M$ aqueous solution of $Br_2$ is added to excess of NaOH in order to disproportionate quantitatively to $Br^-$ and $BrO_3^-$. The resulting solution is made free from $Br^-$ ion by extraction and excess of $OH^-$ neutralized by acidifying the solution. This solution requires 1.5 g of an impure $CaC_2O_4$ sample for complete redox change. Calculate % purity of $CaC_2O_4$ sample.

76. 2 g sample of NaOCl and $CaOCl_2$ are dissolved in water to prepare 100 mL solution. 10 mL of this sample requires 10 mL of 0.15 $M$ acidified $Na_2C_2O_4$ for end point. The clear solution is now treated with excess of $AgNO_3$ solution which precipitates 0.287 g AgCl. Calculate mass percentage of NaOCl and $CaOCl_2$ in mixture.

77. 6.32 g of $KMnO_4$ are allowed to react with a mixture of 4 g of KCl and mg of KBr in presence of concentrated

$H_2SO_4$. If the oxidizing agent is just sufficient to react with both halides completely to liberate halogen, what is the vlaue of $m$? (Atomic mass: K = 39, Br = 80)

78. 1 g of moist sample of KCl and $KClO_3$ was dissolved in water to make 250 mL solution, 25 mL of this solution was treated with $SO_2$ to reduce chlorate to chloride and excess of $SO_2$ was removed by boiling. The total chloride was precipitated as silver chloride. The mass of precipitate was 0.1435 g. In another experiment, 25 mL of original solution was heated with 30 mL of 0.2 $N$ ferrous sulphate solution and unreacted ferrous sulphate required 37.5 mL of 0.08 $N$ solution of an oxidant for complete oxidation. Calculate the molar ratio of chlorate to chloride in the given mixture. $Fe^{2+}$ reacts with $ClO_3^-$ according to equation.

$$ClO_3^- + 6Fe^{2+} + 6H^+ \longrightarrow Cl^- + 6Fe^{3+} + 3H_2O$$

79. An acid solution of $KReO_4$ sample containing 26.83 mg of combined rhenium was reduced by passage through a column of granulated zinc. The effluent solution including the washings from the column, was then titrated with 0.05 $N$ $KMnO_4$. 11.45 mL of the standard $KMnO_4$ was required for the reoxidation of all the rhenium to the perrhenate ion $ReO_4^-$. Assuming that rhenium was the only element reduced, what is the oxidation state to which rhenium was reduced by the zinc column?
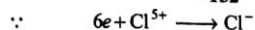
## SOLUTIONS (Numerical Problems)

1. We have,

   Eq. mass of oxidant or reductant

   $$= \frac{\text{Molar mass of oxidant or reductant}}{\text{No. of '} e \text{' lost or gained by one}}$$
   molecule of oxidant or reductant

   (a) $\because$ $\quad 2Fe^{2+} \longrightarrow (Fe^{3+})_2 + 2e$
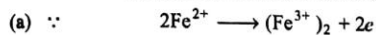
   $\therefore$ Eq. mass of $FeSO_4 = \dfrac{\text{Molar mass of } FeSO_4}{1} = \dfrac{152}{1}$

   $\qquad\qquad = 152$

   $\because$ $\quad 6e + Cl^{5+} \longrightarrow Cl^-$

   $\therefore$ Eq. mass of $KClO_3 = \dfrac{\text{Molar mass of } KClO_3}{6}$

   $\qquad\qquad = \dfrac{122.5}{6} = 20.42$

   (b) $\because$ $\quad S^{4+} \longrightarrow S^{6+} + 2e$

   $\therefore$ Eq. mass of $Na_2SO_3 = \dfrac{M}{2} = \dfrac{126}{2} = 63$

   $\because$ $\quad 3e + Cr^{6+} \longrightarrow Cr^{3+}$

   $\therefore$ Eq. mass of $Na_2CrO_4 = \dfrac{M}{3} = \dfrac{162}{3} = 54$

   (c) $\because$ $\quad 2(Fe^{(8/3)+})_3 \longrightarrow 3Fe_2^{3+} + 2e$
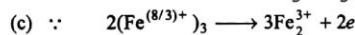
   $\therefore$ Eq. mass of $Fe_3O_4 = \dfrac{M}{1} = \dfrac{232}{1} = 232$

   $\because$ $\quad 3e + Mn^{7+} \longrightarrow Mn^{4+}$

   $\therefore$ Eq. mass of $KMnO_4 = \dfrac{M}{3} = \dfrac{158}{3} = 52.67$

   (d) $\because$ $\quad 2I^- \longrightarrow I_2^0 + 2e$

   $\therefore$ Eq. mass of $KI = \dfrac{M}{1} = \dfrac{166}{1} = 166$

   $\because$ $\quad 6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$
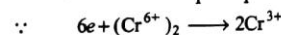
   $\therefore$ Eq. mass of $K_2Cr_2O_7 = \dfrac{M}{6} = \dfrac{294}{6} = 49$

   (e) $\because$ $\quad 2e + Mn^{4+} \longrightarrow Mn^{2+}$

   $\therefore$ Eq. mass of $Mn^{4+} = \dfrac{\text{Atomic mass of Mn}}{2} = \dfrac{55}{2}$

   $\qquad\qquad = 27.5$

   (f) $\because$ $\quad 10e + 2N^{5+} \longrightarrow N_2^0$
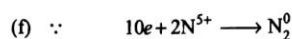
   $\therefore$ Eq. mass of $NO_3^- = \dfrac{\text{Ionic Molar mass}}{5} = \dfrac{62}{5} = 12.4$

   (g) $\because$ $\quad 6e + N_2^0 \longrightarrow 2N^{3-}$
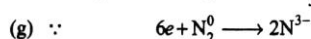
   $\therefore$ Eq. mass of $N_2 = \dfrac{\text{Molar mass of } N_2}{6} = \dfrac{28}{6} = 4.67$

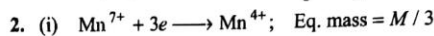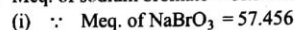   (h) $\because$ $\quad 2S_2^{2+} \longrightarrow S_4^{(5/2)+} + 2e$
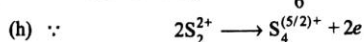
   $\therefore$ Eq. mass of $Na_2S_2O_3 = \dfrac{M}{1} = \dfrac{158}{1} = 158$

   $\because$ $\quad 2e + I_2^0 \longrightarrow 2I^-$

   $\therefore$ Eq. mass of $I_2 = \dfrac{M}{2} = \dfrac{254}{2} = 127$

   (i) $\because$
   $$FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$$
   $$Fe^{2+} \longrightarrow Fe^{3+} + e$$
   $$\underline{C_2^{3+} \longrightarrow 2C^{4+} + 2e}$$
   $$FeC_2O_4 \longrightarrow Fe^{3+} + 2C^{4+} + 3e$$
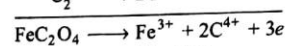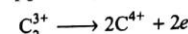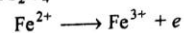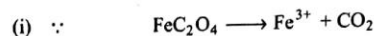
   $\therefore$ Eq. mass of $FeC_2O_4 = \dfrac{M}{3} = \dfrac{144}{3} = 48$

2. (i) $Mn^{7+} + 3e \longrightarrow Mn^{4+}$; Eq. mass $= M/3$

   (ii) $Mn^{7+} + 5e \longrightarrow Mn^{2+}$; Eq. mass $= M/5$

   (iii) $Mn^{7+} + 1e \longrightarrow Mn^{6+}$; Eq. mass $= M/1$
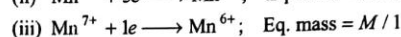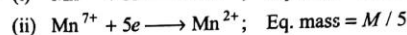
3. Meq. of sodium bromate $= 85.5 \times 0.672 = 57.456$

   (i) $\because$ Meq. of $NaBrO_3 = 57.456$

   $\therefore$ $\qquad \dfrac{w}{E} \times 1000 = 57.456$

   $\therefore$ $\qquad \dfrac{w}{151/6} \times 1000 = 57.456 \qquad \left( \because E_{NaBrO_3} = \dfrac{M}{6} \right)$

   $\therefore$ $\qquad\qquad w = 1.446$ g

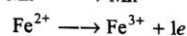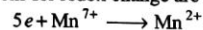   Also, Molarity $= \dfrac{\text{Normality}}{\text{Valency factor}} = \dfrac{0.672}{6} = 0.112M$

   (ii) Similarly use valency factor 5 in place of 6 in this problem and get

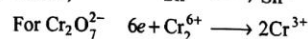   $\qquad\qquad w = 1.735$ g

   and $\qquad\qquad M = 0.1344M$

   **The term valency factor = No. of electrons lost or gained by one molecule of reductant or oxidant**

4. The reactions for redox change are

   $$5e + Mn^{7+} \longrightarrow Mn^{2+}$$
   $$Fe^{2+} \longrightarrow Fe^{3+} + 1e$$

   Now Meq. of $KMnO_4 = $ Meq. of $FeSO_4$

   $0.05 \times 5 \times v = \dfrac{2}{152/1} \times 1000$ $\quad\Big|$ $\because$ Meq. $= N \times V$ in mL

   $\therefore \qquad v = 52.63$ mL $\quad\Big|$ and Meq. $= \dfrac{\text{Mass}}{\text{Eq. mass}} \times 1000$

5. For Sn, $\qquad Sn^{2+} \longrightarrow Sn^{4+} + 2e$

   For $Cr_2O_7^{2-}$ $\quad 6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$

   (a) Meq. of $SnCl_2 = 2000 \times 0.1$
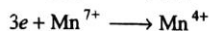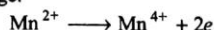
   $\therefore \qquad \dfrac{w}{E} \times 1000 = 200$

   $\therefore \dfrac{w}{189.7/2} \times 1000 = 200 \qquad \left[ \because E_{SnCl_2} = \dfrac{M_{SnCl_2}}{2} \right]$

   $\therefore \qquad w_{SnCl_2} = 18.97$ g

   (b) Normality of $K_2Cr_2O_7$
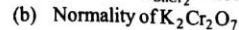
   $= \dfrac{4.9}{M/6} \times \dfrac{1}{0.1} = \dfrac{4.9}{294/6 \times 0.1} = 1N \quad \Big| \quad N = \dfrac{\text{Eq.}}{\text{litre}}$

**6.** For redox change:
$$Mn^{2+} \longrightarrow Mn^{4+} + 2e$$
$$3e + Mn^{7+} \longrightarrow Mn^{4+}$$
$\because$ Meq. of $KMnO_4$ = Meq. of $MnSO_4$
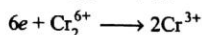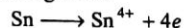$$[\because N = M \times \text{valency factor}]$$
$$N \times 16 = 20 \times 0.2 \times 2$$
$\therefore \qquad N = 0.5$
$\therefore \qquad M = \dfrac{0.5}{3} = 0.167$
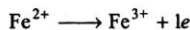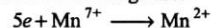$$[\because \text{valency factor for } KMnO_4 = 3]$$

**7.** The redox changes are:
$$Sn \longrightarrow Sn^{4+} + 4e$$
$$6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$$
$\therefore$ Meq. of $Sn$ = Meq. of $K_2Cr_2O_7$
or $\dfrac{1}{E_{Sn}} \times 1000 = \dfrac{1}{10} \times V$
or $\dfrac{1}{\frac{118.7}{4}} \times 1000 = \dfrac{1}{10} \times V \quad \left(\because \text{Eq. mass of } Sn = \dfrac{\text{At. mass}}{4}\right)$
or $\qquad V = 336.98 \text{ mL}$

**8.** Reactions for redox change are:
$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$
$$Fe^{2+} \longrightarrow Fe^{3+} + 1e$$
It is to be noted here that only $FeSO_4 \cdot 7H_2O$ will react with $KMnO_4$ to bring in redox change.
$\because$ Meq. of $FeSO_4 \cdot 7H_2O$ = Meq. of $KMnO_4$
$\dfrac{w}{E} \times 1000 = 5.4 \times 0.1 \quad \therefore \quad \dfrac{w}{\frac{278}{1}} \times 1000 = 0.54$
$\therefore \quad w = 0.150 \text{ g}$
$\therefore$ Mass of $Fe_2(SO_4)_3 \cdot 9H_2O = 5.5 - 0.150 \text{ g} = 5.350 \text{ g}$
$\therefore$ Mole of $Fe_2(SO_4)_3 \cdot 9H_2O = \dfrac{5.350}{562} = 9.5 \times 10^{-3} \text{ mol}$
$$(\because \text{ Molar mass of } Fe_2(SO_4)_3 \cdot 9H_2O = 562)$$
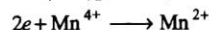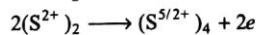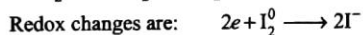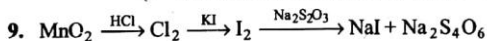
**9.** $MnO_2 \xrightarrow{HCl} Cl_2 \xrightarrow{KI} I_2 \xrightarrow{Na_2S_2O_3} NaI + Na_2S_4O_6$
Redox changes are: $\quad 2e + I_2^0 \longrightarrow 2I^-$
$$2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$$
$$2e + Mn^{4+} \longrightarrow Mn^{2+}$$
The reactions suggest that,
Meq. of $MnO_2$ = Meq. of $Cl_2$ formed
$\qquad\qquad$ = Meq. of $I_2$ liberated
$\qquad\qquad$ = Meq. of $Na_2S_2O_3$ used
$\therefore \quad \dfrac{w}{M/2} \times 1000 = 0.1 \times 1 \times 30$
$$[\because N_{Na_2S_2O_3} = M_{Na_2S_2O_3} \text{ since valency factor} = 1,$$
$$\text{see redox changes for } Na_2S_2O_3]$$
or $w = \dfrac{0.1 \times 1 \times 30 \times M}{2000} = \dfrac{0.1 \times 1 \times 30 \times 87}{2000} \quad (\because M_{MnO_2} = 87)$
$$w_{MnO_2} = 0.1305$$

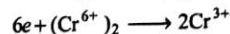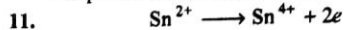$\therefore$ Purity of $MnO_2 = \dfrac{0.1305}{0.5} \times 100 = 26.1\%$

**10.** The element forming acidic oxide is non-metal say $A$. It forms isomorphous of $K_2SO_4$ with KOH, *i.e.*, $K_2AO_4$.
$\therefore \qquad A^0 \longrightarrow A^{6+} + 6e$
$\therefore$ Atomic mass of $A$
= Eq. mass of $A \times$ No. of '$e$' lost $= 13.16 \times 6 = 78.96$
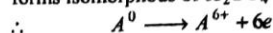
**11.**
$$Sn^{2+} \longrightarrow Sn^{4+} + 2e$$
$$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$$
Since, $Sn^{2+}$ is oxidized by $K_2Cr_2O_7$
$\therefore$ Meq. of $Sn^{2+}$ = Meq. of $K_2Cr_2O_7$ used for tin
$$= N \times V_{\text{in mL}}$$
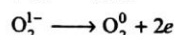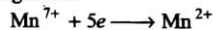$$= \dfrac{2.5}{\frac{294.2}{6} \times 0.50} \times 10 = 1.0197$$
$$\left(\because N = \dfrac{2.5}{\frac{294.2}{6} \times 0.5}\right)$$
$\therefore \qquad \dfrac{w_{Sn^{2+}}}{118/2} \times 1000 = 1.0197$
$\therefore \qquad w_{Sn^{2+}} = 0.06 \text{ g}$
$\therefore \qquad \% \text{ Sn} = \dfrac{0.06}{0.4} \times 100 = 15\%$
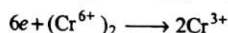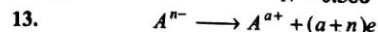
**12.** Redox changes are:
$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$
$$O_2^{1-} \longrightarrow O_2^0 + 2e$$
$\therefore \qquad$ Eq.mass of $H_2O_2 = \dfrac{34}{2}$
Now, $\qquad$ Meq. of $KMnO_4$ = Meq. of $H_2O_2$
$$N.(X) = \dfrac{X}{100 \times 34/2} \times 1000$$
$\therefore \qquad N = 0.588$

**13.**
$$A^{n-} \longrightarrow A^{a+} + (a+n)e$$
$$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$$
$\therefore \qquad$ Meq. of $A^{n-}$ = Meq. of $Cr_2O_7^{2-}$
or $\quad 3.26 \times 10^{-3} \times (a+n) = 1.68 \times 10^{-3} \times 6$
$\therefore \qquad a+n = 3 \quad$ or $\quad a = 3 - n$
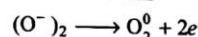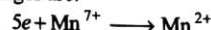
**14.** Redox changes are:
$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$
$$(O^-)_2 \longrightarrow O_2^0 + 2e$$
(a) $\therefore$ Meq. of $H_2O_2$ = Meq. of $KMnO_4$
$$\dfrac{w \times 1000}{34/2} = \dfrac{0.316}{M/5} \times 1000$$
$\therefore \qquad \dfrac{w \times 2 \times 1000}{34} = \dfrac{0.316 \times 5 \times 1000}{158}$
$\therefore \qquad w_{H_2O_2} = 0.17 \text{ g}$
$\because$ 0.2 g impure sample of $H_2O_2$ has 0.17 g pure $H_2O_2$
$\therefore \quad \% \text{ of } H_2O_2 = \dfrac{0.17 \times 100}{0.2} = 85\%$

(b) Now, Eq. of $O_2$ = Eq. of $KMnO_4$

$$\frac{w}{32/2} = \frac{0.316 \times 5}{158}$$

$\therefore \quad w_{O_2} = 0.16\,g$

$\therefore \quad \frac{750}{760} \times V = \frac{0.16}{32} \times 0.0821 \times 300$

$\therefore \quad V_{O_2} = 124.79\,mL$

**15.** Redox changes are: $5e + Mn^{7+} \longrightarrow Mn^{2+}$

$\qquad\qquad\qquad\qquad (C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

$\therefore$ Meq. of oxalate ion

$\qquad = $ Meq. of $KMnO_4$ $\frac{w}{E} \times 1000 = 90 \times \frac{1}{20}$

$$\left[ E_{C_2O_4^{2-}} = \frac{\text{Ionic mass}}{2} \right]$$

$\frac{w}{88} \times 1000 = \frac{9}{2}$

$\therefore \qquad w_{C_2O_4^{2-}} = 0.198\,g$

$\therefore$ 0.3 g $C_2O_4^{2-}$ sample has oxalate ion $= 0.198\,g$

$\therefore$ % of $C_2O_4^{2-}$ in sample $= \frac{0.198 \times 100}{0.3} = 66\%$

**16.** Redox changes are: $2e + (O^-)_2 \longrightarrow 2O^{2-}$

$\qquad\qquad\qquad\qquad 2I^- \longrightarrow I_2 + 2e$

$\qquad\qquad\qquad\qquad 2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$

and $\qquad\qquad 2e + I_2^0 \longrightarrow 2I^{1-}$

$H_2O_2 \xrightarrow{KI} I_2 + H_2O \xrightarrow{Na_2S_2O_3} d\,Na_2S_4O_6 + 2I^-$

$\therefore$ Meq. of $H_2O_2$ = Meq. of KI used = Meq. of $I_2$ liberated

$\qquad\qquad\qquad\qquad = $ Meq. of $Na_2S_2O_3$ used

$\therefore \qquad$ Meq. of $H_2O_2$ = Meq. of $Na_2S_2O_3$ used

$\qquad N \times 50 = 20 \times 0.1 \quad \therefore \quad N_{H_2O_2} = 0.04$

$\therefore$ Strength of $H_2O_2 = N \times E = 0.04 \times \frac{34}{2} = 0.68\,g\,litre^{-1}$

**17.** Redox changes are:

For $H_2C_2O_4$ $\qquad (C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

For $KMnO_4$ $\qquad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

Meq. of oxalic acid in 10 mL solution = Meq. of $KMnO_4$

used for it $= 8.5 \times \frac{1}{10}$

$\therefore$ Meq. of oxalic acid in 200 mL solution $= 8.5 \times \frac{1}{10} \times \frac{200}{10}$

$\therefore \quad \frac{w}{E} \times 1000 = 17$

Formula of oxalic acid is $\qquad\Big|\ \therefore \quad \frac{w}{126/2} \times 1000 = 17$

$\qquad H_2C_2O_4 \cdot 2H_2O \qquad\Big|$

$\therefore$ Molar mass $= 126 \qquad\Big|\ \therefore\ w_{H_2C_2O_4} = 1.071\,g$

$\therefore$ % purity of oxalic acid $= \frac{1.071}{1.2} \times 100 = 89.25\%$

**18.** (a) The redox changes are

$\qquad 2e + (O^-)_2 \longrightarrow 2O^{2-}$

$\qquad\qquad 2I^- \longrightarrow I_2 + 2e$

$\qquad 2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$

$\qquad I_2 + 2e \longrightarrow 2I^-$

Meq. of $H_2O_2$ = Meq. of $I_2$ = Meq. of $Na_2S_2O_3$

$\qquad N \times 25 = 0.1 \times 20 \quad \therefore \quad N_{H_2O_2} = 0.08$

Mass of $H_2O_2$ in one litre $= 0.08 \times \frac{34}{2} = 1.36\,g$

$\therefore \qquad$ % by mass $= 0.136\%$

Also concentration of $H_2O_2$ in terms of volume

$\qquad\qquad\qquad\qquad = \mathbf{0.448\ volume}$

(b) Follow problem 18 (a)

[**Ans. 1.344**]

**19.** The given reactions are:

$MnO_2 + Na_2C_2O_4 + 2H_2SO_4 \longrightarrow MnSO_4 +$
$_{(ppt.)} \qquad\qquad\qquad\qquad 2CO_2 + Na_2SO_4 + 2H_2O$

$\therefore$ Meq. of $MnO_2$ = Meq. of $Na_2C_2O_4 = 10 \times 0.2 \times 2 = 4$

$\because \qquad Mn^{4+} + 2e \longrightarrow Mn^{2+}$

$\therefore$ Valence factor of $MnO_2 = 2$ $\therefore$ mM of $MnO_2 = \frac{4}{2} = 2$

Now, $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 +$
$\qquad\qquad\qquad\qquad\qquad\qquad _{(ppt.)}$
$\qquad\qquad\qquad\qquad\qquad\qquad K_2SO_4 + 2H_2O$

Since, Eq. mass of $MnO_2$ is derived from $KMnO_4$ and $MnSO_4$ both, thus it is better to proceed by mole concept.

$\qquad$ mM of $KMnO_4$ = mM of $MnO_2 \times \frac{2}{5} = \frac{4}{5}$

Also, $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 +$
$\qquad\qquad\qquad\qquad\qquad\qquad K_2SO_4 + 8H_2O + 5O_2$

$\therefore$ mM of $H_2O_2$ = mM of $KMnO_4 \times \frac{5}{2} = \frac{4}{5} \times \frac{5}{2} = 2$

$\therefore \qquad M \times 20 = 2$

$\qquad M_{H_2O_2} = \mathbf{0.1}$

**20.** Limestone $\xrightarrow[CaCO_3]{\text{oxalic acid}} CaC_2O_4 \xrightarrow{KMnO_4}$ decolorizes

$\therefore$ Redox changes are:

For $CaC_2O_4$ $\qquad (C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

For $KMnO_4$ $\qquad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

$\therefore$ Meq. of $CaCO_3$ = Meq. of $CaC_2O_4$ = Meq. of $KMnO_4$

$\because$ Meq. of $CaCO_3$ = Meq. of CaO

$\qquad\qquad\qquad\qquad$ (since CaO is present in $CaCO_3$)

$\therefore$ Meq. of CaO = Meq. of $KMnO_4$

$\qquad \frac{w}{56/2} \times 1000 = 45 \times 0.2$

$\qquad\qquad$ Mass of CaO $= 0.252\,g$

$\therefore$ % of CaO in limestone $= \frac{0.252}{0.56} \times 100 = 45\%$

**21.** The redox changes are:

For $FeSO_4$ $\qquad Fe^{2+} \longrightarrow Fe^{3+} + 1e$

For $KMnO_4$ $\qquad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

$\therefore$ Meq. of $FeSO_4 \cdot 7H_2O$ in 25 mL solution

$\qquad = $ Meq. of $KMnO_4 = 20 \times \frac{1}{10}$

$\therefore$  Meq. of $FeSO_4 \cdot 7H_2O$ in 1 litre solution

$$= 20 \times \frac{1}{10} \times \frac{1000}{25} = 80$$

$\therefore$  $\dfrac{w}{E} \times 1000 = 80$

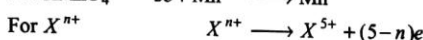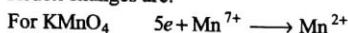(Molar mass of $FeSO_4 \cdot 7H_2O = 278$)  $\therefore$  $\dfrac{w}{\dfrac{278}{1}} \times 1000 = 80$

$\therefore$        $w = 22.24$ g

$\because$  25 g sample has $FeSO_4 \cdot 7H_2O = 22.24$ g

$\therefore$  % of $FeSO_4 \cdot 7H_2O$ in sample $= 22.24 \times \dfrac{100}{25} = \mathbf{88.96\%}$

**22.** Redox changes are:

For $KMnO_4$        $5e + Mn^{7+} \longrightarrow Mn^{2+}$

For $X^{n+}$                $X^{n+} \longrightarrow X^{5+} + (5-n)e$

Now,

Meq. of $X^{n+}$ = Meq. of $KMnO_4$  |  $\because$  Meq. = mole $\times$

$2.68 \times 10^{-3} \times (5-n) \times 1000$  | valency factor $\times 1000$

$\qquad = 1.61 \times 10^{-3} \times 5 \times 1000$

$\therefore$        $n = 1.99$

$\qquad n = 2$

Now,        $X^{2+} \longrightarrow X^{5+} + 3e$
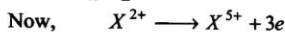
If $a$ is atomic mass of $X$,

$\because$        Eq. mass of $XCl_2 = 56$

$\therefore$  Molar mass of $XCl_2 = 56 \times$ valency factor $= 56 \times 3$

or        $a + 71 = 56 \times 3$

$\therefore$        $a = \mathbf{97}$

**23.** Bleaching powder $\xrightarrow{KI + HCl} I_2 \xrightarrow{Na_2S_2O_3} I^- + Na_2S_4O_6$

The redox changes are:   $2e + I_2 \longrightarrow 2I^-$

$\qquad\qquad\qquad 2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$
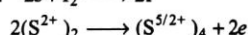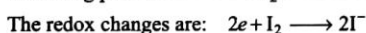
Meq. of bleaching powder = Meq. of available $Cl_2$

$\qquad\qquad\qquad\qquad = $ Meq. of $I_2$ liberated

$\qquad\qquad\qquad\qquad = $ Meq. of $Na_2S_2O_3$ used

$\therefore$  Meq. of available $Cl_2$ in 25 mL bleaching powder solution

$$= \text{Meq. of } Na_2S_2O_3 \text{ used} = 24.35 \times \frac{1}{10}$$
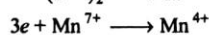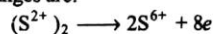
$\therefore$  Meq. of available $Cl_2$ in 500 mL bleaching powder solution

$$= 24.35 \times \frac{1}{10} \times \frac{500}{25} = 48.7$$

$\therefore$  $\dfrac{w}{71/2} \times 1000 = 48.7$  $\therefore$  $w_{Cl_2} = 1.729$ g

$\therefore$  % of available $Cl_2$ in bleaching powder

$$= \frac{1.729}{5.7} \times 100 = \mathbf{30.33\%}$$

**24.** Redox changes are:

$$(S^{2+})_2 \longrightarrow 2S^{6+} + 8e$$
$$3e + Mn^{7+} \longrightarrow Mn^{4+}$$

$\therefore$  Meq. of $KMnO_4$ = Meq. of $S_2O_3^{2-}$

$$0.1 \times 3 \times V = \frac{0.158}{158/8} \times 1000$$

$\qquad\qquad$ ($\because$  Molar mass of $Na_2S_2O_3 = 158$)

$\therefore$        $V = \mathbf{26.67 \ mL}$

**25.** Let Meq. of $Fe_2(SO_4)_3$ and $FeC_2O_4$ are $a$ and $b$ respectively. $KMnO_4$ will oxidize only $FeC_2O_4$ as:

$$2Fe^{2+} \longrightarrow Fe_2^{3+} + 2e$$
$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$
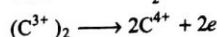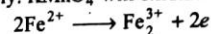
Note that valence factor for $Fe_2(SO_4)_3$ is 2 and for $FeC_2O_4$ is 3.

Meq. of $FeC_2O_4$ of valence factor 3

$\qquad$ = Meq. of $Fe^{2+}$  (v. f. = 1)

$\qquad\qquad\qquad\qquad$ + Meq. of $Ca_2O_4^{2-}$   (v. f. = 2)

$$b = \frac{b}{3} + \frac{2b}{3}$$

$\qquad b = $ Meq. of $KMnO_4$

$\qquad b = 40 \times \dfrac{1}{16} = \dfrac{40}{16}$        ...(1)

$Fe_2^{3+}$ from $Fe_2(SO_4)_3$ and $Fe_2^{3+}$ obtained by oxidation of $FeC_2O_4$ will be converted to $Fe^{2+}$ as,

$$2e + (Fe^{3+})_2 \longrightarrow 2Fe^{2+}$$
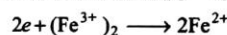
The $CO_2$ formed during oxidation of $FeC_2O_4$ with $KMnO_4$ escapes out.

Now, Meq. of $Fe^{2+}$ so obtained are again oxidized by $KMnO_4$.

$\therefore$  Meq. of $Fe^{2+}$ of $Fe_2(SO_4)_3$ reduction +

$\qquad\qquad\qquad\qquad$ Meq. of $Fe^{2+}$ of $FeC_2O_4$

$\qquad\qquad = $ Meq. of $KMnO_4$

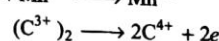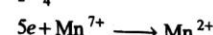$\qquad a + \dfrac{b}{3} = 60 \times \dfrac{1}{16} = \dfrac{60}{16}$        ...(2)

By Eqs. (1) and (2),   $a = \dfrac{140}{48}$,   $b = \dfrac{40}{16}$

$\therefore$  $\dfrac{\text{Meq. of } Fe_2(SO_4)_3 \text{ of valence factor } 2}{\text{Meq. of } FeC_2O_4 \text{ of valence factor } 3} = \dfrac{140}{48} \times \dfrac{16}{40} = \dfrac{7}{6}$

$\therefore$  Ratio of Meq. of $Fe_2(SO_4)_3$ : Meq. of $FeC_2O_4 = \mathbf{7:6}$

**26.** Let $a$ mole of $Cu^{2+}$ and $b$ mole of $C_2O_4^{2-}$ be present in solution.

**Case I:**  The solution is oxidized by $KMnO_4$ which reacts with only $C_2O_4^{2-}$.

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$
$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$

$\therefore$        Meq. of $C_2O_4^{2-}$ = Meq. of $KMnO_4$

$\therefore$        $b \times 2 \times 1000 = 0.02 \times 5 \times 22.6$

$\therefore$        $b = 1.13 \times 10^{-3}$        ...(1)

**Case II:**  After oxidation of $C_2O_4^{2-}$, the resulting solution is neutralized by $Na_2CO_3$, acidified with dilute $CH_3COOH$ and then treated with excess of KI. The liberated $I_2$ required $Na_2S_2O_3$ for its neutralization, *i.e.*,

$$Cu^{2+} \xrightarrow{KI} I_2 \xrightarrow{Na_2S_2O_3} Na_2S_4O_6 + I^-$$
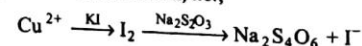
∴ Meq. of $Cu^{2+}$ = Meq. of $I_2$ liberated

= Meq. of $Na_2S_2O_3$ used

| ∴ Meq. of $Cu^{2+}$ = Meq. of $Na_2S_2O_3$ used | Redox changes are: $2Cu^{2+} + 2e \longrightarrow (Cu^+)_2$ |
|---|---|
| $a \times 1 \times 1000 = 11.3 \times 0.05 \times 1$ | $2I^- \longrightarrow I_2 + 2e$ |
| ∴ $a = 5.65 \times 10^{-4}$ | and $2e + I_2 \longrightarrow 2I^{-1}$ |
| ∴ Molar ratio of $\dfrac{Cu^{2+}}{C_2O_4^{2-}} = \dfrac{a}{b} = \dfrac{5.65 \times 10^{-4}}{1.13 \times 10^{-3}} = \dfrac{1}{2}$ | $2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$ |

**27. For KI + $KIO_3$ reaction:**

$$I^{5+} + 4e \longrightarrow I^+$$
$$I^- \longrightarrow I^+ + 2e$$

∴ valence factor of KI = 2 and valence factor of $KIO_3$ = 4

Now, Meq. of KI in 20 mL = $30 \times \dfrac{1}{10} \times 4 = 12$

∴ Meq. of KI in 50 mL = $12 \times \dfrac{50}{20} = 30$

Now, Meq. of KI left after treatment with $AgNO_3$

$$= 50 \times \dfrac{1}{10} \times 4 = 20$$

∴ Meq. of KI (v.f. = 2) used by $AgNO_3$ = 30 − 20 = 10

But in its reaction with $AgNO_3$ valence factor of KI = 1

$$AgNO_3 + KI \longrightarrow AgI + KNO_3$$

∴ Meq. of KI used by $AgNO_3$ (v. f. = 1) = $\dfrac{10 \times 1}{2} = 5$

∴ Meq. of $AgNO_3$ = 5

$$\dfrac{w}{170} \times 1000 = 5$$

∴ $w = 0.85$ g

∴ % purity of $AgNO_3$ in sample = $\dfrac{0.85 \times 100}{1} = 85\%$

**Alternative method:**

milli mole of $KIO_3$ used by 20 mL of KI stock solution

$$= 30 \times \dfrac{1}{10} = 3$$

∴ milli mole of $KIO_3$ used by 50 mL of KI stock solution

$$= 3 \times \dfrac{50}{20} = 7.5$$

milli mole of $KIO_3$ used by KI left in 50 mL solution after reaction with

$$AgNO_3 = \dfrac{1}{10} \times 50 = 5$$

∵ Mole ratio of $KIO_3$ and KI is 1 : 2 in reaction

∴ milli mole of KI in 50 mL stock solution = $7.5 \times 2 = 15$

∴ milli mole of KI left in 50 mL solution after reaction with $AgNO_3$ = $5 \times 2 = 10$

∴ milli mole of KI used for $AgNO_3$ = 15 − 10 = 5

∴ $m$ mole of $AgNO_3$ = 5

(∵ mole ratio of KI and $AgNO_3$ reaction is 1 : 1)

Now for $AgNO_3$: $\dfrac{w}{M} \times 1000 = 5$

∴ $\dfrac{w}{170} \times 1000 = 5$

∴ $w_{AgNO_3} = 0.85$

∴ % of $AgNO_3$ = $0.85 \times \dfrac{100}{1} = 85\%$

**28.** Meq. of $MnO_2$ = Meq. of oxalic acid added −

Meq. of oxalic acid left

$$= 1 \times 50 - 0.1 \times 32 \times 10 \quad \text{(in 250 mL)}$$
$$= 18$$

∴ $\dfrac{w}{E} \times 1000 = 18$  or  $w_{MnO_2} = \dfrac{18 \times 86.9}{2 \times 1000} = 0.7821$ g

$$\left( \because E = \dfrac{86.9}{2} \right)$$

∴ % of $MnO_2$ = $\dfrac{0.7821}{1.6} \times 100 = \mathbf{48.88\%}$

Also Meq. of $MnO_2$ = Meq. of $O_2$ = 18

∴ $\dfrac{w}{8} \times 1000 = 18$

$$w_{O_2} = \mathbf{0.144\ g}$$

∴ % of available $O_2$ = $\dfrac{0.144}{1.6} \times 100 = \mathbf{9}$

**29.**
$$KIO_3 + 5KI \longrightarrow 3K_2O + 3I_2$$

*i.e.*
$$2I^{5+} + 10e \longrightarrow I_2^0$$
$$2I^- \longrightarrow I_2^0 + 2e$$
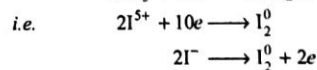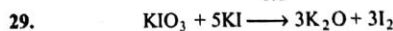
Now the liberated $I_2$ reacts with $Na_2S_2O_3$ to give

$$I_2 + 2e \longrightarrow 2I^-$$
$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$
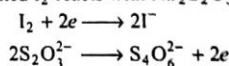
∵ millimole ratio is $I_2 : S_2O_3 :: 1 : 2$,

Thus, m. mole of $I_2$ liberated = m. mole of $Na_2S_2O_3$ used

$$\times \dfrac{1}{2} = 45 \times M \times \dfrac{1}{2}$$

(*M* is molarity of thiosulphate)

Also m. mole of $KIO_3$ = $\dfrac{0.1}{214} \times 1000$

Now, m. mole ratio is $KIO_3 : I_2 :: 1 : 3$

Thus, $\dfrac{\frac{0.1}{214} \times 1000}{\frac{45 M}{2}} = \dfrac{1}{3}$

∴ $M = \dfrac{0.1 \times 1000 \times 3 \times 2}{214 \times 45}$

$$M = \mathbf{0.062}$$

**30.** 1. Pyrolusite contains $MnO_2$.

2. Meq. of oxalic acid added to pyrolusite = $65 \times 1 = 65$

3. $MnO_2$ reacts with oxalic acid as,

$$2e + Mn^{4+} \longrightarrow Mn^{2+}$$
$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$
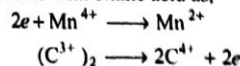
4. Excess of oxalic acid is oxidized by $KMnO_4$

Meq. of oxalic acid left in 100 mL = $50 \times \dfrac{1}{10} = 5$

$\therefore$ Meq. of oxalic acid left in 500 mL $= 5 \times \dfrac{500}{100} = 25$

$\therefore$ Meq. of oxalic acid used for $MnO_2 = 65 - 25 = 40$

$\therefore$                     Meq. of $MnO_2 = 40$

$\because$ Molar mass of $MnO_2 = 87$,   Eq. mass $= \dfrac{87}{2}$

$\therefore$          $\dfrac{w}{87/2} \times 1000 = 40$   $\therefore$   $w_{MnO_2} = 1.74\ g$

$\therefore$ % of $MnO_2$ in pyrolusite $= \dfrac{1.74}{2.6} \times 100 = \mathbf{66.92\%}$

**31. Case I:** $Fe^{2+} \xrightarrow{Zn\ dust\ +\ H_2SO_4} Fe^{2+}$   (*i.e.*, no change)

$2e + (Fe^{3+})_2 \xrightarrow{Zn\ dust\ +\ H_2SO_4} 2Fe^{2+}$
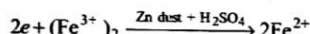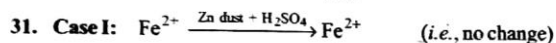
$\because$ Zn dust is used as reducing agent and thus,

$$Zn \longrightarrow Zn^{2+} + 2e$$

Let $a$ Meq. of $Fe^{2+}$ and $b$ Meq. of $Fe^{3+}$ be present in 25 mL solution. In case I, after reduction with Zn,

Meq. of $Fe^{2+}$ + Meq. of $Fe^{2+}$ from $Fe^{3+} = a + b$

Now these are oxidized by $K_2Cr_2O_7$

$\therefore$   Total Meq. of $Fe^{2+}$ = Meq. of $K_2Cr_2O_7$

$$a + b = 34.25 \times \dfrac{1}{10}$$

$\therefore$                     $a + b = 3.425$          ...(1)

**Case II:**  If reduction is not made, the solution contains $Fe^{2+}$ and $Fe^{3+}$ of which only $Fe^{2+}$ are oxidized by $K_2Cr_2O_7$.

$\therefore$          Meq. of $Fe^{2+}$ = Meq. of $K_2Cr_2O_7$

$$a = 22.45 \times \dfrac{1}{10}$$

$$a = 2.245$$          ...(2)

$\therefore$ By Eq. (1),          $b = 3.425 - 2.245 = 1.18$

| $\because$ Meq. of $FeSO_4$ (in 25 mL) $= a = 2.245$ | Meq. of $Fe_2(SO_4)_3$ (in 25 mL) $= b = 1.18$ |
|---|---|
| $\therefore \dfrac{w}{M/1} \times 1000 = 2.245$ | $\therefore \dfrac{w}{M/2} \times 1000 = 1.18$ |
| $\because$ Molar mass of $FeSO_4 = 152$ | $\because$ Molar mass of $Fe_2(SO_4)_3 = 400$ |
| $\therefore$ Mass of $FeSO_4$ in 25 mL $= 0.341 g$ | $\therefore$ Mass of $Fe_2(SO_4)$ in 25 mL $= 0.236 g$ |
| $\therefore$ Strength of $FeSO_4$ $= \mathbf{13.64\ g/litre}$ | $\therefore$ Strength of $Fe_2(SO_4)_3$ $= \mathbf{9.45\ g/litre}$ |

**32.**          $MnSO_4 \cdot 4H_2O \longrightarrow Mn_3O_4$
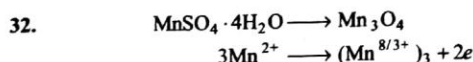
$$3Mn^{2+} \longrightarrow (Mn^{8/3+})_3 + 2e$$

The residue $Mn_3O_4$ is dissolved in $FeSO_4$ which is reduced from $Mn^{8/3+}$ to $Mn^{2+} \cdot (Mn^{8/3+})_3 + 2e \longrightarrow 3Mn^{2+}$. The excess of $FeSO_4$ is titrated by $KMnO_4$. The normality of $KMnO_4$ is determined by another $FeSO_4$.

For normality of $KMnO_4$:   Meq. of $KMnO_4$

$$= \text{Meq. of } FeSO_4$$

$$25 \times N = 30 \times 0.1 \quad \therefore \quad N = \dfrac{3}{25}$$

Now Meq. of $FeSO_4$ added to $Mn_3O_4 = 100 \times 0.1 = 10$

Meq. of $FeSO_4$ left after reaction with $Mn_3O_4$

$$= \text{Meq. of } KMnO_4 \text{ used}$$

$$= 50 \times \dfrac{3}{25} = 6$$

$\therefore$  Meq. of $FeSO_4$ used for $Mn_3O_4 = 10 - 6 = 4$

$\therefore$          Meq. of $Mn_3O_4 = 4$

$\therefore$          Meq. of $MnSO_4 \cdot 4H_2O = 4$

$\therefore$          $\dfrac{w}{3M/2} \times 1000 = 4$

$\because$          $E = \dfrac{M}{2/3}$ for $MnSO_4$ as valence factor is $\dfrac{2}{3}$

$\therefore$          $\dfrac{w \times 2}{3 \times 223} \times 1000 = 4$   $\therefore$   $w = \mathbf{1.338\ g}$

**33.** For acid-base reaction in 25 mL solution:

Meq. of $H_2SO_4$ + Meq. of $H_2C_2O_4$ = Meq. of NaOH

$$a + b = 35.5 \times \dfrac{1}{10} = 3.55$$          ...(1)

For redox change:   Meq. of oxalic acid = Meq. of $KMnO_4$

$$b = 23.45 \times \dfrac{1}{10} = 2.345$$

| $\therefore$ Meq. of $H_2SO_4 = a$ (in 25 mL) | and Meq. of oxalic acid (in 25 mL) $= b = 2.345$ |
|---|---|
| $= 3.55 - 2.345 = 1.205$ | $N_{H_2C_2O_4} = \dfrac{2.345}{25} = 0.0938$ |
| $\therefore N_{H_2SO_4} = \dfrac{1.205}{25} = 0.0482$ | Strength $= N \times E$ $= 0.0938 \times 63$ |
| and Strength $= N \times E = 0.0482 \times 49$ $= \mathbf{2.362\ g\ litre^{-1}}$ | $= \mathbf{5.909\ g\ litre^{-1}}$ |

**34.**          $N_{HCl} = \dfrac{\dfrac{4}{36.5 \times 100}}{1.2 \times 1000} = 1.315$

($\because$ 4% by mass solution means that 100 g solution has 4 g solute)

Now   Meq. of $MnO_2$ = Meq. of HCl

$= $ Meq. of $Cl_2$ formed $= \dfrac{1.78}{11.2} \times 1000 = 158.93$

($\because$ Eq. mass of $Cl_2 = M/2$; $2Cl^- \longrightarrow Cl_2 + 2e$)

$\therefore$          Meq. of HCl $= 158.93$

$N \times V = 158.93$

$\therefore$          $V = \dfrac{158.93}{1.315} = \mathbf{120.85\ mL}$

$\because$ HCl is also used to give $MnCl_2$ and thus, volume used is double than required for reduction of $MnO_2$;

$$= 2 \times 120.85 = \mathbf{241.7\ mL}$$

Also          Meq. of $MnO_2 = 158.93$

$\therefore$          $\dfrac{w}{87/2} \times 1000 = 158.93$

$\therefore$   Mass of $MnO_2 = \mathbf{6.9134\ g}$

**35.** The redox changes are:

For $FeCl_3$          $e + Fe^{3+} \longrightarrow Fe^{2+}$

For $N_2H_6SO_4$          $(N^{2-})_2 \longrightarrow N_2^0 + 4e$

For $KMnO_4$          $5e + Mn^{7+} \longrightarrow Mn^{2+}$
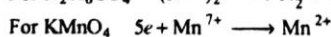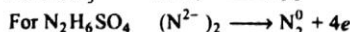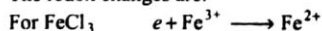
Meq. of $N_2H_6SO_4$ in 10 mL solution

$\quad$ = Meq. of $FeCl_3$ reacting with $N_2H_6SO_4$

$\quad$ = Meq. of $Fe^{2+}$ formed = Meq. of $KMnO_4$

$\therefore$ Meq. of $N_2H_6SO_4$ in 10 mL solution = $20 \times \frac{1}{50} \times 5 = 2$

$\therefore \qquad \frac{w}{M/4} \times 1000 = 2$

$\qquad\qquad$ ($\because$ Molar mass of $N_2H_6SO_4 = 130$)

$\therefore \qquad w = \frac{2 \times 130}{4000} = 0.065$

$\therefore \quad$ Mass of $N_2H_6SO_4$ in 10 mL = 0.065 g

$\therefore \quad$ Mass of $N_2H_6SO_4$ in 1000 mL = **6.5 g litre$^{-1}$**

**36.** The redox changes are:

For reduction of $Fe_2O_3$ by zinc dust

$$2e + (Fe^{3+})_2 \longrightarrow 2Fe^{2+}$$

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

$$\text{Oxidant} + ne \longrightarrow \text{Reductant}$$

Meq. of $Fe_2O_3$ in 25 mL

$\quad$ = Meq. of $Fe^{3+}$ in $Fe_2O_3$ = Meq. of $Fe^{2+}$ formed

$\quad$ = Meq. of oxidant used to oxidize $Fe^{2+}$ again

$\therefore$ Meq. of $Fe_2O_3$ in 25 mL = Meq. of oxidant

$$= 17 \times 0.0167 \times n$$

where $n$ is no. of electrons gained by 1 molecule of oxidant.

$\therefore$ Meq. of $Fe_2O_3$ in 100 mL = $17 \times 0.0167 \times n \times \frac{100}{25}$

$\therefore \qquad \frac{1 \times 55.2 \times 1000}{100 \times M/2} = 17 \times 0.0167 \times n \times 4$

$\because \qquad$ Molar mass of $Fe_2O_3 = 160$

$\therefore \qquad n = \frac{1 \times 55.2 \times 2 \times 1000}{100 \times 160 \times 17 \times 0.0167 \times 4} = 6$

$\therefore$ No. of electrons gained by one molecule of oxidant = **6**

**37.** Redox changes are:

For $CuFeS_2 \qquad\qquad e + Fe^{3+} \longrightarrow Fe^{2+}$

For $K_2Cr_2O_7 \qquad 6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

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

$\therefore$ Meq. of $CuFeS_2$ = Meq. of $Fe^{2+}$ = Meq. of $K_2Cr_2O_7$

$$= 42 \times 0.01 \times 6 = 2.52$$

$\therefore \qquad \frac{w}{183.5/1} \times 1000 = 2.52$

$\qquad\qquad$ ($\because$ Molar mass of $CuFeS_2 = 183.5$)

$\therefore \quad$ Mass of $CuFeS_2 = 0.4624$ g

$\therefore \quad$ % of $CuFeS_2 = \frac{0.4624 \times 100}{0.5} = $ **92.48%**

**38.** Let $\qquad$ mass of $H_2C_2O_4 = a$ g in 1 litre

$\qquad\qquad$ mass of $NaHC_2O_4 = b$ g in 1 litre

For acid-base reaction:

Now (Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$) in 10 mL

$$= 3 \times 0.1$$

$\therefore$ Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in one litre

$$= 3 \times 0.1 \times 100 = 30$$

$\therefore \quad \dfrac{a}{45} \times 1000 + \dfrac{b}{112/1} \times 1000 = 30$ $\qquad$ $\left| \begin{array}{l} \text{E of } H_2C_2O_4 = \dfrac{M}{2} \\ \qquad\qquad = \dfrac{90}{2} = 45 \end{array} \right.$

$\therefore \quad \dfrac{1000a}{45} + \dfrac{1000b}{112} = 30 \;\;...(1)$ $\quad$ $\left| \begin{array}{l} \text{E of } NaHC_2O_4 = \dfrac{M}{1} \\ \qquad\quad \text{(as acid salt)} \\ \qquad\qquad = \dfrac{112}{1} = 112 \end{array} \right.$

For redox change : $\quad C_2^{3+} \longrightarrow 2C^{4+} + 2e$

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$

Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in 10 mL = $4 \times 0.1$

$\therefore$ Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in 1 litre

$$= 4 \times 0.1 \times 100 = 40$$

$\therefore \quad \dfrac{a}{45} \times 1000 + \dfrac{b}{112/2} \times 1000 = 40$ $\quad$ $\left| \begin{array}{l} \because \text{ Eq. mass of } H_2C_2O_4 = \dfrac{M}{2} \end{array} \right.$

$\therefore \quad \dfrac{1000a}{45} + \dfrac{2000b}{112} = 40 \;\;...(2)$ $\quad$ $\left| \begin{array}{l} \text{and} \quad \text{Eq. mass of } NaHC_2O_4 \\ \text{(as reductant)} = \dfrac{M}{2} \end{array} \right.$

Solving Eqs. (1) and (2), we get

$$a = \mathbf{0.90 \ g}$$

$$b = \mathbf{1.12 \ g}$$

**Note :** Also given $a + b = 2.02$ and thus Eq. (1) or (2) can be used to find $a$ and $b$ by using $a + b = 2.02$.

**39.** Let $V$ mL of reducing agent be used for $KMnO_4$ in different medium which act as oxidant.

Acid medium $\qquad n_1e + Mn^{7+} \longrightarrow Mn^{a+} \;\; \therefore \; n_1 = 7 - a$

Neutral medium $\quad n_2e + Mn^{7+} \longrightarrow Mn^{b+} \;\; \therefore \; n_2 = 7 - b$

Alkaline medium $\quad n_3e + Mn^{7+} \longrightarrow Mn^{c+} \;\; \therefore \; n_3 = 7 - c$

$\therefore$ Meq. of reducing agent = Meq. of $KMnO_4$ in acid

$\qquad\qquad\qquad\qquad\qquad$ = Meq. of $KMnO_4$ in neutral

$\qquad\qquad\qquad\qquad\qquad$ = Meq. of $KMnO_4$ in alkali

$= 1 \times n_1 \times 20 \qquad = 1 \times n_2 \times 33.3 \qquad = 1 \times n_3 \times 100$

$$n_1 = 1.665 \; n_2 = 5n_3$$

$\because \;\; n_1, n_2, n_3$ are integers and $n_1 \not> 7$, $\quad \therefore \; n_3 = 1$

$\therefore \qquad\qquad n_1 = 5, \; n_2 = 3$ and $n_3 = 1$

Therefore, different oxidation states of Mn are:

Acid medium $\qquad 5e + Mn^{7+} \longrightarrow Mn^{a+} \qquad \therefore \; a = \mathbf{+2}$

Neutral medium $\quad 3e + Mn^{7+} \longrightarrow Mn^{b+} \qquad \therefore \; b = \mathbf{+4}$

Alkaline medium $\quad 1e + Mn^{7+} \longrightarrow Mn^{c+} \qquad \therefore \; c = \mathbf{+6}$

Now same volume of reducing agent is treated with $K_2Cr_2O_7$ and therefore,

Meq. of reducing agent = Meq. of $K_2Cr_2O_7$

$20 \times 5 = 1 \times 6 \times V$ $\qquad$ $\left| \begin{array}{l} \therefore \; 6e + Cr_2^{6+} \longrightarrow 2Cr^{3+} \end{array} \right.$

$\therefore \;\; V = \dfrac{100}{6} = \mathbf{16.67 \ mL}$ $\qquad$ $\left| \begin{array}{l} \therefore \; N = M \times \text{Valence factor} \end{array} \right.$

**Note :** The conditions are valid only when Mn in each medium exist as monomeric atom, *i.e.*, not as $Mn_z$.

**40.** Redox changes are:

$$Fe \longrightarrow Fe^{2+} + 2e \qquad (in\ H_2SO_4)$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e \qquad (with\ K_2Cr_2O_7)$$
$$6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$$
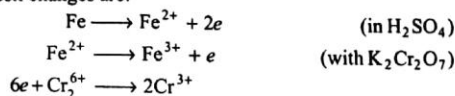
Meq. of $Fe^{2+}$ in 20 mL = Meq. of $K_2Cr_2O_7$

$$= 30 \times \frac{1}{30} = 1$$

$\therefore$ Meq. of $Fe^{2+}$ of valence factor one in 100 mL

$$= \frac{1 \times 100}{20} = 5$$

$\therefore$ Meq. of $Fe^{2+}$ of valence factor two in 100 mL

$$= 5 \times 2 = 10$$

$\therefore$      Meq. of Fe = Meq. of $Fe^{2+}$

$$\frac{w}{M/2} \times 1000 = 10$$

$\therefore$

$$\frac{w}{\frac{56}{2}} \times 1000 = 10$$

$\therefore$
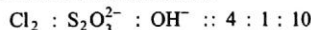
$$w = \frac{56 \times 10}{2 \times 1000} = 0.28\,g$$

$\therefore$ % of Fe in wire $= \frac{0.28}{0.2828} \times 100 = \mathbf{99.0\%}$

**41.** When medium is reported and conc. of medium is desired, then first balance the equation using ion electron method.

$$4Cl_2 + S_2O_3^{2-} + 10OH^- \longrightarrow 2SO_4^{2-} + 8Cl^- + 5H_2O$$

| | | | | | |
|---|---|---|---|---|---|
| Mole | 0.15 | 0.01 | 0.30 | 0 | 0 | 0 |
| before reaction | | | | | | |
| Mole $(0.15 - 4 \times 0.01)$ | 0 | $(0.3 - 0.01 \times 10)$ | 0.02 | 0.08 | 0.05 |
| after reaction = 0.11 | 0 | 0.2 | 0.02 | 0.08 | 0.05 |

Since, mole ratio for combination is

$$Cl_2 : S_2O_3^{2-} : OH^- :: 4 : 1 : 10$$

$\therefore$ **[$OH^-$] left after reaction is 0.2 mole.**

**42.** Meq. of $NH_3$ formed = Meq. of HCl used for $NH_3$

$$= 50 \times 0.15 - 32.10 \times 0.10 = 4.29$$

**Note :** These Meq. of $NH_3$ are derived using valence factor of $NH_3 = 1$. (an acid-base reaction)

In redox change valence factor of $NH_3$ is 8;

$$8e + N^{5+} \longrightarrow N^{3-}$$
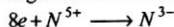
Thus, Meq. of $NH_3$ for valence factor $8 = 8 \times 4.29$

Also, Meq. of $NO_3^- =$ Meq. of $NH_3 = 8 \times 4.29 = 34.32$

$\therefore$     $N_{NO_3^-} = \frac{34.32}{25} = \mathbf{1.37}$    ($N \times V$ in mL = Meq.)

Also,    $M_{NO_3^-} = \frac{1.37}{8} = \mathbf{0.1716}$    ($N = M \times V$ factor)
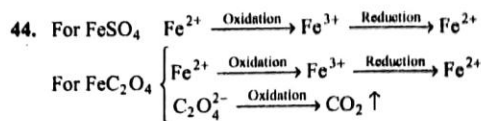
**43.**        $2NaClO_2 + Cl_2 \longrightarrow 2NaCl + 2ClO_2$

Thus,     mole ratio of $\frac{NaClO_2}{ClO_2} = \frac{2}{2}$

Also mole of $NaClO_2 = 2 \times 3.78$    (Mole = $M \times V_{in\ l}$)

$\therefore$     Mole of $ClO_2 = 2 \times 3.78$

Further % yield of the reaction = 97%

$\therefore$ Mole of $ClO_2$ actually formed $= \dfrac{2 \times 3.78 \times 97}{100}$

$$= 7.33\ mol$$

**44.** For $FeSO_4$   $Fe^{2+} \xrightarrow{\ Oxidation\ } Fe^{3+} \xrightarrow{\ Reduction\ } Fe^{2+}$

For $FeC_2O_4$ $\begin{cases} Fe^{2+} \xrightarrow{\ Oxidation\ } Fe^{3+} \xrightarrow{\ Reduction\ } Fe^{2+} \\ C_2O_4^{2-} \xrightarrow{\ Oxidation\ } CO_2 \uparrow \end{cases}$

Let mM or Meq. of $FeSO_4$ and $FeC_2O_4$ be $a$ and $b$ respectively.

$\therefore$ Meq. of

$\underset{in\ FeSO_4}{Fe^{2+}} + \underset{in\ FeC_2O_4}{Meq.\ of\ Fe^{2+}} + \underset{in\ FeC_2O_4}{Meq.\ of\ C_2O_4^{2-}} = \underset{KMnO_4\ used}{Meq.\ of}$

$\underset{a \times 1}{} + \underset{b \times 1}{} + \underset{b \times 2}{} = 40 \times \frac{1}{15} = \frac{8}{3}$

$\therefore$           $a + 3b = \frac{8}{3}$       ...(1)

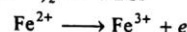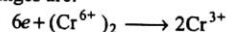After reduction of mixture only $Fe^{2+}$ ions are formed from $Fe^{3+}$ since $CO_2$ escapes out in air.

$\therefore$ Meq. of $Fe^{2+}$ of $FeSO_4$ + Meq. of $Fe^{2+}$ of $FeC_2O_4$

$$= Meq.\ of\ KMnO_4\ used$$

$a \times 1 + b \times 1 = 25 \times \frac{1}{15} = \frac{5}{3}$

$\therefore$          $a + b = 5/3$       ...(2)

By Eqs. (1) and (2),     $a = 7/6$,   $b = 1/2$

$\therefore$ Ratio of Fe in $FeSO_4$ and $FeC_2O_4 = \frac{a}{b} = \frac{7}{3}$

**45.** Redox changes are:

$$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

Meq. of $K_2Cr_2O_7$ in 1 mL = Meq. of Fe

$$= \frac{0.006}{56} \times 1000 = \frac{6}{56}$$

$\therefore$ Meq. of $K_2Cr_2O_7$ in 15.05 mL

$$= \frac{6}{56} \times 15.05 = 1.612$$

$\therefore$ Meq. of $Fe^{2+}$ left unused = Meq. of $K_2Cr_2O_7$ used

$$= 1.612$$

Now Meq. of ferrous ammonium sulphate added

$$= 50 \times 0.12 = 6$$

Meq. of ferrous ammonium sulphate left unused = 1.612

$\therefore$ Meq. of ferrous ammonium sulphate used for sample

$$= 6 - 1.612 = 4.388$$

$\therefore$    Meq. of Cr = 4.388   or   $\frac{w}{E} \times 1000 = 4.388$

$\therefore$     $w_{Cr} = \frac{4.388 \times 52}{1000 \times 3} = 0.0761$    ($\because E_{Cr} = 52/3$)

$\therefore$     % Cr $= \frac{0.0761}{0.5} \times 100 = \mathbf{15.20\%}$

Also    Meq. of $Cr_2O_3 = 4.388$   or   $\frac{w}{E} \times 1000 = 4.388$

$w_{Cr_2O_3} = \frac{4.388 \times 152}{6 \times 1000} = 0.1112\,g \left( \because E_{Cr_2O_3} = \frac{152}{6} \right)$

$\therefore$     % $Cr_2O_3 = \frac{0.1112}{0.5} \times 100 = \mathbf{22.23\%}$

**46.** Redox changes are:

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

$$2N^- \longrightarrow (N^+)_2 + 4e$$

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$
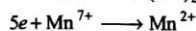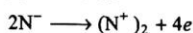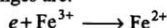
Meq. of $Fe^{2+}$ formed by $NH_2OH$ in 50 mL dilute solution

$$= \text{Meq. of } KMnO_4 \text{ used} = 12 \times 0.02 \times 5 = 1.2$$

$\therefore$  Meq. of $NH_2OH$ in 50 mL dilute solution = 1.2

$\therefore$  Meq. of $NH_2OH$ in 1000 mL dilute solution

$$= 1.2 \times \frac{1000}{50} = 24$$

$\therefore$  Meq. of $NH_2OH$ in 10 mL of original solution

$$= \text{Meq. of } NH_2OH \text{ in } 1000 \text{ mL dilute solution} = 24$$

( $\because$ Meq. of solute does not change on dilution)

$\therefore$ $\qquad \dfrac{w}{33/2} \times 1000 = 24$

$$w_{NH_2OH} = 0.396 \, g$$

$\therefore$ Mass of $NH_2OH$ in 10 mL original solution = 0.396 g

$\therefore$ Mass of $NH_2OH$ in 1 litre original solution

$$= \frac{0.396 \times 1000}{10} = \mathbf{39.6 \, g / litre}$$

**47.** $\therefore$  Meq. of $NaHSO_3$ = Meq. of $NaIO_3$

$$= N \times V = \frac{5.8}{198/6} \times 1000$$

[Eq. mass of $NaIO_3 = M/6$; because $I^{5+} + 6e \longrightarrow I^-$]

Meq. of $NaHSO_3 = 175.76$

$\therefore$ $\qquad \dfrac{w}{M/2} \times 1000 = 175.76$

$\therefore$ $\qquad w_{NaHSO_3} = \dfrac{175.76 \times 104}{2000} = \mathbf{9.14 \, g}$

Also Meq. of $I^-$ formed in I step using valence factor 6

$$= 175.76$$

In II step valence factor of $I^-$ is 1 and valence factor of $IO_3^-$ is 5.

Thus,  Meq. of $I^-$ formed using valence factor $1 = \dfrac{175.76}{6}$

Also  Meq. of $NaIO_3$ used in step II $= \dfrac{175.76}{6}$

$\therefore$ $\qquad N \times V = \dfrac{175.76}{6}$

or  $\dfrac{5.8}{198/5} \times V = \dfrac{175.76}{6}$   $\therefore$  $V_{NaIO_3} = \mathbf{200 \, mL}$

**48.** Meq. of oxalate salt as acid in 30 mL = Meq. of NaOH used

$$= 27 \times 0.12$$

Meq. of oxalate salt as acid in one litre $= \dfrac{27 \times 0.12 \times 1000}{30}$

or  $\dfrac{9.15}{\text{Molar mass of salt}/Y} \times 1000 = \dfrac{27 \times 0.12 \times 1000}{30}$ ...(1)

( $\because$ $Y$ is replaceable H-atom $\therefore$ $E_{salt} = M/Y$)
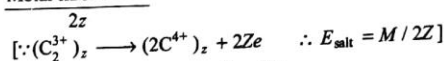
Also Meq. of oxalate salt as reductant in 30 mL

$$= \text{Meq. of } KMnO_4 \text{ used} = 36 \times 0.12$$

$\therefore$  Meq. of oxalate salt as reductant in 1 litre

$$= \frac{36 \times 0.12 \times 1000}{30}$$

or  $\dfrac{9.15}{\dfrac{\text{Molar mass of salt}}{2z}} \times 1000 = \dfrac{36 \times 0.12 \times 1000}{30}$ ...(2)

$[\because (C_2^{3+})_z \longrightarrow (2C^{4+})_z + 2Ze$   $\therefore E_{salt} = M/2Z]$

$\therefore$ By Eqs. (1) and (2),  $\dfrac{Y}{2Z} = \dfrac{27}{36}$

$\therefore$ $\qquad 4Y = 6Z$ ...(3)

Also,  Total cationic charge = total anionic charge

$\therefore$ $\qquad X + Y = 2Z$ ...(4)
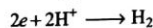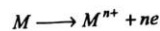
By Eqs. (3) and (4), $X : Y : Z :: 1 : 3 : 2$

These are in simplest ratio.

$\therefore$  Molecular formula is $KH_3(C_2O_4)_2 \cdot nH_2O$.

Now Molar mass of salt $= 39 + 3 + 176 + 18n = 218 + 18n$ ...(5)

By Eq. (1) and putting,  $Y = 3$

$\qquad\qquad\qquad\qquad M = 254.16$ ...(6)

$\therefore$  By Eqs. (5) and (6),  $n = 2$

$\therefore$  Oxalate salt is $\mathbf{KH_3(C_2O_4)_2 \cdot 2H_2O}$

**49.** Metal is $M$

$$M \longrightarrow M^{n+} + ne$$

$$2e + 2H^+ \longrightarrow H_2$$

$\therefore$  Meq. of metal or Meq. of $M^{n+}$ = Meq. of $H_2$

$$= \frac{43.9}{11200} \times 1000$$

( $\because$ 11200 mL $H_2$ = 1 equivalent)

$$\frac{0.1}{51/n} \times 1000 = 3.92$$

$\therefore$ $\qquad n = 2$

Now  $M^{2+} \longrightarrow M^{a+} + (a-2)e$

$$5e + Mn^{7+} \longrightarrow Mn^{2+}$$
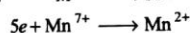
$\therefore$  Meq. of $M^{2+}$ = Meq. of $KMnO_4$

$\dfrac{0.1}{51/(a-2)} \times 1000 = 58.8 \times 0.1$   $\therefore$   $a = 5$

$\therefore$  Different oxidation states of metal are **2** and **5**.

**50.** For the reaction:  $Fe + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4$

$\because$  964 g $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ gives 3

$\qquad\qquad\qquad\qquad\qquad \times 152 g$ $FeSO_4$

$\therefore$  1.25 g $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ gives

$$= \frac{3 \times 152 \times 1.25}{964} \, g$$

$$= 0.5913 \, g \, FeSO_4$$

$FeSO_4$ formed is now oxidized by $KMnO_4$

$\therefore$ $\qquad$ Meq. of $FeSO_4$ = Meq. of $KMnO_4$

$\dfrac{0.5913}{152/1} \times 1000 = 0.107 \times V$   $\therefore$   $V = \mathbf{36.36 \, mL}$

Similarly, if Cu is used

$$Cu + Fe_2(SO_4)_3 \longrightarrow 2FeSO_4 + CuSO_4$$

$\because$ $\qquad$ 964 g salt gives $= 2 \times 152 g$ $FeSO_4$

$\therefore$  1.25 g salt gives $= \dfrac{2 \times 152 \times 1.25}{964} g = 0.3942 g$ $FeSO_4$

$\therefore$ $\qquad$ Meq. of $FeSO_4$ = Meq. of $KMnO_4$

$$\frac{0.3942}{152/1} \times 1000 = 0.107 \times V \quad \therefore \quad V = \textbf{24.24 mL}$$

**51.** For, $Fe_3O_4 \longrightarrow 3FeO; \quad 2e + Fe_3^{8/3+} \longrightarrow 3Fe^{2+}$  ...(i)
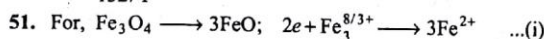
Thus, valence factor for $Fe_3O_4$ is 2 and for FeO is 2/3

For, $Fe_2O_3 \longrightarrow 2FeO; \quad 2e + Fe_2^{3+} \longrightarrow 2Fe^{2+}$  ...(ii)
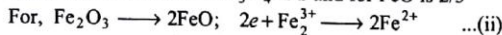
Thus, valence factor for $Fe_2O_3$ is 2 and for FeO is 1.

Let Meq. of $Fe_3O_4$ and $Fe_2O_3$ be $a$, $b$ respectively.

$\therefore$ Meq. of $Fe_3O_4$ + Meq. of $Fe_2O_3$

$\qquad$ = Meq. of $I_2$ liberated = Meq. of hypo used

$$a + b = \frac{11 \times 0.5 \times 100}{20} = 27.5 \qquad ...(iii)$$

Now, the $Fe^{2+}$ ions are again oxidized to $Fe^{3+}$ by $KMnO_4$.

Note that in the change $Fe^{2+} \rightarrow Fe^{3+} + e$; valence factor of $Fe^{2+}$ is 1.

Thus, Meq. of $Fe^{2+}$ (from $Fe_3O_4$) +

$\qquad\qquad\qquad\qquad$ Meq. of $Fe^{2+}$ (from $Fe_2O_3$)

$\qquad\qquad$ = Meq. of $KMnO_4$ used

$$\begin{bmatrix} \text{If valence factor for } Fe^{2+} \text{ is } 2/3 \text{ from Eq. (1),} \\ \text{then Meq. of } Fe^{2+} \text{ (from } Fe_3O_4 \text{)} = a \\ \text{If valence factor for } Fe^{2+} \text{ is 1 then Meq. of } Fe^{2+} \\ \text{(from } Fe_3O_4 \text{)} = 3a/2 \\ \text{Similarly, from Eq. (ii), Meq. of } Fe^{2+} \text{ from } Fe_2O_3 = b \end{bmatrix}$$

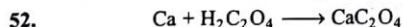$$\therefore \quad \frac{3a}{2} + b = 0.25 \times 5 \times 12.8 \times \frac{100}{50} = 32$$

or $\qquad 3a + 2b = 64 \qquad\qquad$ ...(iv)

From Eqs. (iii) and (iv),

$$\text{Meq. of } Fe_3O_4 = a = 9 \quad \left| \begin{array}{l} \text{and Meq. of} \\ Fe_2O_3 = b = 18.5 \end{array} \right.$$

$$\therefore w_{Fe_3O_4} = \frac{9 \times 232}{2 \times 1000} = 1.044 \text{ g} \left| w_{Fe_2O_3} = \frac{18.5 \times 160}{2 \times 1000} = 1.48 \text{ g} \right.$$

$$\therefore \quad \text{\% of } Fe_3O_4 = \frac{1.044 \times 100}{3} = \textbf{34.8}$$

and $\qquad \text{\% of } Fe_2O_3 = \frac{1.48 \times 100}{3} = \textbf{49.33}$

**52.** $\qquad\qquad Ca + H_2C_2O_4 \longrightarrow CaC_2O_4$

The Meq. of $H_2C_2O_4$ solution added to precipitate Ca as $CaC_2O_4$ is derived as:

25 mL of $H_2C_2O_4$ is diluted 4 folds, *i.e.*, to 100 mL

Now Meq. of dil. $H_2C_2O_4$ in 25 mL

$\qquad\qquad\qquad\qquad$ = Meq. of $KMnO_4$ used

$\qquad\qquad\qquad\qquad$ = $24.1 \times 0.1025 = 2.47025$

$\therefore$ Meq. of $H_2C_2O_4$ in 100 mL dilute solution

$$= \frac{2.47025 \times 100}{25} = 9.881$$

$\therefore$ Meq. of $H_2C_2O_4$ in 25 mL conc. solution = 9.881

Meq. of $H_2C_2O_4$ left after precipitation of $Ca_2C_2O_4$ in one fourth filtrate

$\qquad\qquad$ = Meq. of $KMnO_4$ used = $5 \times 0.1025$

$\therefore$ Total Meq. of $H_2C_2O_4$ left = $5 \times 0.1025 \times 4 = 2.05$

$\therefore$ Meq. of $H_2C_2O_4$ used for Ca = $9.881 - 2.05 = 7.831$

$\therefore \qquad\qquad$ Meq. of Ca = 7.831

$$\frac{w}{40/2} \times 1000 = 7.831 \quad \therefore \quad w_{Ca} = 0.1566 \text{ g}$$

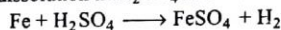$\therefore \quad$ % of Ca in substance = $\frac{0.1566}{1.048} \times 100 = \textbf{14.94\%}$

**53.** $\qquad$ Meq. of $Fe^{2+}$ = Meq. of $KMnO_4$
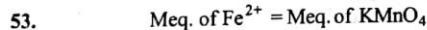
$\qquad$ Meq. of $Fe^{2+}$ = $47.2 \times 0.112 = 5.2864$

$\therefore \qquad Fe^{2+} \longrightarrow Fe^{3+} + e$
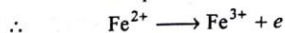
$\qquad$ Meq. of $Fe^{2+}$ = 5.2864 $\qquad$ (valence factor = 1)

Fe ore on dissolution in $H_2SO_4$ show valence factor 2

$\qquad\qquad\qquad Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

$\therefore$ Meq. of $Fe^{2+}$ of valence factor 2 = $5.2864 \times 2$

$\therefore \qquad$ Meq. of Fe = $5.2864 \times 2$

$$\frac{w}{\frac{56}{2}} \times 1000 = 5.2864 \times 2 \quad \therefore \quad w_{Fe} = 0.296 \text{ g}$$

$\therefore \qquad$ % purity of Fe = $\frac{0.296 \times 100}{0.804} = \textbf{36.82\%}$

Now $\qquad Fe_3O_4 \longrightarrow 3Fe$
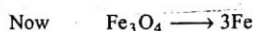
$3 \times 56$ g Fe is obtained from 232 g $Fe_3O_4$

$\therefore 0.296$ g Fe is obtained = $\frac{232 \times 0.296}{56 \times 3} = 0.409$ g $Fe_3O_4$

$\therefore \qquad$ % of $Fe_3O_4 = \frac{0.409}{0.804} \times 100 = \textbf{50.87\%}$

**54.** Meq. of reductant in 25 mL = Meq. of $KMnO_4$
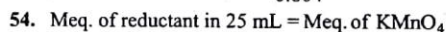
$\qquad\qquad\qquad\qquad = 20 \times 0.01 \times 5$

$\therefore$ Meq. of reductant in 1 litre = $20 \times 0.01 \times 5 \times 40 = 40$

Reductant shows the change $A_2^{+a} \longrightarrow 2A^{+b} + 2e$

$\therefore \qquad$ Eq. mass of reductant = $\frac{\text{Molar mass}}{2}$

$\because \qquad$ Meq. of reductant = 40

$\therefore \qquad \frac{w}{M/2} \times 1000 = 40 \quad \therefore \quad \frac{2.52 \times 2 \times 1000}{M} = 40$

$\therefore \qquad\qquad M = \textbf{126}$

**55.** $\qquad$ Meq. of $H_2SO_4$ = Meq. of NaOH
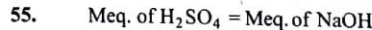
$\qquad N \times 10.27 = 10.35 \times 0.1297 \therefore N_{H_2SO_4} = 0.1307$

$\qquad V_{H_2SO_4}$ used for $KNaCO_3$ = $41.72 - 1.91$ mL

Meq. of $H_2SO_4$ used for $NaKCO_3$ = Meq. of $H_2SO_4$ added

$\qquad\qquad\qquad\qquad$ – Meq. of $H_2SO_4$ used by NaOH

$\qquad = (0.1307 \times 41.72) - 1.91 \times 0.1297 = 5.2050$

Also for the change

$\qquad NaKC_4H_4O_6 \cdot 4H_2O \longrightarrow NaKCO_3 + CO_2 \uparrow + H_2O \uparrow$
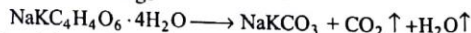
Now Meq. of $NaKCO_3$ using valency factor 2 during its neutralization with $H_2SO_4$ = 5.2050

$\therefore \qquad$ Mass of $NaKCO_3 = \frac{5.2050 \times 122}{2 \times 1000} = 0.3175$ g

$\therefore$ For 1 : 1 mole ratio of conversion, mass of Rochelle salt

$$= \frac{282}{122} \times 0.3175 = 0.7339 \text{ g}$$

$\therefore$ % purity of Rochelle salt = $\frac{0.7339}{0.9546} \times 100 = \textbf{76.87\%}$

**56.** The reactions are:

$\qquad 5e + Mn^{7+} \longrightarrow Mn^{2+} \quad$ and $\quad 2I^- \longrightarrow I_2 + 2e$

$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$
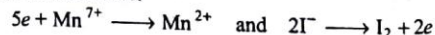
Let mass of $KMnO_4$ and $K_2Cr_2O_7$ be $a$ and $b$ g respectively.

$\therefore$ Meq. of $KMnO_4$ + Meq. of $K_2Cr_2O_7$ = Meq. of $I_2$

= Meq. of hypo = $60 \times 0.1$

$\therefore \quad \dfrac{a}{158/5} \times 1000 + \dfrac{b}{294/6} \times 1000 = 6$ ...(i)

Also given $\qquad a + b = 0.24$ ...(ii)

$\therefore \qquad a = 0.098\,g$ *i.e.*, mass of $KMnO_4$

$b = 0.142\,g$ *i.e.*, mass of $K_2Cr_2O_7$

Also, mass of Mn in 0.098 g $KMnO_4 = \dfrac{55 \times 0.098}{158}$

$= 0.034\,g$

Mass of Cr in 0.142 g $K_2Cr_2O_7 = \dfrac{52 \times 2 \times 0.142}{294} = 0.050\,g$

$\therefore \qquad$ % of Mn in sample $= \dfrac{0.034 \times 100}{0.24} = \mathbf{14.17\%}$

$\therefore \qquad$ % of Cr in sample $= \dfrac{0.050 \times 100}{0.24} = \mathbf{20.83\%}$

**57.** The redox changes are :
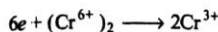
$5e + Mn^{7+} \longrightarrow Mn^{2+}$

$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$2I^- \longrightarrow I_2^0 + 2e$

$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$
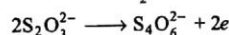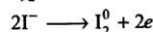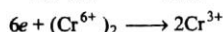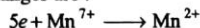
Let $K_2Cr_2O_7$ and $KMnO_4$ be $a$ and $b$ g respectively

$\therefore \qquad a + b = 0.5$ ...(1)

Further Meq. of $KMnO_4$ + Meq. of $K_2Cr_2O_7$

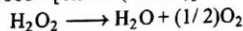= Meq. of KI = Meq. of $I_2$ liberated = Meq. of $Na_2S_2O_3$

$\dfrac{a}{294/6} \times 1000 + \dfrac{b}{158/5} \times 1000 = 100 \times 0.15$ ...(2)

By Eqs. (1) and (2) $a = 0.073$, $b = 0.427$

$\therefore$ % of $K_2Cr_2O_7 = \mathbf{14.6\%}$ and % of $KMnO_4 = \mathbf{85.4\%}$

**58.** Meq. of $H_2O_2$ = Meq. of $I_2$

$(w/17) \times 1000 = [0.508/(254/2)] \times 1000 \quad \therefore w = 0.068\,g$

$H_2O_2 \longrightarrow H_2O + (1/2)O_2$

$\because$ 34 g $H_2O_2$ gives 11.2 litre $O_2$,

$\therefore$ 0.068 g gives $(11.2 \times 0.068)/34 = 22.4$ mL $O_2$

$\therefore \qquad$ Volume strength of $H_2O_2 = 22.4/5 = \mathbf{4.48\%}$

**59.** Let Molar mass of $AO$ and $A_2O_3$ be $m$ and $n$ respectively.

$\therefore \qquad m = a + 16$ ...(1)

and $\qquad n = 2a + 48$ ...(2)

where $a$ is Atomic mass of $A$.

Now suppose $X$ and $Y$ g of $AO$ and $A_2O_3$ are present in mixture

Then $\qquad X + Y = 2.198$ ...(3)

Also Meq. of $AO$ + Meq. of $A_2O_3$ = Meq. of $K_2Cr_2O_7$

$\dfrac{X}{(a+16)/5} \times 1000 + \dfrac{Y}{(2a+48)/8} \times 1000 = 0.015 \times 6 \times 1000$

...(4)

$\because \qquad A^{2+} \longrightarrow A^{7+} + 5e$

$A_2^{3+} \longrightarrow 2A^{7+} + 8e$

$6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$
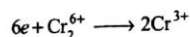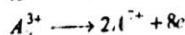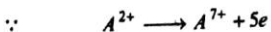
$\therefore$ By Eq. (4), $\quad \dfrac{5X}{a+16} + \dfrac{8Y}{2a+48} = 0.09$ ...(5)

Also, mole $AO_4^-$ by $AO$ + mole of $AO_4^-$ by $A_2O_3 = 0.0187$

$\dfrac{X}{a+16} + \dfrac{2Y}{2a+48} = 0.0187$ ...(6)

$\because$ Mole ratio of $AO : AO_4^- :: 1 : 1$, $A_2O_3 : AO_4^{-1} :: 1 : 2$

Solving Eqs. (3), (5) and (6) $a = \mathbf{100}$

**60.** In (a): $Se^{4+} \longrightarrow Se^{6+} + 2e$

$10e + 2Br^{5+} \longrightarrow Br_2^0 \qquad \therefore$ Eq. mass $KBrO_3 = M/5$;
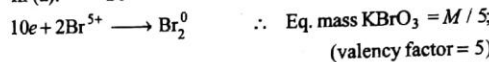
(valency factor = 5)

In (b): $6e + Br^{5+} \longrightarrow Br^{1-} \quad \therefore$ Eq. mass $KBrO_3 = M/6$;

$As^{3+} \longrightarrow As^{5+} + 2e$ (valency factor = 6)
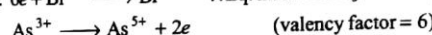
Let Meq. of $BrO_3^-$ of valency factor 6 = Meq. of $AsO_2^-$

$= 5.1 \times \dfrac{1}{25} \times 2 = 0.408$

Meq. of $BrO_3^-$ of valency factor 5 added

$= 20 \times \dfrac{1}{60} \times 5 = \dfrac{5}{3} = 1.67$

Left Meq. of $BrO_3^-$ of valency factor 5 $= \dfrac{0.408 \times 5}{6} = 0.34$

$\therefore$ Meq. of $BrO_3^-$ used for $SeO_3^{2-} = 1.67 - 0.34 = 1.33$

$\therefore$ Meq. of $SeO_3^{2-} = 1.33$ or $\dfrac{w}{127/2} \times 1000 = 1.33$

$\therefore \qquad W_{SeO_3^{2-}} = \mathbf{0.084\,g}$

**61.** Meq. of $I_2$ used $= 20.10 \times 0.05 = 1.005$

Let Meq. of $As_2O_3$ and Meq. of $As_2O_5$ in mixture be $a$ and $b$ respectively. On addition of $I_2$ to mixture, $As_2^{3+}$ is converted to $As_2^{5+}$.

$\therefore$ Meq. of $As_2O_3$ = Meq. of $I_2$ used = 1.005

= Meq. of $As^{5+}$ formed

or $\qquad a = 1.005$ ...(1)

After reaction with $I_2$, mixture contains all the arsenic in +5 oxidation state which is then titrated using KI + hypo. Thus,

Meq. of $As_2O_3$ as $As^{5+}$ + Meq. of $As_2O_5$ as $As^{5+}$

= Meq. of liberated $I_2$ = Meq. of hypo used

or $\qquad a + b = \dfrac{1.1113}{248} \times 1000$ or $a + b = 4.481$ ...(2)

By Eqs. (1) and (2), $b = 4.481 - 1.005 = 3.476$

$\therefore$ Mass of $As_2O_3 = \dfrac{\text{Meq.} \times \text{Eq. mass}}{1000} = \dfrac{1.005 \times 198}{4 \times 1000}$

$= 0.0497\,g$

and Mass of $As_2O_5 = \dfrac{3.476 \times 230}{4 \times 1000} = 0.1999\,g$

$\therefore \qquad$ Mass of mixture = 0.0497 + 0.1999 = **0.2496 g**

**62.** (a) $\qquad Cu^0 \longrightarrow Cu^{2+} + 2e$

$N^{5+} + e \longrightarrow N^{4+}$
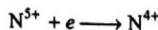
$\therefore$   Eq. of Cu = Eq. of $NO_2$

$$\frac{w}{63.6/2} = \frac{1 \times 1.04}{0.0821 \times 298}$$

$$\left( \because \text{mole of } NO_2 = \text{Eq. of } NO_2 = \frac{PV}{RT} \right)$$

$\therefore \qquad w_{Cu} = \mathbf{1.35\ g}$

$\therefore \qquad w_{Zn} = 1.50 - 1.35 = \mathbf{0.15\ g}$

$\qquad \% \text{ of Cu} = \dfrac{1.35}{1.5} \times 100 = 90\%$

$\therefore \qquad \% \text{ of Zn} = \dfrac{0.15}{1.5} \times 100 = \mathbf{10\%}$

(b) Thus, 1 g brass contains 0.9 g Cu and 0.1 g Zn

$\therefore$ Meq. of $HNO_3$ $\qquad\quad$ and Meq. of $HNO_3$
$\qquad\quad$ = Meq. of Zn $\qquad\qquad\quad$ = Meq. of Cu

or

$3 \times 8 \times V_1 = \dfrac{0.1}{65/2} \times 1000$ $\qquad$ or $3 \times V_2 = \dfrac{0.9}{63.6/2} \times 1000$

$\therefore \quad V_1 = 0.128$ mL $\qquad\qquad \therefore \quad V_2 = 9.43$ mL

$(\because N^{5+} + 8e \rightarrow N^{3-})$

$\therefore$ Total volume of $HNO_3$ used = 0.128 + 9.43 = **9.558 mL**

**63.** Meq. of alkali added = $30 \times 0.04 = 1.2$

Meq. of alkali left = $22.48 \times 0.024 = 0.54$

$\therefore$ Meq. of alkali used for $SO_2$ and $H_2O_2$

$\qquad = 1.2 - 0.54 = 0.66$

$\therefore$ Mass of alkali used $= \dfrac{0.66 \times 40}{1000} = 0.0264$ g

$\because$   80 g NaOH reacts with 64 g $SO_2$.

$\therefore$   0.0264 g NaOH reacts $= \dfrac{64 \times 0.0264}{80} = 0.021$ g $SO_2$

Now $\because$   64 g $SO_2$ required = 32 g S

$\therefore$   0.021 g $SO_2$ required $= \dfrac{32 \times 0.021}{64} = 0.0105$ g

$\therefore$   % of S $= \dfrac{0.0105}{5.6} \times 100 = \mathbf{0.1875\%}$

**64.** Since, Cu will react with ferric sulphate to reduce $Fe^{3+}$ to $Fe^{2+}$. The reduced state of iron is further oxidized by $KMnO_4$.

Thus, Meq. of $KMnO_4$ used

$\qquad$ = Meq. of iron sulphate oxidized

$\qquad$ = Meq. of ferric sulphate used by Cu

$\qquad$ = Meq. of Cu

$\therefore \qquad$ Meq. of Cu = Meq. of $KMnO_4$ used

$$\frac{0.108}{63.6/n} \times 1000 = 33.7 \times 0.1$$

$\therefore \qquad n \approx 2$ (integer)

It is thus, clear that during reduction of $Fe^{3+}$, Cu is oxidized to $Cu^{2+}$. Thus reaction is:

$$\mathbf{Cu + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 2FeSO_4}$$

**65.** The reactions are

$\qquad H_2O + 2KI + O_3 \longrightarrow 2KOH + I_2 + O_2$

Also $\qquad 2e + I_2 \longrightarrow 2I^-$

and $\qquad 2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$

$\therefore$ Meq. of $I_2$ = Meq. of $Na_2S_2O_3 = 1.5 \times 0.01 = 1.5 \times 10^{-2}$

or $\qquad$ mM of $I_2 = \dfrac{1.5 \times 10^{-2}}{2} = 7.5 \times 10^{-3}$

$\therefore \qquad$ mM of $O_3 =$ mM of $I_2 = 7.5 \times 10^{-3}$

$\qquad\qquad\qquad (\because$ Mole ratio of $O_3 : I_2 :: 1 : 1)$

$\therefore \quad P'_{O_3} = \dfrac{nRT}{V} = \dfrac{7.5 \times 10^{-6} \times 0.0821 \times 300}{10}$

$\qquad\qquad = 184.725 \times 10^{-7}$ atm

$\therefore$ Vol. % of $O_3 = 184.725 \times 10^{-7} \times 100 = \mathbf{1.847 \times 10^{-3}\%}$

**66.** $\qquad O_3 + 2KI + H_2O \longrightarrow 2KOH + I_2 + O_2$

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

$\therefore$ Millimole of $O_3$ = Millimole of $I_2$

$\qquad\qquad = \dfrac{1}{2} \times$ mM of $Na_2S_2O_3$

$\qquad\qquad\qquad\qquad (mM = M \times V_{in\ mL})$

$\qquad = \dfrac{1}{2} \times 40 \times \dfrac{1}{10} = 2$ mM = 0.002 mole

Total millimole of $O_2$ and $O_3$ in mixture are calculated from $PV = nRT$

$\qquad 1 \times 1 = n \times 0.0821 \times 273 \quad \therefore \quad n = 0.044$ mole

$\therefore \qquad$ Mole of $O_2 = 0.044 - 0.002 = 0.042$

Now $\qquad$ mass of $O_2 = 0.042 \times 32$ g = 1.344 g

$\qquad\qquad$ mass of $O_3 = 0.002 \times 48$ g = 0.096 g

$\therefore \qquad$ % of $O_3 = \dfrac{0.096}{1.44} \times 100 = 6.7\%$

No. of photon or molecules of ozone

$\qquad = \dfrac{0.096 \times 6.023 \times 10^{23}}{48} = \mathbf{1.2 \times 10^{21}}$

**67.** Meq. of $MnO_4^-$ added $= 200 \times 0.75 \times 5 = 750$

$\because \qquad Mn^{7+} + 5e \longrightarrow Mn^{2+} \qquad\qquad \therefore \quad N = M \times 5$

Meq. of $MnO_4^-$ left unused = Meq. of $Fe^{2+}$ used

$\qquad\qquad\qquad\qquad = 175 \times 1 \times 1 = 175$

$\because \qquad\qquad Fe^{2+} \longrightarrow Fe^{3+} + e \qquad \therefore \quad N = M \times 1$

Now Meq. of $MnO_4^-$ used $= 750 - 175 = 575$

$MnO_4^-$ is used for $Cu_2S$ and CuS to give.

For $Cu_2S$: $\qquad Cu_2^+ \longrightarrow 2Cu^{2+} + 2e$

$\qquad\qquad\qquad\quad S^{2-} \longrightarrow S^{4+} + 6e$

$\qquad\qquad\qquad Cu_2S \longrightarrow 2Cu^{2+} + S^{4+} + 8e$

For CuS: $\qquad S^{2-} \longrightarrow S^{4+} + 6e$

Let $Cu_2S$ and CuS be $a$ and $b$ g respectively

$\therefore \qquad\qquad a + b = 10 \qquad\qquad\qquad ...(1)$

$\therefore$ Meq. of $MnO_4^-$ used = Meq. of $Cu_2S$ + Meq. of CuS

$\qquad 575 = \dfrac{a}{159.2/8} \times 1000 + \dfrac{b}{95.6/6} \times 1000 \quad ...(2)$

$\therefore$ Solving Eqs. (1) and (2), $\quad a = 4.206$ g

$\qquad\qquad\qquad\qquad\qquad\qquad b = 5.794$ g

$\therefore \qquad$ % of CuS in mixture $= \dfrac{5.794}{10} \times 100 = \mathbf{57.94\%}$

**68.** NaCN *vs.* KMnO$_4$ : $C^{2+} \longrightarrow C^{4+} + 2e$

$$3e + Mn^{7+} \longrightarrow Mn^{4+}$$
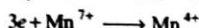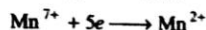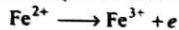
Meq. of KMnO$_4$ added $= 50 \times 0.33 \times 3 = 49.5$

(v.f. of KMnO$_4$ = 3)

Meq. of KMnO$_4$ (v.f. = 5) left after reaction with NaCN
= Meq. of FeSO$_4$ used $= 500 \times 0.06 \times 1 = 30$

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

$$Mn^{7+} + 5e \longrightarrow Mn^{2+}$$

$\therefore$ Meq. of KMnO$_4$ (v.f. = 3) left $= \dfrac{30 \times 3}{5} = 18$

$\therefore$ Meq. of NaCN in sample $= 49.5 - 18 = 31.5$
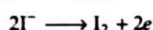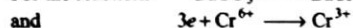
$$\frac{w}{49/2} \times 1000 = 31.5$$

$\therefore$ $\qquad\qquad w = 0.7718\,g$

$\therefore$ **% of NaCN = 77.18**

**69.** Suppose mass of BaCO$_3$, CaCO$_3$ and CaO are $a, b, c$ be respectively.

$$a + b + c = 1.249 \qquad\qquad ...(1)$$

For the reactions $\quad$ BaCO$_3 \longrightarrow$ BaCrO$_4$

and $\qquad\qquad 3e + Cr^{6+} \longrightarrow Cr^{3+}$

$$2I^- \longrightarrow I_2 + 2e$$

Meq. of BaCO$_3$ = Meq. of BaCrO$_4$ = Meq. of I$_2$

or $\qquad \dfrac{a}{197/3} \times 1000 = 20 \times 0.05 \times \dfrac{100}{10}$

$\therefore$ $\qquad\qquad a = 0.657\,g \qquad\qquad ...(2)$

The Eq. mass of BaCrO$_4$ is $M/3$ and thus for BaCO$_3$ it should be $M/3$.

Also for acid-base reaction

Meq. of BaCO$_3$ + Meq. of CaCO$_3$ = Meq. of CO$_2$

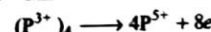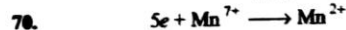$$\frac{a}{197/2} \times 1000 + \frac{b}{100/2} \times 1000 = \frac{168 \times 44}{22400 \times 22} \times 1000$$

$\therefore$ $\qquad\qquad 200a + 394b = 295.5 \qquad ...(3)$

By Eqs. (2) and (3) $\qquad b = 0.416\,g$

$\therefore$ By Eq. (1) $\quad 0.657 + 0.416 + c = 1.249$

$\therefore$ $\qquad\qquad c = 0.176$

or $\qquad$ % of CaO $= \dfrac{0.176 \times 100}{1.249} = $ **14.09%**

**70.** $\qquad\qquad 5e + Mn^{7+} \longrightarrow Mn^{2+}$

$$(P^{3+})_4 \longrightarrow 4P^{5+} + 8e$$

Thus, $\quad$ Meq. of KMnO$_4 = \dfrac{100 \times 5 \times 1000}{158} = 3164.56$

$\qquad\qquad$ Meq. of P$_4$O$_6 = \dfrac{100 \times 8 \times 1000}{219.9} = 3638.02$

$\therefore$ $\qquad$ Meq. of P$_4$O$_6$ in excess $= 473.46$

$\therefore$ $\dfrac{w \times 8 \times 1000}{219.9} = 473.46$ $\therefore$ $w_{P_4O_6}$ in excess $=$ **13.01 g**

**71.** As$_2$O$_3$ sample $= 12.0\,g$. It reacts with NaHCO$_3$ to give Na$_3$AsO$_3$. Its reaction with I$_2$ shows the changes:

$$(As^{3+})_2 \longrightarrow (As^{5+})_2 + 4e;$$

$$I_2 + 2e \longrightarrow 2I^-$$
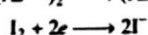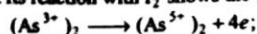
Meq. of As$_2$O$_3$ in 25 mL = Meq. of I$_2$ = $22.4 \times N$ ...(1)

Also $N$ of I$_2$ can be evaluated as:

Meq. of I$_2$ = Meq. of hypo = $N \times V$

The reaction are: $\quad I_2 + 2e \longrightarrow 2I^-$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$
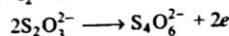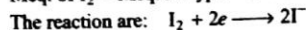
$$N \times 25 = \frac{24.8}{248 \times 1} \times 25$$

$\therefore$ $\qquad\qquad N_{I_2} = \dfrac{N}{10}$

$\therefore$ Meq. of As$_2$O$_3$ in 25 mL $= 22.4 \times \dfrac{1}{10} = 2.24$

or $\quad$ Meq. of As$_2$O$_3$ in 250 mL $= 2.24 \times \dfrac{250}{25} = 22.4$

or $\qquad \dfrac{w}{E} \times 1000 = 22.4$

$$\frac{w}{\frac{198}{4}} \times 1000 = 22.4$$

$\therefore$ $\qquad w_{As_2O_3} = \dfrac{22.4 \times 198}{4 \times 1000} = 1.1088$

$\therefore$ **% of As$_2$O$_3$** $= \dfrac{1.1088}{12} \times 100 = $ **9.24%**

**72.** $\qquad\qquad Sn^{2+} \longrightarrow Sn^{4+} + 2e$

$$2e + (O^-)_2 \longrightarrow 2O^{2-}$$
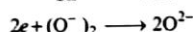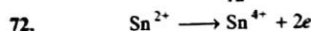
Meq. of H$_2$O$_2$ used = Meq. of Sn$^{2+}$ $= 100 \times 2 \times 2 = 400$

$\therefore$ Meq. of H$_2$O$_2$ taken $= \dfrac{200 \times 10 \times 2 \times 1000}{100 \times 34} = 1176.47$

$\therefore$ $\quad$ Meq. of H$_2$O$_2$ left $= 1176.47 - 400 = 776.47$

$m$ mole of H$_2$O$_2$ left $= \dfrac{776.47}{2}$

Now $\qquad H_2O_2 \longrightarrow H_2O + \dfrac{1}{2}O_2$
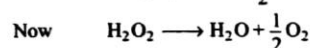
or $\qquad m$ mole of O$_2$ formed $= \dfrac{776.47}{2 \times 2} = 194.12$

$\therefore$ $V = \dfrac{nRT}{P} = \dfrac{194.12 \times 10^{-3} \times 0.0821 \times 293}{1} = $ **4.67 litre**

**73.** For $A_x(CO_3)_y(OH)_z$ : $\quad 2x = 2y + z \qquad ...(1)$
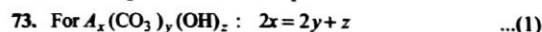
The reaction of salt with H$_2$SO$_4$ uses carbonate ions as well as hydroxide ions.

**In case of phenolphthalein :** Half of the salt is neutralized as carbonate is converted to bicarbonate and OH$^-$ ions are completely neutralized.

Meq. of H$_2$SO$_4 = \dfrac{1}{2}$ Meq. of salt for carbonate +

$\qquad\qquad\qquad\qquad\qquad$ Meq. of salt for OH$^-$

$$\frac{10 \times 1 \times 100}{50} = \frac{1}{2} \times \frac{1.7225 \times 1000}{\frac{M}{2y}} + \frac{1.7225 \times 1000}{\frac{M}{z}}$$

or $\qquad 20 = \dfrac{1722.5y}{M} + \dfrac{1722.5z}{M} \qquad ...(2)$

**In case of methyl orange :** Salt is completely neutralized.

$$\frac{15 \times 1 \times 100}{50} = \frac{1.7225 \times 1000}{\frac{M}{2y}} + \frac{1.7225 \times 1000}{\frac{M}{z}}$$

or
$$30 = \frac{3445y}{M} + \frac{1722.5z}{M} \qquad ...(3)$$

By subtracting Eq. (2) from Eq. (3).
$$10 = \frac{1722.5y}{M} \qquad ...(4)$$

By Eqs. (2) and (4), $10 = \frac{1722.5z}{M} \qquad ...(5)$

$\therefore$ By Eqs. (4) and (5), $y = z \qquad ...(6)$

Also from Eqs. (1) and (6), $x = 1.5y$

Thus for simplest ratio $x : y : z :: 1.5 : 1 : 1$ or $3 : 2 : 2$

Therefore formula of salt is $A_3(CO_3)_2(OH)_2$

**74.** $(Cu^+)_2 \longrightarrow Cu^{2+} + Cu$
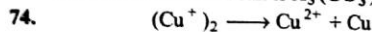
The solution after dissolution of $Cu_2O$ in dil. $H_2SO_4$ contains $Cu^{2+}$ and $Cu$ ions. $Cu^{2+}$ ions react with KI to give $CuI_2$ which is converted to $CuI$ and $I_2$.

$$Cu^{2+} + 2I \longrightarrow CuI_2 \longrightarrow CuI + \frac{1}{2}I_2$$
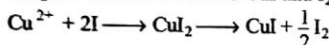
Millimole of KI taken $= \frac{8.3}{166} \times 1000 = 50$

Now, KI left unused reacts with oxidizing agent to liberate $I_2$ again.

$$2I^- \xrightarrow{\text{Oxidant}} I_2 \xrightarrow{2Na_2S_2O_3} Na_2S_4O_6 + 2NaI$$
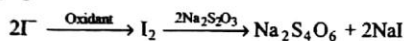
$\therefore$ Millimole of KI left = Millimole of $Na_2S_2O_3$ used
(mole ratio of $I^-$ to $Na_2S_2O_3$ is $1 : 1$)
$$= 10 \times 1.0 = 10$$

Therefore, millimole of KI used for $Cu^{2+} = 50 - 10 = 40$

$\therefore$ Millimole of $Cu_2O = 20$

$$\begin{bmatrix} Cu_2^+ \longrightarrow 2Cu^{2+} \\ \therefore \text{Mole ratio } Cu_2^+ : Cu^{2+} :: 1 : 2 \end{bmatrix}$$
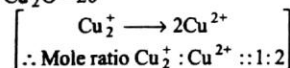
or $\frac{w}{M} \times 1000 = 20$

$$\frac{w \times 1000}{142} = 20 \quad \therefore \quad w_{Cu_2O} = 2.84$$

$\therefore$ % of $Cu_2O = \frac{2.84 \times 100}{3} = \mathbf{94.67}$

**75.** $3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$
(mole ratio $Br_2 : BrO_3^- :: 3 : 1$)
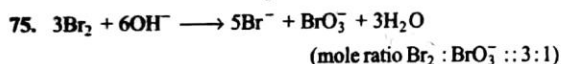
$BrO_3^-$ and $C_2O_4^{2-}$ reacts to give redox change as:

$$6e + Br^{5+} \longrightarrow Br^- \quad \text{(valence factor of } BrO_3^- = 6)$$
$$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$$
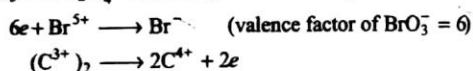
Millimole of $Br_2$ taken $= 10 \times 1.0 = 10$

$\therefore$ Millimole of $BrO_3^-$ formed $= \frac{10}{3}$

Also, Meq. of $CaC_2O_4$ = Meq. of $BrO_3^- = \frac{10}{3} \times 6 = 20$

or $\frac{w \times 1000}{128/2} = 20 \quad \therefore \quad w_{CaC_2O_4} = 1.28\,g$

$\therefore$ % of $CaC_2O_4 = \frac{1.28}{1.5} \times 100 = \mathbf{85.33}$

**76.** $2e + Cl^+ \longrightarrow Cl^- \qquad$ ($OCl^-$ changes to $Cl^-$)
$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e \qquad$ ($C_2O_4^{2-}$ change to $CO_2$)
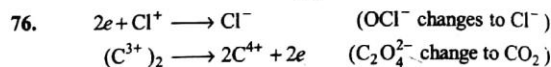
Let $a$ and $b$ millimole of $NaOCl$ and $CaOCl_2$ be present in mixture.

Meq. of $NaOCl$ + Meq. of $CaOCl_2$ = Meq. of $Na_2C_2O_4$
$$2a + 2b = 10 \times 0.15 \times 2 \times \frac{100}{10} = 30$$

$\therefore \qquad 2a + 2b = 30 \qquad ...(1)$

Also millimole of $Cl^-$ from $NaOCl$ +
millimole of $Cl^-$ from $CaOCl_2$
= millimole of $AgCl$

or $a + 2b = \frac{0.287}{143.5} \times 1000 \times \frac{100}{10} = 20$

$$a + 2b = 20 \qquad ...(2)$$

By Eqs. (1) and (2), $a = 10, b = 5$

$\therefore$ % of $NaOCl = 10 \times 74.5 \times 10^{-3} \times \frac{100}{2} = \mathbf{37.25}$

% of $CaOCl_2 = 5 \times 127 \times 10^{-3} \times \frac{100}{2} = \mathbf{31.75}$

**77.** Equivalent of $KMnO_4 = \frac{6.32}{31.6} = 0.2$

Equivalent of $KCl = \left[\frac{4}{74.5}\right] = 0.0537$

Equivalent of $KBr = \left[\frac{m}{119}\right]$

$\therefore \qquad 0.2 = 0.0537 + \frac{m}{119} \qquad \therefore \quad m = \mathbf{17.41\,g}$

**78.** Let mM of $Cl^-$ and $ClO_3^-$ be $a$ and $b$ respectively

$\therefore \qquad a + b = $ mM of $AgCl = \frac{0.1435}{143.5} \times 1000 = 1$

Also, Meq. of $KClO_3 = 6a \quad \because \ 6e + Cl^{5+} \longrightarrow Cl^-$

and Meq. of $FeSO_4$ used for $KClO_3$
$$= 30 \times 0.2 - 37.5 \times 0.08 = 6 - 3 = 3$$

$\therefore \qquad 6a = 3$

$\therefore \qquad a = \frac{1}{2} \quad$ and $\quad b = \frac{1}{2}$

i.e., $5 \times 10^{-3}$ **mole each, (1 : 1)**

**79.** Meq. of $KMnO_4$ = Meq. of $ReO_4^{1-}$ = Meq. of $Re$

$1145 \times 0.05 = $ Meq. of $ReO_4^{1-}$ = Meq. of $Re$

$\therefore \qquad$ Meq. of $Re$ from $Re^{n+}$ to $ReO_4^- = 0.5725$

or $\frac{26.83 \times 10^{-3}}{186.2/(7-n)} \times 1000 = 0.5725$

$\therefore \quad 7 - n = \frac{0.5725 \times 186.2}{26.83 \times 10^{-3} \times 1000} = 4 \quad \therefore \ n = 3$

$\therefore$ Oxidation state is $Re^{3+}$.

# ● SINGLE INTEGER ANSWER PROBLEMS ●

1. '$n$' factor of $FeC_2O_4$ during its oxidation by acidified $KMnO_4$ is .......

2. An element $A$ in a compound has oxidation state $A^{n-}$. If $1.68 \times 10^{-3}$ mole of $K_2Cr_2O_7$ are required for complete oxidation of $3.26 \times 10^{-3}$ mole of $ABD$ for oxidation to $A^{n-}$ to elemental state. The value of $n$ is .......

3. 1.6 g pyrolusite ore was titrated with 50 cm$^3$ of 1.0 $N$ oxalic acid and some sulphuric acid. The oxalic acid left was raised to 250 mL in a flask 25 mL of this solution when treated with 0.1 $N$ $KMnO_4$ required 32 mL of the solution. The percentage of available oxygen in pyrolusite is :

4. 1 g sample of $Fe_2O_3$ solid of 55.2% purity is dissolved in acid and reduced by heating the solution with Zn dust. The resultant solution is cooled and made upto 100 mL. An aliquot of 25 mL of this solution requires 17 mL of 0.0167$M$ solution of an oxidant for titration. The number of electrons taken up by oxidant in the above titration is .......

5. 0.31 g of an alloy of Fe + Cu was dissolved in excess dilute $H_2SO_4$ and the solution was made upto 100 mL. 20 mL of this solution required 3 mL of $\dfrac{N}{30}$ $K_2Cr_2O_7$ solution for exact oxidation. The % purity (in closest value) of Fe in wire is :

6. The reaction $Cl_2(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + Cl^-$ to be carried out in basic medium. 1.5 mole of $Cl_2$ are allowed to react can with 0.1 mole of $S_2O_3^{2-}$ in presence of 3.0 mole of $OH^-$. Mole of $OH^-$ left after the reaction is .......

7. Equivalent mass of $O_3$ in the reaction : $2O_3 \longrightarrow 3O_2$ is .......

8. '$n$' factor for $H_2S$ during its oxidation to $SO_2$ is .......

9. '$n$' factor for $Cu_2S$ in the reaction
$Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + SO_2 + Mn^{2+}$ is:

10. A 5.6 g sample of limestone is dissolved in acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed with water and dissolved in dil. $H_2SO_4$. The solution required 40 mL of 0.25 $N$ $KMnO_4$ solution for titration. The % of CaO in limestone is .......

11. 80 mL of $M/24$ $K_2Cr_2O_7$ solution oxidises 22.4 mL $H_2O_2$ solution. The volume strength of $H_2O_2$ solution is .......

12. 10 mL of 0.2 $M$ solution of $K_xH(C_2O_4)_y$ requires 8 mL of 0.2 $M$ acidified $KMnO_4$ solution. The value of $x$ is .......

13. '$n$' factor for $SO_2$ in $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$ is .......

14. 30 mL of 0.3 $M$ $MnSO_4$ is completely oxidised by 3 mL of $KMnO_4$ of unknown normality, each forming $Mn^{4+}$ oxidation state. The normality of $KMnO_4$ is .......

15. 2 $M$ solution of $HNO_3$ is reduced to NO by suitable reductant. The normality of $HNO_3$, if $HNO_3$ is used like this is .......

16. '$n$' factor for S in $SO_2$ is 4 and in $SO_3$ is 6. The '$n$' factor of S in $SO_2 + \dfrac{1}{2}O_2 \longrightarrow SO_3$ is .......

17. '$n$' factor of $C_2H_5OH$ in the reactions is....
$C_2H_5OH \longrightarrow CH_3CHO$

18. 4 mole each of $Hg^{2+}$ and $I^-$ will form how much mole of $[HgI_4]^{2-}$

19. 2.5 mole of $Fe_2(C_2O_4)_3$ requires how much mole of $KMnO_4$ for its complete oxidation in acidic medium?

20. $C_3H_8$ is completely oxidised to $CO_2$ and $H_2O$, the ratio of equivalent mass of $CO_2$ formed and $C_3H_8$ taken is.....

21. The number of mole of $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ oxidised by 4 mole of acidified $KMnO_4$ is.....

22. $CrO_5$ reacts with $H_2SO_4$ to give $Cr_2(SO_4)_3$, $H_2O$ and $O_2$. The mole of $O_2$ released during the reaction of 4 mole of $CrO_5$ with excess of $H_2SO_4$.

23. 2 mole of $FeC_2O_4$ are oxidised by '$X$' mole of $KMnO_4$ whereas 2 mole of $FeSO_4$ are oxidised by '$Y$' mole of $KMnO_4$. The ratio of $X : Y$ is.....

24. Number of $H_2O_2$ mole needed to convert two mole of $Cr(OH)_3$ in alkaline medium to sodium chromate is.....

25. $6 \times 10^{-3}$ mole $K_2Cr_2O_7$ reacts completely with $9 \times 10^{-3}$ mole $X^{n+}$ to give $XO_3^-$ and $Cr^{3+}$. The value of $n$ is ......

26. Mole of $KMnO_4$ required to oxidise a mixture of 2 mole each of $FeSO_4$, $FeC_2O_4$ and $Fe_2(C_2O_4)_3$ in acid medium.

27. Mole of $K_2Cr_2O_7$ required to oxidise one mole of $Fe_2(C_2O_4)_3$ in acid medium.

28. Equivalent mass of nitrogen in the reaction :
$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$ is $\dfrac{M}{X}$. The value of $X$ is .........

29. A 1.10 g sample of copper ore is dissolved and $Cu^{2+}$ formed are titrated with excess of KI. The liberated iodine requires 12.12 mL of 0.10 $N$ $Na_2S_2O_3$ solution for titration. The % of copper by mass in sample is .........

30. 9.824 g of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot X \, H_2O$ were dissolved in 250 mL of solution. 20 mL of this solution required 20 mL of $KMnO_4$ containing 3.52 g of 90% by mass $KMnO_4$ dissolved per litre. The value of '$X$' is .........

**31.** A 0.56 g sample of limestone is dissolved in acid and calcium is precipitated as calcium oxalate. The precipitate is filtered, washed and dried and then dissolved in $H_2SO_4$. The solution required 4mL of 0.25 $N$ $KMnO_4$ for oxidation of oxalate. The % of CaO in limestone is .........

**32.** Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation.
$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$
under conditions where 1 mole of gas occupies $50\,dm^3$, $100\,cm^3$, of $XM$ solution of $H_2O_2$ produces $5\,dm^3$ of $O_2$. Thus $X$ is ...........

**33.** 15g sample of an alloy containing Cu (at mass 63.6) and Zn reacts completely with $3M$ $HNO_3$ as :
$$Cu + HNO_3 \longrightarrow Cu^{2+} + NO_2(g) + H_2O$$
$$Zn + HNO_3 \longrightarrow Zn^{2+} + NH_4^+ + H_2O$$

The liberated $NO_2(g)$ was found to occupy 4.647 litre at 1 atm and 300 K. The mass of Zn (to the closest value) in alloy is .......

**34.** $n$-factor of $Mn_2O_7$ in the change :
$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2 \text{ is .........}$$

**35.** $n$-factor for $Fe_3O_4$ in its reaction during its oxidation to $Fe_2O_3$ is ..........

**36.** Number of mole of $As_2S_3$ required to reduce 56 mole of $HNO_3$ according to equation :
$$As_2S_3 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO$$

**37.** Reaction of $Br_2$ with $Na_2CO_3$ in aqueous solution gives sodium bromide and sodium bromate with evolution of $CO_2$ gas. The number of sodium bromide molecules involved in the balanced chemical equation is :

[IIT 2011]

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## ANSWERS

| | | | | | | |
|---|---|---|---|---|---|---|
| **1.** Three | **2.** Three | **3.** Nine | **4.** Six | **5.** Nine | **6.** Two | **7.** Eight |
| **8.** Six | **9.** Eight | **10.** Five | **11.** Five | **12.** Three | | |
| **13.** Five | **14.** Two | **15.** Six | **16.** Two | **17.** Two | **18.** One | **19.** Three |
| **20.** Three | **21.** Five | **22.** Seven | **23.** Three | **24.** Three | | |
| **25.** One | **26.** Four | **27.** One | **28.** Six | **29.** Seven | **30.** Six | **31.** Five |
| **32.** Two | **33.** Nine | **34.** Six | **35.** One | **36.** Six | | |
| **37.** Five | | | | | | |

# OBJECTIVE PROBLEMS (One Answer Correct)

1. Four mole of $Cl_2$ undergoes disproportionation involving in all six moles electrons. The No. of mole of $Cl_2$ losing electron and gaining electrons are respectively :
   (a) 1, 3
   (b) 3, 1
   (c) 2, 2
   (d) none of these

2. Number of mole of $K_2Cr_2O_7$ in acidic medium required to oxidise one mole of $Cu_3P$ to $CuSO_4$ and $H_3PO_4$ is :
   (a) 11/6
   (b) 6/11
   (c) 3/5
   (d) 5/3

3. Equivalent mass of $As_2S_5$ in $As_2S_5 + HNO_3 \longrightarrow$ $H_2SO_4 + NO_2 + H_3AsO_4 + H_2O$ is :
   (a) $M/20$
   (b) $M/40$
   (c) $M/10$
   (d) $M/5$

4. 4 mole of $FeC_2O_4$ are oxidised separately by acidified $KMnO_4$ and $K_2Cr_2O_7$. The mole ratio of $KMnO_4$ and $K_2Cr_2O_7$ is :
   (a) 6/5
   (b) 5/6
   (c) 24/5
   (d) $5/2n$

5. Which of the following is not disproportionation reaction?
   (a) $\begin{matrix} CHO \\ | \\ COOH \end{matrix} \xrightarrow{OH^-} \begin{matrix} CH_2OH \\ | \\ COOH \end{matrix} + \begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$
   (b) $KO_2 + H_2O + CO_2 \longrightarrow KHCO_3 + O_2$
   (c) $KClO_3 \longrightarrow KClO_4 + KCl$
   (d) $PbO_2 + H_2O \longrightarrow PbO + H_2O_2$

6. Which of the following is intermolecular redox change?
   (a) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$
   (b) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$
   (c) $2KClO_3 \longrightarrow 2KCl + 3O_2$
   (d) $PbO_2 + H_2O \longrightarrow PbO + H_2O_2$

7. For the reaction : $4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$, which statement is wrong :
   (a) It is disproportionation reaction
   (b) It is intramolecular redox
   (c) $CrO_5$ acts as oxidant and reductant both
   (d) Cr acts as oxidant whereas O acts as reductant

8. In which of the reaction oxygen is not an oxidant :
   (a) $N_2 + \frac{1}{2}O_2 \longrightarrow N_2O$ (b) $C + O_2 \longrightarrow CO_2$
   (c) $F_2 + \frac{1}{2}O_2 \longrightarrow F_2O$ (d) $C + \frac{1}{2}O_2 \longrightarrow CO$

9. The equilibrium : $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$ exist at pH = 4. The concentration of $[CrO_4^{2-}]$ at equilibrium is :
   (a) $4 \times K_c \times [Cr_2O_7^{2-}]$
   (b) $2 \times \sqrt{K_c \cdot [Cr_2O_7^{2-}]}$
   (c) $10^4 \times \sqrt{K_c \times [Cr_2O_7^{2-}]}$
   (d) $10^{-8} \times K_c \times [Cr_2O_7^{2-}]$

10. 1 mole each of $FeC_2O_4$ and $FeSO_4$ is oxidised separately by $1 M$ $KMnO_4$ in acid medium. The volume ratio of $KMnO_4$ used for $FeC_2O_4$ and $FeSO_4$ is :
    (a) 1
    (b) 2
    (c) 3
    (d) 4

11. What is wrong about 6.07% strength $H_2O_2$?
    (a) Its normality is 3.57 $N$
    (b) Its molarity is 1.785 $M$
    (c) Its volume strength is 20 volume
    (d) Volume strength = 5.6 × molarity

12. A 100 mL sample of blackish water was made ammoniacal and the sulphide ion in solution were titrated with 16.50 mL of 0.02000 $M$ $AgNO_3$. The concentration of $H_2S$ in the water in ppm is :
    (a) 5.60
    (b) 560
    (c) 56
    (d) 0.560

13. Titration of $I_2$ produced from 0.1045 g of primary standard $KIO_3$ required 30.72 mL of sodium thiosulphate as shown below:
    $$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$
    $$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$
    The molarity of sodium thiosulphate ion is :
    (a) 0.095
    (b) 0.079
    (c) 0.084
    (d) 0.064

14. The mass of 1 g-equivalent of $V_2O_5$ used in the reaction $Zn + V_2O_5 \longrightarrow ZnO + V$ is : (atomic mass of V $= A$)
    (a) $\frac{A}{5}$
    (b) $\frac{A + 80}{5}$
    (c) $\frac{2A + 80}{5}$
    (d) $\frac{2A + 80}{10}$

15. An element $A$ forms an acidic oxide which with KOH forms a salt isomorphous to $K_2SO_4$. If eq. mass of $A$ is 13, the atomic mass of $A$ is :
    (a) 78
    (b) 80
    (c) 26
    (d) 52

16. Equivalent mass of $Fe_3O_4$ and $Fe_2O_3$ in the change $Fe_3O_4 \longrightarrow Fe_2O_3$ is respectively. $M_1$ and $M_2$ are molar mass of $Fe_3O_4$ and $Fe_2O_3$ respectively :
    (a) $M_1, \frac{3M_2}{2}$
    (b) $\frac{M_1}{3}, \frac{M_2}{2}$
    (c) $\frac{M_1}{2}, \frac{M_2}{3}$
    (d) $M_1, \frac{3M_2}{2}$

17. A definite amount of reducing agent is oxidised by 20 mL of 1 $M$ $KMnO_4$ in acid medium, then the same amount of reducing agent is oxidised t. same state by how many mL of 1 $M$ $KMnO_4$ in neutral medium it self changing to $Mn^{4+}$ state :
    (a) 3 mL
    (b) 33.3 mL
    (c) 12 mL
    (d) 24 mL

**18.** 5 g mixture $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ is completely oxidised by 5.5 mL of 0.1 M $KMnO_4$ in acid medium. The % of $FeSO_4 \cdot 7H_2O$ in mixture is :
(a) 15.29      (b) 3.058
(c) 20.24      (d) 25.29

**19.** The number of mole of $KMnO_4$ that will be needed to react with one mole of sulphite ions in acidic solution is:
(a) 2/5      (b) 3/5
(c) 4/5      (d) 1

**20.** Mole of $H_2O_2$ required for decolorising 1 mole of acidified $KMnO_4$ are :
(a) 1/2      (b) 3/2
(c) 5/2      (d) 7/2

**21.** 2 mole, equimolar mixture of $Na_2C_2O_4$ and $H_2C_2O_4$ required $V_1$ L of 0.1 M $KMnO_4$ in acidic medium for complete oxidation. The same amount of the mixture required $V_2$L of 0.1 M NaOH. The ratio of $V_1$ to $V_2$ is :
(a) 2 : 1      (b) 4 : 5
(c) 5 : 4      (d) 2 : 5

**22.** If $a$ g of $NaHC_2O_4$ is completely reduced by 100 mL of 0.02 M $KMnO_4$ in acid medium and $b$ g of $NaHC_2O_4$ required to neutralise completely 100 mL of 0.2 M NaOH, then :
(a) $a = b$      (b) $2a = b$
(c) $a = 2b$      (d) $b = 4a$

**23.** Ratio of mole of $FeSO_4$ oxidised by equal volume of equimolar $K_2Cr_2O_7$ and $KMnO_4$ solution in acidic medium is :
(a) 6 : 5      (b) 5 : 6
(c) 5 : 3      (d) 3 : 5

**24.** When $BrO_3^-$ ion reacts with $Br^-$ ion in acid medium, $Br_2$ is liberated. The equivalent mass of $Br_2$ in the reaction is :
(a) $\dfrac{5M}{3}$      (b) $\dfrac{3M}{5}$
(c) $\dfrac{4M}{6}$      (d) $\dfrac{5M}{8}$

**25.** In $Fe^{2+}$ vs $MnO_4^-$ titration, $HNO_3$ is not used because it :
(a) oxidises $Mn^{2+}$      (b) reduces $MnO_4^-$
(c) oxidises $Fe^{2+}$      (d) reduces $Fe^{3+}$ formed

**26.** 1 mole of equimolar mixture of $Fe_2(C_2O_4)_3$ and $FeC_2O_4$ requires $X$ mole of $KMnO_4$ in acid medium for complete oxidation. The value of $X$ is :
(a) 0.9      (b) 0.6
(c) 1.2      (d) 0.8

**27.** Number of $MnO_4^-$ ions present in 1 litre of 5 N $KMnO_4$ is :
(a) $N_A$      (b) $5N_A$
(c) $\dfrac{2N_A}{10}$      (d) $\dfrac{5N_A}{10}$

**28.** 1 litre solution of $KIO_3$ of unknown molarity is given to titrate with KI in strong acid medium. 50 mL solution of $KIO_3$ requires 10 mL of 0.1 M KI for complete reduction to $I_2$. The molarity of $KIO_3$ solution is :
(a) $4 \times 10^{-3}$ M      (b) $4 \times 10^{-4}$ M
(c) $4 \times 10^{-5}$ M      (d) $4 \times 10^{-2}$ M

**29.** 10g of $Fe_3O_4$ is oxidised completely by 50 mL of 0.1 M $KMnO_4$ solution. The mass in g of $Fe_2O_3$ in $Fe_3O_4$ is :
(a) 1.8      (b) 8.2
(c) 4.1      (d) 5.9

**30.** How many mole of $KMnO_4$ are needed to oxidise a mixture of 1 mole each of $FeSO_4$, $FeC_2O_4$ and $Fe_2(C_2O_4)_3$ completely in acid medium :
(a) 5      (b) 2
(c) 4      (d) 6

**31.** The anion nitrate is converted into $NH_4^+$ ion. The equivalent mass of $NO_3^-$ is :
(a) 6.20      (b) 7.75
(c) 10.5      (d) 21.0

**32.** If $Cl_2$ is passed into hot NaOH solution, oxidation number of chlorine changes from :
(a) 0 to + 5      (b) 0 to −2
(c) 0 to +1      (d) 0 to +7

**33.** $M$ is the molar mass of $KMnO_4$. The equivalent mass of $KMnO_4$ when it is converted into $K_2MnO_4$ is :
(a) $M$      (b) $M/3$
(c) $M/5$      (d) $M/7$

**34.** The equivalent mass of $MnSO_4$ is half its molar mass when it is converted to :
(a) $Mn_2O_3$      (b) $MnO_2$
(c) $MnO_4^-$      (d) $MnO_4^{2-}$

**35.** The number of mole of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acidic medium is :
(a) $\dfrac{3}{5}$      (b) $\dfrac{2}{5}$
(c) $\dfrac{4}{5}$      (d) 1

**36.** $9 \times 10^{-3}$ mole of $X^{n+}$ are oxidised to $XO_3^-$ by $6 \times 10^{-3}$ mole of $K_2Cr_2O_7$. If atomic mass of $X$ is $A$, then equivalent mass of $X^{n+}$ will be :
(a) $A$      (b) $\dfrac{A}{2}$
(c) $\dfrac{A}{3}$      (d) $\dfrac{A}{4}$

**37.** If molar mass of $AsCl_3$ is 228.5. It is oxidised to $AsCl_5$. The equivalent mass of $AsCl_3$ is :
(a) 228.5      (b) 114.25
(c) 76.16      (d) 57.12

**38.** In the disproportionation : $H_3PO_2 \longrightarrow PH_3 + H_3PO_3$; the $n$ factor of $H_3PO_2$ is :

(a) $\dfrac{3}{4}$   (b) $\dfrac{4}{3}$

(c) $\dfrac{2}{3}$   (d) $\dfrac{3}{2}$

**39.** Number of mole of $KMnO_4$ required for 1 mole of $Hg_2S$ in the reaction :

$Hg_2S + MnO_4^- + H^+ \longrightarrow Hg^{2+} + SO_4^{2-} + Mn^{2+} + H_2O$

are same as required for the change 5 mole of :

(a) $N_2$ to $NO_2$   (b) $C_2H_5OH$ to $CH_3CHO$

(c) $NO$ to $HNO_3$   (d) $NH_3$ to $NO$

**40.** Photosynthesis is a redox reaction *i.e.,*

$$X CO_2 + X H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} (CH_2O)_n + X O_2;$$ which one

is not correct about it :

(a) carbon is reduced and oxygen is oxidised

(b) it may be classified as intermolecular redox reaction

(c) $O_2$ released comes from $H_2O$

(d) equivalent mass of $CO_2$ is 11 and of $H_2O$ is 4.5

**41.** In standardisation of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent mass of $K_2Cr_2O_7$ is : **(IIT 2001)**

(a) $M/2$   (b) $M/6$

(c) $M/6$   (d) $M$

**42.** In alkaline medium, $MnO_4^-$ oxidises $I^-$ to : **(IIT 2004)**

(a) $IO_3^-$   (b) $I_2$

(c) $IO_4^-$   (d) $IO^-$

**43.** Consider a titration of potassium dichromate solution with acidified Mohr's salt. The number of mole of Mohr's salt required per mole of dichromate is : **(IIT 2007)**

(a) 3   (b) 4

(c) 5   (d) 6

**44.** The oxidation number of Mn in the product of alkaline oxidative fusion of $MnO_2$ is : **(IIT 2009)**

(a) 2   (b) 4

(c) 6   (d) 8

## SOLUTIONS (One Answer Correct)

1. (a) $2e + Cl_2 \longrightarrow 2Cl^- \times 3$

   (The lowest oxidation state of Cl is –I)

   $$\dfrac{Cl_2 \longrightarrow 2Cl^{3+} + 6e}{4Cl_2 \longrightarrow 6Cl^- + 2Cl^{3+}}$$

2. (a) $6Cu_3P + 124H^+ + 11Cr_2O_7^{2-} \longrightarrow 18Cu^{2+} +$

   $\qquad\qquad\qquad\qquad 6H_3PO_4 + 22Cr^{3+} + 53H_2O$

3. (b) $(As^{5+})_2 \longrightarrow 2As^{5+}$,     No redox

   $(S^{2-})_5 \longrightarrow 5S^{6+} + 40e$,    $E_{As_2S_5} = M/40$

4. (a) $Fe^{2+} \longrightarrow Fe^{3+} + e$     $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

   $\dfrac{(C^{3+})_2 \longrightarrow 2C^{4+} + 2e \quad (Cr^{6+})_2 + 6e \longrightarrow 2Cr^{3+}}{FeC_2O_4 \longrightarrow Fe^{3+} + 2C^{4+} + 3e}$

   $\therefore$ 4 mole $FeC_2O_4 \equiv \dfrac{12}{5}$ mole $KMnO_4$

   $\qquad\qquad\qquad \equiv 2$ mole $K_2Cr_2O_7$

5. (d) It is intermolecular redox change.

6. (d) —do—

7. (a) $3e + Cr^{6+} \longrightarrow Cr^{3+}$

   $O^{-1} \longrightarrow O_2^0 + 2e$

8. (c) $F_2$ is oxidant and $O_2$ is reductant (0 to +2)

9. (c) $K_c = \dfrac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}]}$

   $\therefore [CrO_4^{2-}] = \sqrt{10^8 \times [Cr_2O_7^{2-}] \times K_c}$

10. (c) $Fe^{2+} + C_2O_4^{2-} \longrightarrow Fe^{3+} + 2CO_2^{4+} + 3e$

    $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

    $Fe^{2+} + SO_4^{2-} \longrightarrow Fe^{3+} + SO_4^{2-} + e$

    Meq. of $FeC_2O_4 =$ Meq. of $KMnO_4$,

    $\qquad 1 \times 3 \times 1000 = 1 \times 5 \times V_1$

    Meq. of $FeSO_4 =$ Meq. of $KMnO_4$

    $\qquad 1 \times 1 \times 1000 = 1 \times 5 \times V_2$

    $\therefore \qquad \dfrac{V_1}{V_2} = 3$

11. (d) 6.07% strength of $H_2O_2$ means 6.07 g $H_2O_2$ in 100 mL solution.

    20 volume $H_2O_2$ means of 1 mL $H_2O_2$ solution gives 20 mL $O_2$

    Also, % strength $= \dfrac{17}{56} \times$ vol. strength;

    volume strength $= 5.6 \times N = 11.2 \times M$

12. (c) Meq. of $H_2S =$ Meq. of $S^{2-} =$ Meq. of $AgNO_3$

    $\qquad\qquad = 16.50 \times 0.02 = 0.33$

    $\dfrac{w}{17} \times 1000 = 0.33 \quad \therefore w_{H_2S} = 5.6 \times 10^{-3}$

    $\therefore$ ppm of $H_2S = \dfrac{5.6 \times 10^{-3} \times 10^6}{10^2} = 56$

13. (a) $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

    $\dfrac{3I_2 + 6S_2O_3^{2-} \longrightarrow 6I^- + 3S_4O_6^{-2}}{IO_3^- + 6S_2O_3^{2-} + 6H^+ \longrightarrow I^- + 3S_4O_6^{2-}}$

    Mole of $KIO_3 = 6$ mole of $S_2O_3^{2-}$

    Mole of $KIO_3 = \dfrac{0.1045}{214} = 4.88 \times 10^{-4}$

    $\therefore$ Mole of $S_2O_3^{2-}$ used $= 4.88 \times 10^{-4} \times 6$

    Mole of $S_2O_3^{2-} = 2.93 \times 10^{-3}$

    $\dfrac{M \times 30.72}{1000} = 2.93 \times 10^{-3}$

    $\therefore \qquad\qquad M = 0.095$

14. (d) $10e + (V^{5+})_2 \longrightarrow 2V^0$

    $\therefore \quad E = \dfrac{M}{10} = \dfrac{2A + 80}{10}$

15. (a) $A \longrightarrow$ oxide of $A \xrightarrow{KOH}$ Isomorph of $K_2SO_4$, *i.e.*,

    $K_2AO_4$

    $\qquad\qquad A^0 \longrightarrow A^{6+} + 6e$

    $\therefore$ atomic mass $=$ eq. mass $\times$ v.f. $= 13 \times 6 = 78$

16. (a) $2(Fe^{8/3+})_3 \longrightarrow 3(Fe^{3+})_2 + 2e$

    $\therefore \quad E_{Fe_3O_4} = \dfrac{M}{1}$ and $E_{Fe_2O_3} = \dfrac{M}{2/3}$

17. (b) $Mn^{7+} + 5e \longrightarrow Mn^{2+}$ (Acid med.)

    $Mn^{7+} + 3e \longrightarrow Mn^{4+}$ (Neutral med.)

    $\therefore$ Meq. of $KMnO_4$ in acid medium

    $\qquad\qquad =$ Meq. of $KMnO_4$ in neutral medium.

    $\qquad 1 \times 5 \times 20 = 1 \times 3 \times V$

    $\therefore \qquad V = 33.3$ mL

18. (a) Meq. of $KMnO_4 =$ Meq. of $FeSO_4 \cdot 7H_2O$

    $5.5 \times 0.1 \times 5 = \dfrac{w}{278} \times 1000$   $(Mn^{7+} + 5e \longrightarrow Mn^{2+})$

    $\therefore \qquad w = 0.7645$      $(Fe^{2+} \longrightarrow Fe^{3+} + 1e)$

    $\therefore$ % of $FeSO_4 \cdot 7H_2O = \dfrac{0.7645}{5} \times 100 = 15.29$

19. (a) $\qquad S^{4+} \longrightarrow S^{6+} + 2e$     $\times 5$

    $Mn^{7+} + 5e \longrightarrow Mn^{2+}$     $\times 2$

20. (c) $Mn^{7+} + 5e \longrightarrow Mn^{2+}$     $\times 2$

    $\qquad (O^{-1})_2 \longrightarrow O_2^0 + 2e$     $\times 5$

21. (d) Let mole of $Na_2C_2O_4$ and $H_2C_2O_4$ be $a, b$ respectively, then $a + b = 2$ and $a = b$ (equimolar)

    Eq. of $Na_2C_2O_4 + H_2C_2O_4 = V_1 \times 0.1 \times 5$

    $\qquad\qquad\qquad\qquad (Mn^{7+} + 5e \longrightarrow Mn^{2+})$

    $2a + 2b = 0.5 V_1$    $(\because a = b)$        ...(i)

    $\therefore \qquad\qquad V_1 = 8$ L

    Eq. of $H_2C_2O_4 = V_2 \times 0.1 \times 1$

    $\qquad\qquad 2b = 0.1 V_2$

$\therefore \qquad V_2 = 20\,L$

$\therefore \qquad \dfrac{V_1}{V_2} = \dfrac{8}{20} = \dfrac{2}{5}$

22. (d) Meq. of $NaHC_2O_4$ = Meq. of $KMnO_4$

$$\dfrac{a \times 2}{M} \times 1000 = 100 \times 0.02 \times 5 = 10$$

Also Meq. of $NaHC_2O_4$ = Meq. of NaOH

$$\dfrac{b \times 1 \times 1000}{M} = 100 \times 0.2 = 20$$

$\therefore \quad \dfrac{2a}{b} = \dfrac{10}{20}$

or $\quad b = 4a$

23. (a) $6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$5e + Mn^{3+} \longrightarrow Mn^{2+}$

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

One mole of $K_2Cr_2O_7$ will oxidise 6 mole $Fe^{2+}$

One mole of $KMnO_4$ will oxidise 5 mole $Fe^{2+}$

24. (b) $10e + 2Br^{5+} \longrightarrow (Br^0)_2$

$\dfrac{2Br^- \longrightarrow (Br^0)_2 + 2a}{2Br^{5+} + 10Br^- \longrightarrow 6Br_2}$

$6$ mole of $Br_2 = 2$ mole $Br^{5+}$

$\qquad\qquad = 10$ eq. $Br^{5+}$

$\qquad\qquad = 10$ eq. $Br_2$

$\therefore \quad 1$ mole $Br_2 = \dfrac{10}{6}$ eq. $Br_2 = \dfrac{5}{3}$ eq. $Br_2$

$\therefore \qquad\qquad n = \dfrac{5}{3}$

$\therefore \qquad\qquad E_{Br_2} = \dfrac{M}{5/3} = \dfrac{3M}{5}$

25. (c) $HNO_3$ will also oxidise $Fe^{2+}$

26. (a) $KMnO_4$ will oxidise $Fe^{2+}$ to $Fe^{3+}$ and $C_2O_4^{2-}$ to $CO_2$

$(C_2^{3+})_3 \longrightarrow 6C^{4+} + 6e$

$(C_2^{3+}) \longrightarrow 2C^{4+} + 2e$

and $\qquad Fe^{2+} \longrightarrow Fe^{3+} + e$

Meq. of $C_2O_4^{2-}$ in $Fe_2(C_2O_4)_3$ + Meq. of $FeC_2O_4$

$\qquad = $ Meq. of $KMnO_4$

$\qquad = X \cdot 5 \qquad$ (Total mole of $FeC_2O_4 = 0.5$ and mole of $Fe_2(C_2O_4)_3 = 0.5$)

$0.5 \times 6 + 0.5 \times 3 = X \cdot 5$

$\therefore \qquad\qquad X = 0.9$

27. (a) $\qquad$ Eq. of $KMnO_4 = 5 \times 1 = 5$

$\therefore \quad$ mole of $KMnO_4 = 1 \qquad$ (mole $\times$ V.f. = Eq.)

28. (a) $10e + 2I^{5+} \longrightarrow (I^0)_2$

$2I^- \longrightarrow (I^0)_2 + 2e$

Meq. of $KIO_3$ = Meq. of $I^-$

$50 \times M \times 5 = 10 \times 0.1 \times 1$

$\therefore \qquad$ Molarity $= \dfrac{1}{250} = 4 \times 10^{-3}$ M

29. (b) Meq. of $Fe^{2+}$ in $Fe_3O_4 = 50 \times 0.1 \times 5 = 25 = $ Meq. of FeO

mm of $Fe^{2+}$ in $Fe_3O_4 = 25 = $ mm of FeO

$\therefore \quad w_{FeO} = \dfrac{25 \times 72}{1000} = 1.8$ g

$\therefore \quad w_{Fe_2O_3} = 10 - 1.8 = 8.2$ g

30. (b) $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

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

$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

$[(C^{3+})_2]_3 \longrightarrow 6C^{4+} + 6e$

Eq. of $KMnO_4$ = Eq. of $FeSO_4$ + Eq. of $FeC_2O_4$ + Eq. of $Fe_2(C_2O_4)_3$

$\qquad = 1 \times 1 + 1 \times 3 + 1 \times 6$

$M \times 5 = 10$

$M = 2$

31. (b) $8e + N^{+5} \longrightarrow N^{-3}$

$\therefore \quad E_{NO_3^-} = \dfrac{62}{8} = 7.75$

32. (a) $Cl_2 + OH^- \longrightarrow ClO_3^- + Cl^-$

33. (a) $Mn^{7+} + e \longrightarrow Mn^{6+}$

$\therefore \quad E = \dfrac{M}{1}$

34. (b) $Mn^{2+} \longrightarrow Mn^{4+} + 2e$

$\therefore \quad E = \dfrac{M}{2}$

35. (a) $\qquad Fe^{2+} \longrightarrow Fe^{3+} + e$

$\dfrac{(C^{3+})_2 \longrightarrow 2C^{4+} + 2e}{FeC_2O_4 \longrightarrow Fe^{3+} + 2C^{4+} + 3e] \times 5}$

$Mn^{7+} + 5e \longrightarrow Mn^{2+}] \times 3$

or 5 mole $FeC_2O_4 \equiv 3$ mole $KMnO_4$

36. (d) $6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$X^{n+} \longrightarrow X^{5+} + (5-n)e$

$\therefore$ Meq of $K_2Cr_2O_7$ = Meq of $X^{+n}$

$6 \times 6 \times 10^{-3} = 9 \times 10^{-3} \times (5-n)$

$\therefore \quad n = 1$

$\therefore \quad X^{1+} \longrightarrow X^{5+} + 4e$

$\therefore$ E of $X^{n+} = \dfrac{A}{4}$

37. (b) $As^{3+} \longrightarrow As^{5+} + 2e$

$\therefore$ Eq. mass $= \dfrac{\text{molar mass}}{2} = \dfrac{228.5}{2} = 114.25$

38. (b) $4e + P^{+1} \longrightarrow P^{-3}$

$\dfrac{P^{+1} \longrightarrow P^{+3} + 2e}{3P^+ \longrightarrow P^{-3} + 2P^{+3}}$

$3H_3PO_2 \longrightarrow PH_3 + 2H_3PO_3$

3 mole $H_3PO_2 = 1$ mole $PH_3$

$\qquad = 4$ eq. $PH_3 = 4$ eq. $H_3PO_2$

$\therefore$ 1 mole $H_3PO_2 = \dfrac{4}{3}$ eq. $H_3PO_2$

or $n$ factor $= \dfrac{4}{3}$

**39.** (b) $(Hg^{+1})_2 \longrightarrow 2Hg^{2+} + 2e$

$\dfrac{S^{-2} \longrightarrow S^{6+} + 8e}{Hg_2S \longrightarrow 2Hg^{2+} + S^{6+} + 10e}$

for (b) $(C^{-2})_2 \longrightarrow (2C^{-1}) + 2e$

$\therefore 5C_2H_5OH \longrightarrow 10CH_3CHO$

$5e + Mn^{7+} \longrightarrow Mn^{2+}$

**40.** (d) $4e + C^{4+} \longrightarrow C^0$

$2(O^{-2}) \longrightarrow O_2^0 + 4e$
(of $H_2O$)

$\therefore$ Equivalent mass of $CO_2 = \dfrac{44}{4} = 11$

and Equivalent mass of $H_2O = \dfrac{18}{2} = 9$

**41.** (b) $6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

$\therefore E = M/6$

**42.** (a) $2MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-$

**43.** (d) $Fe^{2+} \longrightarrow Fe^{3+} + e] \times 6$

$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$

**44.** (c) $2MnO_2 + 4KOH + O_2 \longrightarrow K_2MnO_4 + 2H_2O$

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### Redox Titrations                                                                 **311**

## OBJECTIVE PROBLEMS (More Than One Answer Correct)

**1.** 100 mL of 0.1 $M$ $NaHC_2O_4$ is neutralised by $V_1$ mL of 0.1 $M$ NaOH and $V_2$ mL of a $M$ $KMnO_4$ separately, then for complete neutralisation :

(a) volume of NaOH required = 200 mL

(b) if $M$ of $KMnO_4$ is 0.1 $M$ then $\dfrac{V_1}{V_2} = 5:1$

(c) if $M$ of $KMnO_4$ is 0.1 $M$ then $V_2 = 20$ mL

(d) if $M$ of $KMnO_4$ is 0.2 $M$ then $V_2 = 2$ mL

**2.** A mixture of $Na_2C_2O_4$ and $H_2C_2O_4$ requires 100 mL of 0.1 $M$ $KMnO_4$ for complete neutralisation. The same mixture on neutralisation by a base requires 50 mL of 0.2 $M$ NaOH solution. Which one are correct?

(a) Mole ratio of $Na_2C_2O_4$ and $H_2C_2O_4 = 4:1$

(b) Equivalent ratio of $Na_2C_2O_4$ and $H_2C_2O_4 = 4:1$

(c) Mole of $C_2O_4^{2-}$ in mixture $= 25 \times 10^{-3}$

(d) Mole ratio of $Na_2C_2O_4$ and $H_2C_2O_4 = 1:4$

**3.** Quantitative estimation of $Fe^{2+}$ can be made by $KMnO_4$ in acidified medium. In which medium it can be estimated by $KMnO_4$?

(a) In $H_2SO_4$          (b) In $HNO_3$

(c) In HCl               (d) all of these

**4.** Which are correct about the reaction?

$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$

(a) Eq. mass of $FeS_2$ is $M/11$

(b) Eq. mass of $SO_2 = M/5$

(c) 1 mole of $FeS_2$ requires 7/4 mole of $O_2$

(d) S has $-2$ oxidation state in $FeS_2$

**5.** Which of the following are primary standards?

(a) $As_2O_3$            (b) $H_2C_2O_4$

(c) NaOH                (d) $Na_2CO_3$

**6.** Which of the followings are not valid reactions for iodometric titrations?

(a) $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$

(b) $8HNO_3 + 6I^- \longrightarrow 6NO_3^- + 2NO + 2I_2 + 4H_2O$

(c) $CuSO_4 + 2KI \longrightarrow Cu_2I_2 + I_2 + K_2SO_4$

(d) $Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

**7.** In which of the following reactions $O_2$ is oxidant?

(a) $F_2 + \dfrac{1}{2}O_2 \longrightarrow F_2O$   (b) $3O_3 \longrightarrow 2O_2$

(c) $CO + \dfrac{1}{2}O_2 \longrightarrow CO_2$   (d) $N_2 + O_2 \longrightarrow 2NO$

**8.** Reduction of the metal centre in aqueous permanganate ion involves :                                              **(IIT 2011)**

(a) 3 electrons in neutral medium

(b) 5 electrons in neutral medium

(c) 3 electrons in alkaline medium

(d) 5 electrons in acidic medium

## SOLUTIONS (More Than One Answer Correct)

1. (b, c)  Meq. of $NaHC_2O_4 = 100 \times 0.1 = 10$

   Meq. of NaOH required $= 10 = V_1 \times 0.1 \times 1$

   (v.f. of NaOH $= 1$)

   $V_1 = 100$ mL

   Meq. of $KMnO_4$ required $= 10 = V_2 \times a \times 5$

   (v.f. of $KMnO_4 = 5$)

   $\therefore \quad V_2 = \dfrac{10}{5a} \quad \therefore \quad \dfrac{V_1}{V_2} = \dfrac{100 \times 5a}{10}$

   if $M_{KMnO_4} = 0.1M$, then $10 = V_2 \times 0.1 \times 5$

   $\therefore \qquad\qquad V_2 = 20$ mL

2. (a,b,c)  Meq. of $KMnO_4 = 100 \times 0.1 \times 5 = 50$

   $= $ Meq. of $Na_2C_2O_4 + $ Meq. of $H_2C_2O_4$

   $\qquad\qquad\qquad\quad a \qquad + \qquad b$

   $\therefore \qquad\qquad a + b = 50$

   Meq. of NaOH $= 50 \times 0.2 = 10 = $ Meq. of $H_2C_2O_4$

   $\therefore \qquad\qquad b = 10$

   $\therefore \qquad\qquad a = 40$

   milli mole of $Na_2C_2O_4 = \dfrac{a}{2}$

   $\therefore$  milli mole of $C_2O_4 = \dfrac{a}{2} + \dfrac{b}{2} = \dfrac{a+b}{2} = \dfrac{40+10}{2} = 25$

   milli mole of $H_2C_2O_4 = \dfrac{b}{2}$

3. (a)  $HNO_3$ also oxidises $Fe^{2+}$ whereas $KMnO_4$ oxidises HCl.

4. (a,b,c)  $2Fe^{2+} \longrightarrow (Fe^{3+})_2 + 2e$
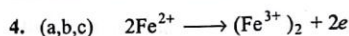
   Eq. mass of $FeS_2 = \dfrac{M}{22/2} = \dfrac{M}{11}$

   $2(S^{-1})_2 \longrightarrow 4(S^{4+}) + 20e$

   Eq. mass of $SO_2 = \dfrac{M}{20/4} = \dfrac{M}{5}$

   $\therefore \quad 4e + O_2^0 \longrightarrow 2(O^{-2})$

   $\therefore \quad 4 FeS_2 + 7O_2 \longrightarrow 2Fe_2O_3$
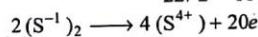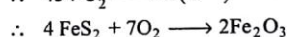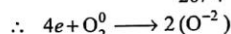
   S has $-1$ oxidation state.

5. (a,b)  Primary standard solutions are those whose solution of exact normality can be prepared by weighing desired amount of its pure sample.

6. (b)  In strong acidic medium either I produced in reaction tend to be oxidised to $I^-$ or starch used to detect end point is decomposed and hydrolysed.

7. (c,d)  In the reaction of $F_2$ and $O_2$, $F_2$ is oxidant.

8. (a,c,d)

   In acidic medium : $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

   In neutral medium : $Mn^{7+} + 3e \longrightarrow Mn^{4+}$

   In alkaline solution : $Mn^{7+} + e \longrightarrow Mn^{6+}$

   Note that in **alkaline medium**, $Mn^{6+}$ is further reduced to $Mn^{4+}$

   $\qquad\qquad Mn^{6+} + 2e \longrightarrow Mn^{4+}$

   Thus over all reaction may give

   $\qquad\qquad Mn^{7+} + 3e \longrightarrow Mn^{4+}$

# COMPREHENSION BASED PROBLEMS

**Comprehension 1:** Estimation of $CuSO_4$ is made by iodometric titrations. In a given titration $CuSO_4$ reacts with KI in acidic medium to liberate $I_2$.

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

Mercuric per iodate $Hg_5(IO_6)_2$ reacts with a mixture of KI and HCl following the equation:

$$Hg_5(IO_6)_2 + 34KI + 24HCl \longrightarrow$$
$$5K_2HgI_4 + 8I_2 + 24KCl + 12H_2O$$

The liberated iodine is titrated against $Na_2S_2O_3$ solution. One mL of which is equivalent to 0.0499 g of $CuSO_4 \cdot 5H_2O$. Molar mass of $Hg_5(IO_6)_2 = 1448.5$ and molar mass of $CuSO_4 \cdot 5H_2O = 249.5$.

**[1]** Equivalent mass of $CuSO_4 \cdot 5H_2O$ is :

(a) $\dfrac{M}{2}$      (b) $\dfrac{M}{1}$

(c) $\dfrac{M}{3}$      (d) $M$

**[2]** The reaction of $Na_2S_2O_3$ and $I_2$ gives oxidation product as:

(a) $I^-$      (b) $S_2O_3^{2-}$

(c) $S_4O_6^{2-}$      (d) $SO_4^{2-}$

**[3]** Volume in mL of $Na_2S_2O_3$ solution will be required to react with $I_2$ liberated from 0.76245 g of $Hg_5(IO_6)_2$ :

(a) 40 mL      (b) 10 mL

(c) 20 mL      (d) 30 mL

**Comprehension 2:** 2.5 g sample of copper is dissolved in excess of $H_2SO_4$ to prepare 100 mL of 0.02 $M$ $CuSO_4$ (aq.). 10 mL of 0.02 $M$ solution of $CuSO_4$ (aq.) is mixed with excess of KI to show the following changes.

$$CuSO_4 + 2KI \longrightarrow K_2SO_4 + CuI_2$$
$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

The liberated iodine is titrated with hypo ($Na_2S_2O_3$) and requires $V$ mL of 0.1 $M$ hypo solution for its complete reduction.

**[1]** The volume ($V$) of hypo required is :

(a) 2 mL      (b) 20 mL

(c) 1 mL      (d) 10 mL

**[2]** Percentage of purity of sample is :

(a) 10.16      (b) 5.08

(c) 2.54      (d) 1.27

**[3]** The mass of $I_2$ liberated in the reaction of 10 mL of 0.02 $M$ solution with $KI_{excess}$ is :

(a) 0.051 g      (b) 0.0254 g

(c) 0.102 g      (d) 0.204 g

**[4]** The colour of solution developed during addition of KI $CuSO_4$ is :

(a) violet due to dissolution of liberated $I_2$

(b) brownish yellow due to dissolution of liberated $I_2$

(c) red due to the formation of $CuI_2$

(d) brown due to the formation of $Cu_2I_2$

**[5]** Select the correct statement :

1. The reaction belongs to iodometric titration
2. The reaction belongs to iodimetric titration
3. $Cu_2I_2$ formed during the reaction is white
4. Starch is used as indicator in this titration

(a) 1, 3, 4      (b) 2, 3, 4

(c) 1, 3      (d) 2, 3

**Comprehension 3:** $K_2Cr_2O_7$ acts as a good oxidizing agent in acidic medium.

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

In alkaline solution, orange colour of $Cr_2O_7^{2-}$ changes to yellow colour due to formation of $CrO_4^{2-}$ and again yellow colour changes to orange colour on changing the solution to acidic medium.

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{Orange}}{2Cr_2O_7^{2-}} + H_2O$$

$CrO_4^{2-}$ and $Cr_2O_7^{2-}$ exist in equilibrium at pH = 4 and are interconvertible by altering the pH of the solution. When heated with $H_2SO_4$ and metal chloride, $K_2Cr_2O_7$ gives vapours of chromyl chloride ($CrO_2Cl_2$). Chromyl chloride ($CrO_2Cl_2$) when passed into aqueous NaOH solution, yellow colour solution of $CrO_4^{2-}$ is obtained. This on reaction with lead acetate gives yellow ppt. of $PbCrO_4$.

When $H_2O_2$ is added to an acidified solution of dichromate ion, a complicated reaction occurs. The products obtained depend on the pH and concentration of Cr.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO(O_2)_2 + 5H_2O$$

A deep blue-violet coloured peroxo compound, $CrO(O_2)_2$, called chromic peroxide is formed. This decomposes rapidly in aqueous solution into $Cr^{3+}$ and oxygen.

**[1]** What happens when a solution of potassium chromate is treated with an excess of dilute nitric acid?

(a) $Cr^{3+}$ and $Cr_2O_7^{2-}$ are formed

(b) $Cr_2O_7^{2-}$ and $H_2O$ are formed

(c) $CrO_4^{2-}$ is reduced to +3 state of Cr

(d) $CrO_4^{2-}$ is reduced to 0 state of Cr

**[2]** Which of the following statement is wrong when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. $H_2SO_4$?

(a) A deep red vapour is evolved

(b) The vapour when passed through NaOH solution gives a yellow solution of $Na_2CrO_4$
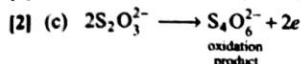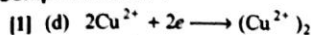
(c) Chlorine gas is formed

(d) Chromyl chloride is formed

[3] The $CrO_3$ on reaction with HCl and NaOH($aq.$) gives respectively:

(a) $CrO_2Cl_2, CrO_4^{2-}$     (b) $Cr(OH)_2, CrO_4^{2-}$

(c) $Cl_2, Cr_2O_7^{2-}$     (d) $Cl_2, Cr(OH)_3$

[4] Number of mole of $K_2Cr_2O_7$ reduced by one mole of $Sn^{2+}$ ions in acidic medium is :

(a) $\frac{1}{3}$     (b) 3

(c) $\frac{1}{6}$     (d) 6

[5] The equivalent mass of barium in $BaCrO_4$ used as an oxidizing agent in acidic medium is (atomic mass of Ba = 137.34 and Cr = 52)

(a) 137.34     (b) 85.78

(c) 114.45     (d) 68.67

[6] The equivalent mass of $KIO_3$ in the reaction

$$2Cr(OH)_3 + OH^- + KIO_3 \longrightarrow 2CrO_4^{2-} + KI + 5H_2O$$

(a) Molar mass     (b) $\frac{M}{3}$

(c) $\frac{M}{6}$     (d) $\frac{M}{2}$

[7] When $H_2O_2$ is added to an acidified solution of $K_2Cr_2O_7$, then :

(a) solution turns green due to formation of $Cr_2O_3$ and reduction of Cr takes place

(b) solution turns blue due to formation of $CrO(O_2)_2$ and no redox change

(c) a deep blue-violet coloured compound $CrO(O_2)_2$ due to reduction of Cr

(d) solution gives green ppt. $CrO(O_2)_2$ due to oxidation of Cr

[8] The colour of $Cu_2Cr_2O_7$ solution in water is :

(a) green     (b) blue

(c) orange     (d) black

[9] Which statement about $CrO_5$ is wrong?

(a) Oxidation number of Cr in $CrO_5$ is +6

(b) $CrO_5$ has butterfly structure

(c) It has one oxygen atom attached with double bond with Cr and four oxygen atoms attached with single bond with chromium

(d) It has four peroxide bond

[10] The $[CrO_4^{2-}]$ ions at equilibrium for the reaction

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+ \text{ at pH} = 4 \text{ is :}$$

(a) $10^{-4} [Cr_2O_7^{2-}] \cdot K_C$

(b) $10^{-8} [Cr_2O_7^{2-}] \cdot K_C$

(c) $10^{+4} [(Cr_2O_7^{2-}) \cdot K_C]^{1/2}$

(d) $10^{-4} [Cr_2O_7^{2-}]^{1/2} \cdot K_C$

**Comprehension 4 :** Redox changes are of three types. These includes, intermolecular redox reaction, intramolecular redox reactions and disproportionation.

The equivalent mass '$E$' of reductant or oxidant is given by the expression :

$$E_{red/oxi} = \frac{\text{Molar mass of reductant or oxidant}}{\text{Number of electron lost or gained by 1 molecule of reductant or oxidant}}$$

[1] The equivalent mass of cyanogen $(CN)_2$ in the redox change is :

$$(CN)_2 + H_2O \longrightarrow HCN + HOCN$$

(a) $\frac{M}{2}$     (b) $M$

(c) $\frac{M}{3}$     (d) $\frac{M}{24}$

[2] The equivalent mass of $KClO_3$ in the redox reaction is :

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

(a) $\frac{M}{6}$     (b) $\frac{M}{2}$

(c) $\frac{M}{3}$     (d) $\frac{M}{5}$

[3] The equivalent mass of $Fe_2(C_2O_4)_3$ in the redox reaction is :

$$5Fe_2(C_2O_4)_3 + 6KMnO_4 + 24H_2SO_4 \longrightarrow$$
$$5Fe_2(SO_4)_3 + 6MnSO_4 + 30CO_2 + 24H_2O$$

(a) $\frac{M}{2}$     (b) $\frac{M}{6}$

(c) $\frac{M}{3}$     (d) $\frac{M}{4}$

**Comprehension 5 :** Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry.                    (IIT 2012)

[1] Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is :

(a) $Cl_2O$     (b) $Cl_2O_7$

(c) $ClO_2$     (d) $Cl_2O_6$

[2] 25 mL of household bleach solution was mixed with 30 mL of 0.50 $M$ KI and 10 mL of 4 $N$ acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 $N$ $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is :

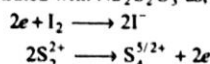(a) 0.48 $M$     (b) 0.96 $M$

(c) 0.24 $M$     (d) 0.024 $M$

**═══ SOLUTIONS ═══**

## Comprehension 1

[1] (d) $2Cu^{2+} + 2e \longrightarrow (Cu^{2+})_2$

[2] (c) $2S_2O_3^{2-} \longrightarrow \underset{\substack{\text{oxidation} \\ \text{product}}}{S_4O_6^{2-}} + 2e$

[3] (a) $\because$ 1 mole $Hg_5(IO_6)_2$ or 1448.5 g gives = 8 mole $I_2$

$\therefore$ 0.7245 g $Hg_5(IO_6)_2$ will give

$= \dfrac{8 \times 0.7245}{1448.5}$ mole $I_2$

$= 4.0 \times 10^{-3}$ mole $I_2$

This $I_2$ is titrated with $Na_2S_2O_3$ as,

$2e + I_2 \longrightarrow 2I^-$

$2S_2^{2+} \longrightarrow S_4^{5/2+} + 2e$

Meq. of $Na_2S_2O_3$ = Meq. of $I_2 = 4 \times 10^{-3} \times 10^3 \times 2 = 8$

Meq. of $Na_2S_2O_3$ in one mL = Meq. of $CuSO_4$

$= \dfrac{0.0499}{249/1} \times 1000 = 0.20$

$\therefore \quad 0.20 \times V = 8 \quad \therefore \quad V = 40$ mL

## Comprehension 2

[1] (a) The reactions are :

$2(Cu^{2+}) + 2e \longrightarrow (Cu^+)_2, E = \dfrac{M}{1}$

$2(I^{-1}) \longrightarrow I_2 + 2e, E_{I^-} = \dfrac{M}{1}$

$2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e,$
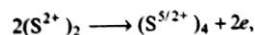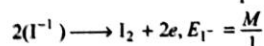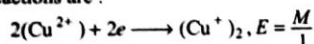
$E_{Na_2S_2O_3} = \dfrac{M}{1}$

Meq. of $CuSO_4$ = Meq. of $Na_2S_2O_3$

= Meq. of $I_2$ liberated

$10 \times 0.02 \times 1 = V \times 0.1 \times 1$

$\therefore \qquad V = 2$ mL

[2] (b) Meq. of $CuSO_4$ in 100 mL $= 100 \times 0.02 = 2$

$\therefore \quad w_{CuSO_4} = \dfrac{2 \times 249.6}{1000} = 0.499$ g

$\therefore \quad w_{Cu} = \dfrac{0.499 \times 63.6}{249.6} = 0.127$ g

$\therefore \quad \%$ of Cu $= \dfrac{0.127}{2.5} \times 100 = 5.08$
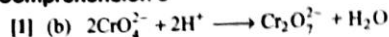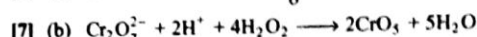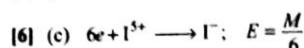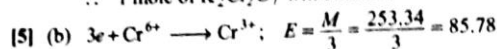
[3] (b) Eq. of $I_2$ = Eq. of $CuSO_4$

$= \dfrac{10 \times 0.02}{1000} = 2 \times 10^{-4}$

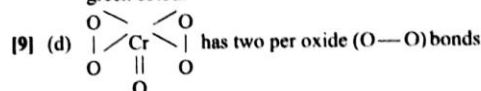$\therefore \qquad \dfrac{w}{254/2} = 2 \times 10^{-4}$

$\therefore \qquad w_{I_2} = 0.0254$ g

[4] (b) Liberated iodine on dissolution in solution of $Cu_2I_2$ and KI develops brown colour.

[5] (a) If $I_2$ is used as intermediate, the process is iodometric.

## Comprehension 3

[1] (b) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

[2] (c) $4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow$
$\qquad 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O$

[3] (a) $CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O$

$CrO_3 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O$

[4] (a) $[Sn^{2+} \longrightarrow Sn^{4+} + 2e] \times 3$

$6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$
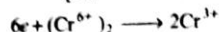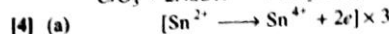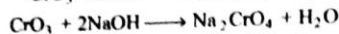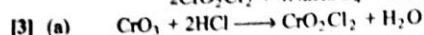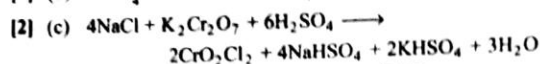
$\therefore$ 1 mole of $K_2Cr_2O_7$ will oxidise 3 mole of $Sn^{2+}$

[5] (b) $3e + Cr^{6+} \longrightarrow Cr^{3+}$; $E = \dfrac{M}{3} = \dfrac{253.34}{3} = 85.78$

[6] (c) $6e + I^{5+} \longrightarrow I^-$; $E = \dfrac{M}{6}$

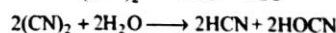[7] (b) $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow 2CrO_5 + 5H_2O$

(Not a redox change)

[8] (a) $Cu^{2+}$ ions are blue and $Cr_2O_7^{2-}$ ions are orange to give green colour

[9] (d) $\underset{O}{\overset{O}{\underset{\|}{\overset{\diagdown}{\underset{|}{\phantom{x}}}}}} \overset{\diagup O}{\underset{Cr}{\diagdown}} \overset{\phantom{x}}{\underset{O}{\overset{\diagup O}{|}}}$ has two per oxide (O—O) bonds

[10] (c) $K_C = \dfrac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}]}$

$\therefore \quad [CrO_4^{2-}]^2 = \dfrac{[Cr_2O_7^{2-}] \times K_C}{[H^+]^2} = \dfrac{K_C[Cr_2O_7^{2-}]}{(10^{-4})^2}$

$= 10^4 [K_C \cdot Cr_2O_7^{2-}]^{1/2}$

## Comprehension 4

[1] (b) $2e + (C^{3+})_2 \longrightarrow 2C^{2+}$

$\dfrac{(C^{3+})_2 \longrightarrow 2C^{4+} + 2e}{(C^{3+})_2 \longrightarrow 2C^{2+} + 2C^{4+}}$

$2(CN)_2 + 2H_2O \longrightarrow 2HCN + 2HOCN$

2 mole $(CN)_2$ = 2 mole HCN

$= 2 \times 1$ eq. HCN $\qquad$ (V.f. for HCN = 1)

$= 2$ eq. $(CN)_2$

$\therefore$ 1 mole of $(CN)_2 = 1$ eq. $(CN)_2$

or V.f. for $(CN)_2 = 1$

$\therefore E = M$

[2] (a) $6e + Cl^{5+} \longrightarrow Cl^{-1}$

$\dfrac{2(O^{-2})_3 \longrightarrow 3(O_2^0) + 12e}{\therefore \quad 2KClO_3 \longrightarrow 2KCl + 3O_2}$

2 mole $KClO_3 = 2$ mole KCl
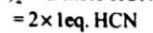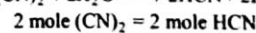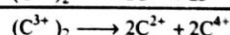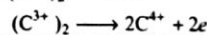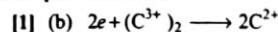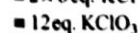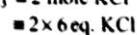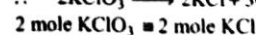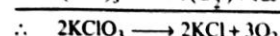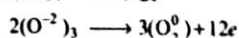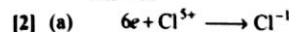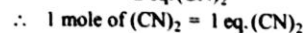
$= 2 \times 6$ eq. KCl

$= 12$ eq. $KClO_3$

$\therefore$ 1 mole $KClO_3 \equiv 6$ eq. $KClO_3$

$\therefore$ v.f. for $KClO_3 \equiv 6$

$\therefore \qquad E_{KClO_3} = \dfrac{M}{6}$

[3] (b) $(C_2^{3+})_3 \longrightarrow 6C^{4+} + 6e$

$\qquad \underline{Mn^{7+} + 5e \longrightarrow Mn^{2+}}$

$\therefore 5Fe_2(C_2O_4)_3 + 6KMnO_4 + 24H_2SO_4 \longrightarrow$

$\qquad\qquad 5Fe_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$
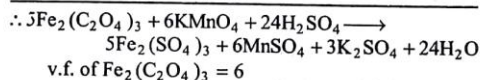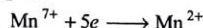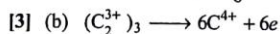
v.f. of $Fe_2(C_2O_4)_3 = 6$

**Comprehension 5**

13. (a) $\underset{\text{(Bleaching powder)}}{Ca(OCl)Cl} \longrightarrow Ca^{2+} + \bar{O}Cl + Cl^-$
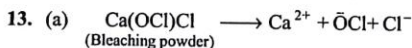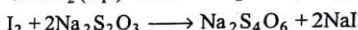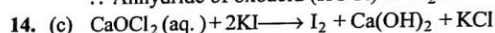
Thus bleaching powder contains $OCl^-$ *i.e.*, part of oxoacid $HOCl$ and $Cl^-$ *i.e.*, part of $HCl$.

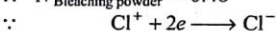Oxidation no. of Cl in oxoacid = +1.

Thus, oxide of Cl with same ox. no. is $Cl_2O$

$\therefore$ Anhydride of oxoacid (HOCl) is $Cl_2O$.

14. (c) $CaOCl_2(aq.) + 2KI \longrightarrow I_2 + Ca(OH)_2 + KCl$

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

Thus Meq. of $Na_2S_2O_3$ used = Meq. of $I_2$ formed

$\qquad\qquad\qquad\qquad$ = Meq. of bleaching powder

or $\qquad 48 \times 0.25 =$ Meq. of bleaching powder $= N \times 25$

$\therefore \quad N_{\text{Bleaching powder}} = 0.48$

$\because \qquad\qquad Cl^+ + 2e \longrightarrow Cl^-$

Thus, *n*-factor for bleaching powder = 2

$\therefore \quad M_{\text{Bleaching powder}} = \dfrac{0.48}{2} = 0.24$

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## ▲▲ STATEMENT EXPLANATION PROBLEMS ▲

Read the statements (S) and explanations (E) given below. Choose the correct choices a, b, c and d from the options

(a) S is correct but E is wrong

(b) S is wrong but E is correct

(c) Both S and E are correct and E is correct explanation of S

(d) Both S and E are correct but E is not correct explanation of S

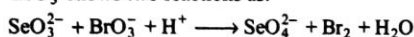1. **S :** The equivalent mass of NaCN in its conversion to NaOCN by $KMnO_4$ is $M/2$

    **E :** The reaction is : $C^{2+} \longrightarrow C^{4+} + 2e$
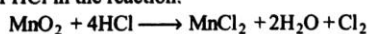
2. **S :** The $I_3^-$ reacts with $H_3AsO_3$ as:

    $H_3AsO_3 + KI_3 + H_2O \longrightarrow H_3AsO_4 + KI + 2HI$
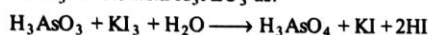
    **E :** Equivalent mass of $KI_3 = 210$.

3. **S :** $BrO_3^-$ shows two reactions as:

    $SeO_3^{2-} + BrO_3^- + H^+ \longrightarrow SeO_4^{2-} + Br_2 + H_2O$

    $AsO_2^{2-} + BrO_3^- + H^+ \longrightarrow Br^- + AsO_4^- + H_2O$
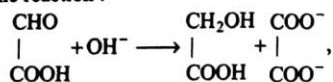
    **E :** The ratio of equivalent mass of $BrO_3^-$ in two reactions is 5/6.

4. **S :** One equivalent of $MnO_2$ reacts with 2 equivalent of HCl in the reaction:

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

    **E :** One equivalent of $MnO_2$ reacts with one equivalent of HCl.

5. **S :** The reaction :

    $\begin{array}{l} CHO \\ | \\ COOH \end{array} + OH^- \longrightarrow \begin{array}{l} CH_2OH \\ | \\ COOH \end{array} + \begin{array}{l} COO^- \\ | \\ COO^- \end{array},$
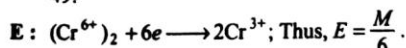
    is Cannizzaro's reaction.

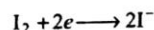    **E :** This is an example of disproportionation reaction.

6. **S :** In acidic medium, equivalent mass of $K_2Cr_2O_7$ is 49.

    **E :** $(Cr^{6+})_2 + 6e \longrightarrow 2Cr^{3+}$; Thus, $E = \dfrac{M}{6}$.

7. **S :** Iodimetric titration are redox titrations.

    **E :** The iodine solution acts as an oxidant to reduce the reductant.

    $I_2 + 2e \longrightarrow 2I^-$

8. **S :** The redox titrations in which liberated $I_2$ is used as oxidant are called as iodometric titration.

    **E :** Addition of KI of $CuSO_4$ liberates $I_2$ which is estimated against hypo solution.

9. **S :** $KMnO_4$ acts as oxidant as well as self indicator in its titration with ferrous ammonium sulphate solution in acidic medium.

    **E :** $KMnO_4$ reduces itself to $Mn^{2+}$ ions and oxidises $Fe^{2+}$ to $Fe^{3+}$ as well as after redox reaction is complete, the $KMnO_4$ at the equivalence point imparts pink colour.

10. **S :** The equivalence point refers the condition where equivalents of one species react with same number of equivalent of other species.

    **E :** The end point of titration is exactly equal to equivalence point.

11. **S :** The equivalent mass of $KMnO_4$ when it is converted to $K_2MnO_4$ is equal to its molar mass.

    **E :** $Mn^{7+} + e \longrightarrow Mn^{6+} \quad \therefore \quad E = \dfrac{M}{1}$
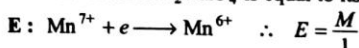
12. **S :** The number of equivalent per mole of $H_2S$ used in its oxidation to $SO_2$ is six.

    **E :** $S^{2-} \longrightarrow S^{4+} + 6 \quad \therefore$ Equivalent = Mole $\times$ 6.
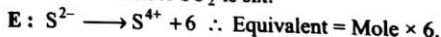
13. **S :** Starch is generally used as absorption indicator in iodometric or iodimetric titrations.

    **E :** Starch imparts blue colour with iodine.

14. **S :** The colour of $KMnO_4$ discharges slowly in the beginning by the oxalic acid but fastens after sometime.

    **E :** The $Mn^{2+}$ ion act as auto catalyst for the reaction.

15. **S :** $KMnO_4$ has different equivalent mass in acid, neutral or alkaline medium.

    **E :** In different medium change in oxidation number shown by manganese is altogether different.

## ANSWERS (Statement Explanation Problems)

1. (c) $E = M/2$

2. (c) $E = M/2$ because $2e + (I^{-1/3})_3 \longrightarrow 3I^-$.

3. (a) (i) $\quad E_{BrO_3^-} = \dfrac{M}{5}$

　　(ii) $\quad E_{BrO_3^-} = \dfrac{M}{6}$

$$10e + 2Br^{5+} \longrightarrow Br^0;$$
$$6e + Br^{5+} \longrightarrow Br^{-1}$$

$$\therefore \quad \text{Ratio} = \dfrac{6}{5}$$

4. (a) 1 mole $MnO_2 \equiv 4$ mole HCl

$$2 \text{ eq. } MnO_2 \equiv 4 \text{ eq. HCl}$$

5. (c) Both are facts.

6. (c) One mole of $K_2Cr_2O_7$ shows a change of six N electrons.

7. (c) The electrons liberated during oxidation of species are used by $I_2$ to get itself reduced.

8. (c) $\quad 2KI + CuSO_4 \longrightarrow CuI_2 + K_2SO_4$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$
$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

9. (c) The explanation is correct reason of the statement.

10. (a) The equivalent point is nearly same but not exactly same to end point. However for all practical purposes the two are taken same.

11. (c) One mole of $KMnO_4$ shows a change of N electrons.

12. (c) Equivalent = Mole × valence factor.

13. (c) The explanation is correct reason of the statement.

14. (c) $KMnO_4$ is reduced to $MnO_2$ by oxalic acid. The redox change is catalysed by $Mn^{2+}$ ions *i.e.*, autocatalysis.

15. (c) $5e + Mn^{7+} \longrightarrow Mn^{2+}$ (Acidic)

$$3e + Mn^{7+} \longrightarrow Mn^{4+} \text{ (Alkaline or neutral)}$$
$$1e + Mn^{7+} \longrightarrow Mn^{6+} \text{ (Neutral or alkaline)}$$

# MATCHING TYPE PROBLEMS

## Type I : Only one match is possible

**1.**

| Half Reactions | | *n*-factor of reactant |
|---|---|---|
| A. | $Bi_2S_3 \rightarrow Bi^{5+} + S$ | (a) 6 |
| B. | $FeS_2 \rightarrow Fe^{3+} + 2SO_2$ | (b) 10 |
| C. | $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3$ | (c) 11 |
| D. | $Al_2(Cr_2O_7)_3 \rightarrow Al^{3+} + Cr^{3+}$ | (d) 18 |

**2.**

| Reaction | | *n*-factor of reactant |
|---|---|---|
| A. | $Fe_3O_4 \rightarrow Fe_2O_3$ | (a) 4/3 |
| B. | $Fe_2O_3 \rightarrow Fe_3O_4$ | (b) 2/3 |
| C. | $P_2H_4 \rightarrow PH_3 + P_4H_2$ | (c) 1 |
| D. | $H_3PO_2 \rightarrow PH_3 + H_3PO_3$ | (d) 5/3 |
| E. | $I_2 \rightarrow I^- + IO_3^-$ | (e) 6/5 |

## Type II : More than one match are possible

**3.**

| Titration | | Reagents |
|---|---|---|
| A. | Iodimetric | (a) $AgNO_3$ *vs.* $KCl$ |
| B. | Iodometric | (b) $N_2H_4$ *vs.* $I_2$ |
| C. | Redox | (c) $CuSO_4$ *vs.* $KI$ |
| D. | Acid-Base | (d) $H_2C_2O_4$ *vs.* $KMnO_4$ |
| E. | Precipitation | (e) $H_2C_2O_4$ *vs.* $NaOH$ |

**4.**

| Reaction | | Equivalent mass of reactant |
|---|---|---|
| A. | $Fe(SCN)_2 \rightarrow$ $Fe^{3+} + SO_4^{2-} + CO_3^{2-} + NO_3^-$ | (a) $\dfrac{M}{28}$ |
| B. | $As_2S_3 \rightarrow As^{5+} + SO_4^{2-}$ | (b) $\dfrac{M}{33}$ |
| C. | $CrI_3 \rightarrow Cr_2^{6+} + I^{5+}$ | (c) $\dfrac{M}{27}$ |
| D. | $CrI_3 \rightarrow Cr_2^{6+} + I^{7+}$ | (d) $\dfrac{M}{21}$ |
| E. | $CrI_3 \rightarrow Cr^{6+} + I^{7+}$ | |

## Type III : Only one match from each list

**5.**

| List A | List B | List C |
|---|---|---|
| A. $CH_4$ | (i) $E = M/8$ | (a) $C^{2+} \rightarrow C^{4+}$ |
| B. $CO$ | (ii) $E = M/2$ | (b) $C^{4-} \rightarrow C^{4+}$ |
| C. $C_2O_4^{2-}$ | (iii) $E = M/12$ | (c) $C^{3+} \rightarrow C^{4+}$ |
| D. $C_2H_4$ | | (d) $C^{2-} \rightarrow C^{4+}$ |

**6.**

| Redox change | Equivalent mass | Number of electrons involved in change |
|---|---|---|
| A. $MnO_2 \rightarrow Mn_2O_3$ | i. $E_{MnO_2} = M/2$ | (a) 4 |
| B. $MnO_2 \rightarrow MnSO_4$ | ii. $E_{MnO_2} = M/4$ | (b) 2 |
| C. $MnO_2 \rightarrow Mn$ | iii. $E_{MnO_2} = M/1$ | (c) 3 |
| D. $KMnO_4 \rightarrow Mn_2O_3$ | iv. $E_{MnO_4} = M/4$ | (d) 8 |
| E. $KMnO_4 \rightarrow MnO_2$ | v. $E_{MnO_4} = M/3$ | |

# ANSWERS

1. A–b;  B–c;  C–a;  D–d
2. A–c;  B–b;  C–e;  D–a; E–d
3. A–b;  B–c;  C–b,c,d;  D–e;  E–a

4. A–b;  B–a, d;  C–c, d; D–c;  E–c
5. A–i–b;  B–ii–a;  C–ii–c;  D–iii–d
6. A–iii–b;  B–i–b;  C–ii–a;  D–iv–d;  E–v–c