

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

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

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

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:

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

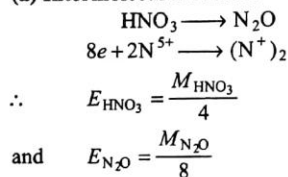
This equation gives mass of substance whose Eq. mass is substituted.

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.

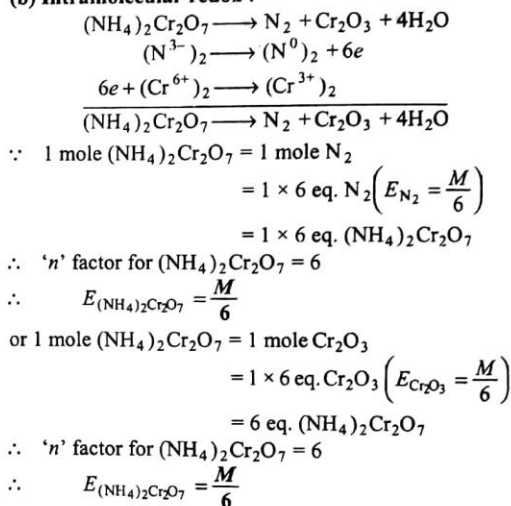
5. In case balanced equation is given, it is always advised to proceed with mole concept to avoid complications in equivalent mass determination.

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

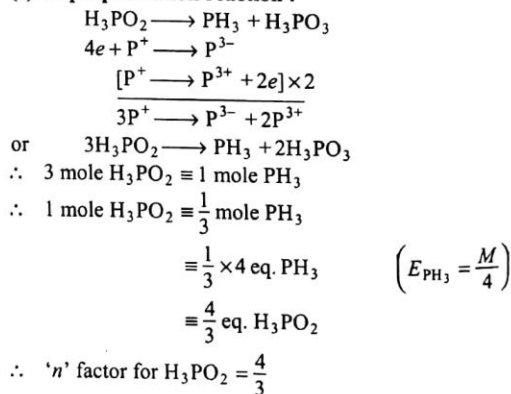
(a) Intermolecular redox :



(b) Intramolecular redox :



(c) Disproportionation reaction :



$$\begin{aligned} \therefore E_{\text{H}_3\text{PO}_2} &= \frac{M}{4/3} = \frac{3M}{4} \\ \text{or } 3 \text{ mole H}_3\text{PO}_2 &\equiv 2 \text{ mole H}_3\text{PO}_3 \\ \text{or } 1 \text{ mole H}_3\text{PO}_2 &\equiv \frac{2}{3} \text{ mole H}_3\text{PO}_3 \\ &\equiv \frac{2}{3} \times 2 \text{ eq. H}_3\text{PO}_3 \quad \left(E_{\text{H}_3\text{PO}_3} = \frac{M}{2} \right) \end{aligned}$$

$$\begin{aligned} &\equiv \frac{4}{3} \text{ eq. H}_3\text{PO}_2 \\ \therefore \text{'n' factor for H}_3\text{PO}_2 &= \frac{4}{3} \\ \therefore E_{\text{H}_3\text{PO}_2} &= \frac{M}{4/3} = \frac{3M}{4} \end{aligned}$$

● NUMERICAL PROBLEMS ●

- Calculate the equivalent mass of each oxidant and reductant in:
 - $\text{FeSO}_4 + \text{KClO}_3 \longrightarrow \text{KCl} + \text{Fe}_2(\text{SO}_4)_3$
 - $\text{Na}_2\text{SO}_3 + \text{Na}_2\text{CrO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{Cr}(\text{OH})_3$
 - $\text{Fe}_3\text{O}_4 + \text{KMnO}_4 \longrightarrow \text{Fe}_2\text{O}_3 + \text{MnO}_2$
 - $\text{KI} + \text{K}_2\text{Cr}_2\text{O}_7 \longrightarrow \text{Cr}^{3+} + 3\text{I}_2$
 - $\text{Mn}^{4+} \longrightarrow \text{Mn}^{2+}$
 - $\text{NO}_3^- \longrightarrow \text{N}_2$
 - $\text{N}_2 \longrightarrow \text{NH}_3$
 - $\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$
 - $\text{FeC}_2\text{O}_4 \longrightarrow \text{Fe}^{3+} + \text{CO}_2$
- 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)
- What is the mass of sodium bromate and molarity of solution to prepare 85.5 mL of 0.672N solution when half cell reactions are?
 - $\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \longrightarrow \text{Br}^- + 3\text{H}_2\text{O}$
 - $2\text{BrO}_3^- + 12\text{H}^+ + 10\text{e}^- \longrightarrow \text{Br}_2 + 6\text{H}_2\text{O}$
 (IIT 1987)
- How many mL of 0.05M KMnO_4 (acidic) are required to oxidize 2.0 g of FeSO_4 in dilute solution?
- Dichromate ion in acid solution oxidizes stannous ion as $3\text{Sn}^{2+} + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \longrightarrow 3\text{Sn}^{4+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
 - If SnCl_2 is the source of Sn^{2+} , how many gram of SnCl_2 would be contained in 2 litre of 0.1N solution?
 - If $\text{K}_2\text{Cr}_2\text{O}_7$ is the source of $\text{Cr}_2\text{O}_7^{2-}$, what is the normality of solution containing 4.9 g $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.1 litre of solution? (IIT 1987)
- 20 mL of 0.2M 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.
- Metallic tin in the presence of HCl is oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ to stannic chloride. What volume of decinormal dichromate solution would be reduced by 1 g of tin? (MLNR 1994)
- 5.5g of a mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ required 5.4 mL of 0.1N KMnO_4 solution for complete oxidation. Calculate mole of hydrated ferric sulphate in mixture. (IIT 1989)
- 0.5 g sample containing MnO_2 is treated with HCl, liberating Cl_2 . The Cl_2 is passed into a solution of KI and 30.0 cm³ of 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in sample. (Atomic mass of Mn = 55) (Roorkee 1994)
- 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.
- In an ore, the only oxidizable material is Sn^{2+} . This ore is titrated with a dichromate solution containing 2.5 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.5 litre. A 0.40g sample of the ore required 10.0 cm³ of titrant to reach equivalence point. Calculate the percentage of tin in ore. (Roorkee 1993)
- 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.
- An element A in a compound ABD has an oxidation No. A^{n-} . It is oxidized by $\text{Cr}_2\text{O}_7^{2-}$ in acid medium. In an experiment 1.68×10^{-3} mole of $\text{K}_2\text{Cr}_2\text{O}_7$ was required for 3.26×10^{-3} mole of the compound ABD. Calculate new oxidation state of A.
- 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:
 - Purity of H_2O_2
 - Volume of dry O_2 evolved at 27°C and 750 mm P.
 (IIT 1985)
- 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.
- 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $0.1N$ $\text{Na}_2\text{S}_2\text{O}_3$ 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 $0.3N$ 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 $0.2M$ 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 up to 1 litre. 25 mL of this solution required 20 mL of $N/10$ KMnO_4 for complete oxidation. Calculate % of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in given sample.
22. KMnO_4 oxidizes X^{n+} ion to XO_3^- , itself changing to Mn^{2+} in acid solution. 2.68×10^{-3} mole of X^{n+} requires 1.61×10^{-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 $N/10$ $\text{Na}_2\text{S}_2\text{O}_3$. Calculate % of available Cl_2 in bleaching powder. (Roorkee 1990)
24. A solution of $0.1M$ KMnO_4 is used for the reaction:

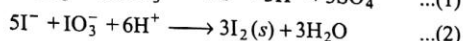
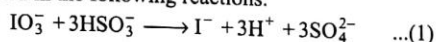
$$\text{S}_2\text{O}_3^{2-} + 2\text{MnO}_4^- + \text{H}_2\text{O} \longrightarrow \text{MnO}_2 + \text{SO}_4^{2-} + \text{OH}^-$$
 What volume of solution in mL will be required to react with 0.158 g of $\text{Na}_2\text{S}_2\text{O}_3$? (MLNR 1991)
25. A sample of $\text{Fe}_2(\text{SO}_4)_3$ and FeC_2O_4 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 .
 H_2SO_4 . On again oxidation by same KMnO_4 , 60 mL were required. Calculate the ratio of Meq. of $\text{Fe}_2(\text{SO}_4)_3$ and FeC_2O_4 in mixture.
26. A solution of 0.2 g of a compound containing Cu^{2+} and $\text{C}_2\text{O}_4^{2-}$ ions on titration with $0.02M$ 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 $0.05M$ $\text{Na}_2\text{S}_2\text{O}_3$ for complete reduction. Find out mole ratio of Cu^{2+} and $\text{C}_2\text{O}_4^{2-}$ 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:

$$\text{KIO}_3 + 2\text{KI} + 6\text{HCl} \longrightarrow 3\text{ICl} + 3\text{KCl} + 3\text{H}_2\text{O}$$
 (IIT 1992)
28. 1.6 g of pyrolusite ore was treated with 50 cm^3 of $1.0N$ 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 $0.1N$ 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 up to 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 $\text{K}_2\text{Cr}_2\text{O}_7$ for oxidation. Before reduction with zinc, 25 mL of the same solution required 22.45 mL of same $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Calculate the strength of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ in solution.
32. A sample of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ 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 $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in sample. (Roorkee 2001)
33. A solution contains mixture of $\text{H}_2\text{C}_2\text{O}_4$ and H_2SO_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:
- Normality of $\text{H}_2\text{C}_2\text{O}_4$ and H_2SO_4 .
 - Strength of $\text{H}_2\text{C}_2\text{O}_4$ and H_2SO_4 .
- Assume molar mass of $\text{H}_2\text{C}_2\text{O}_4 = 126$
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:
- $$\text{MnO}_2 + 4\text{HCl} \longrightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$$
35. A sample of hydrazine sulphate ($\text{N}_2\text{H}_6\text{SO}_4$) 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, $4\text{Fe}^{3+} + \text{N}_2\text{H}_4 \longrightarrow \text{N}_2 + 4\text{Fe}^{2+} + 4\text{H}^+$
- $$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$$
- (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 0.0167M 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 ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$) and was obtained as solution. In the absence of any interfering radical, the solution required 42 mL of 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$ for titration. Calculate % of CuFeS_2 in sample.
38. A mixture of $\text{H}_2\text{C}_2\text{O}_4$ 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 $\text{H}_2\text{C}_2\text{O}_4$ and NaHC_2O_4 in mixture. (IIT 1990)
39. An equal volume of reducing agent is titrated separately with 1M 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 $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $N/30$ $\text{K}_2\text{Cr}_2\text{O}_7$ solution for exact oxidation. Calculate % purity of Fe in wire.
41. The reaction $\text{Cl}_2(\text{g}) + \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{Cl}^-$ is to be carried out in basic medium. Starting with 0.15 mole of Cl_2 , 0.010 mole $\text{S}_2\text{O}_3^{2-}$ 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:
- $$\text{NO}_3^- + \text{Mg}(\text{s}) + \text{H}_2\text{O} \longrightarrow \text{Mg}(\text{OH})_2(\text{s}) + \text{OH}^-(\text{aq.}) + \text{NH}_3(\text{g})$$
- A 25.0 mL sample of NO_3^- solution was treated with Mg. The $\text{NH}_3(\text{g})$ 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 $\text{Cl}_2(\text{g})$ into concentrated solution of sodium chlorite $\text{NaClO}_2 \cdot \text{NaCl}(\text{aq.})$ 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 $\text{NaClO}_2(\text{aq.})$? (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 $\text{K}_2\text{Cr}_2\text{O}_7$. (1 mL of $\text{K}_2\text{Cr}_2\text{O}_7 = 0.006 \text{ g Fe}$). Also find % of Cr_2O_3 in sample.
46. Hydroxylamine reduces iron III according to the equation $4\text{Fe}^{3+} + 2\text{NH}_2\text{OH} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} + 4\text{Fe}^{2+} + 4\text{H}^+$. Iron II thus produced is estimated by titration with standard KMnO_4 solution. The reaction is
- $$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$$
- 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.



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 $\text{K}_x\text{H}_y(\text{C}_2\text{O}_4)_z \cdot n\text{H}_2\text{O}$ 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 $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ containing 1.25 g of the salt was boiled with iron when the reaction $\text{Fe} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow 3\text{FeSO}_4$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{H}_2\text{C}_2\text{O}_4$. The excess of $\text{C}_2\text{O}_4^{2-}$ in one fourth of filtrate

was back titrated with 5 mL of 0.1025 N KMnO_4 . To determine the conc. of $\text{H}_2\text{C}_2\text{O}_4$ 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 $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (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 $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 was treated with excess of KI in acidic medium. Iodine liberated required 100 cm³ of 0.15N sodium thiosulphate solution for titration. Find the mass per cent of each in the mixture. (Roorkee 1995)
58. A 5.0 cm³ 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 $\text{K}_2\text{Cr}_2\text{O}_7$ 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) $\text{SeO}_3^{2-} + \text{BrO}_3^- + \text{H}^+ \longrightarrow \text{SeO}_4^{2-} + \text{Br}_2 + \text{H}_2\text{O}$
 (b) $\text{BrO}_3^- + \text{AsO}_2^- + \text{H}_2\text{O} \longrightarrow \text{Br}^- + \text{AsO}_4^{3-} + \text{H}^+$

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 ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) for complete reaction. Calculate mass of mixture. The reactions are:
- $$\text{As}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O} \longrightarrow \text{As}_2\text{O}_5 + 4\text{H}^+ + 4\text{I}^-$$
- $$\text{As}_2\text{O}_5 + 4\text{H}^+ + 4\text{I}^- \longrightarrow \text{As}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O}$$
62. 1.5 g of brass containing Cu and Zn reacts with 3M HNO_3 solution, the following reactions take place.
- $$\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}^{2+} + \text{NO}_2(\text{g}) + \text{H}_2\text{O}$$
- $$\text{Zn} + \text{H}^+ + \text{NO}_3^- \longrightarrow \text{NH}_4^+ + \text{Zn}^{2+} + \text{H}_2\text{O}$$
- The liberated $\text{NO}_2(\text{g})$ 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:
- $$\text{SO}_2(\text{g}) + \text{H}_2\text{O}_2(\text{aq.}) + 2\text{OH}^-(\text{aq.}) \longrightarrow \text{SO}_4^{2-}(\text{aq.}) + 2\text{H}_2\text{O}(\text{l})$$
- 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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?
 (IIT May 1997)
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 $\text{Na}_2\text{S}_2\text{O}_3$. 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 ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in one litre. Calculate the percentage of arsenious oxide in the sample. (Atomic mass of As = 75)
 (Roorkee 1999)
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 $\text{A}_x(\text{CO}_3)_y(\text{OH})_z$ 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

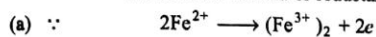
- as indicator required 15 mL of same acid. Deduce the formula of salt.
74. A 3.0 g sample of Cu_2O is dissolved in dil. H_2SO_4 where it undergoes disproportionation quantitatively. The solution is filtered off and 8.3 g pure KI crystals are added to clear filtrate in order to precipitate CuI with evolution 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{C}_2\text{O}_4$ 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 value of m ? (Atomic mass: $\text{K} = 39$, $\text{Br} = 80$)
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.
- $$\text{ClO}_3^- + 6\text{Fe}^{2+} + 6\text{H}^+ \longrightarrow \text{Cl}^- + 6\text{Fe}^{3+} + 3\text{H}_2\text{O}$$
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,

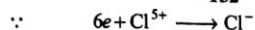
Eq. mass of oxidant or reductant

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



$$\therefore \text{Eq. mass of FeSO}_4 = \frac{\text{Molar mass of FeSO}_4}{1} = \frac{152}{1}$$

$$= 152$$



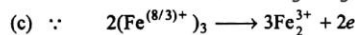
$$\therefore \text{Eq. mass of KClO}_3 = \frac{\text{Molar mass of KClO}_3}{6} = \frac{122.5}{6} = 20.42$$



$$\therefore \text{Eq. mass of Na}_2\text{SO}_3 = \frac{M}{2} = \frac{126}{2} = 63$$



$$\therefore \text{Eq. mass of Na}_2\text{CrO}_4 = \frac{M}{3} = \frac{162}{3} = 54$$



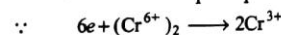
$$\therefore \text{Eq. mass of Fe}_3\text{O}_4 = \frac{M}{1} = \frac{232}{1} = 232$$



$$\therefore \text{Eq. mass of KMnO}_4 = \frac{M}{3} = \frac{158}{3} = 52.67$$



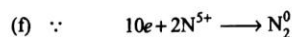
$$\therefore \text{Eq. mass of KI} = \frac{M}{1} = \frac{166}{1} = 166$$



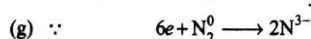
$$\therefore \text{Eq. mass of K}_2\text{Cr}_2\text{O}_7 = \frac{M}{6} = \frac{294}{6} = 49$$



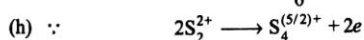
$$\therefore \text{Eq. mass of Mn}^{4+} = \frac{\text{Atomic mass of Mn}}{2} = \frac{55}{2} = 27.5$$



$$\therefore \text{Eq. mass of NO}_3^- = \frac{\text{Ionic Molar mass}}{5} = \frac{62}{5} = 12.4$$



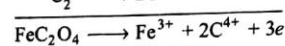
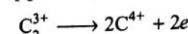
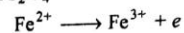
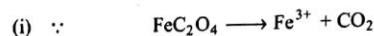
$$\therefore \text{Eq. mass of N}_2 = \frac{\text{Molar mass of N}_2}{6} = \frac{28}{6} = 4.67$$



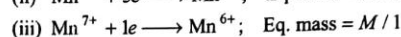
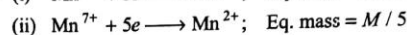
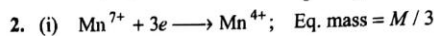
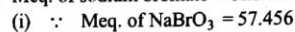
$$\therefore \text{Eq. mass of Na}_2\text{S}_2\text{O}_3 = \frac{M}{1} = \frac{158}{1} = 158$$



$$\therefore \text{Eq. mass of I}_2 = \frac{M}{2} = \frac{254}{2} = 127$$



$$\therefore \text{Eq. mass of FeC}_2\text{O}_4 = \frac{M}{3} = \frac{144}{3} = 48$$

3. Meq. of sodium bromate = $85.5 \times 0.672 = 57.456$ 

$$\therefore \frac{w}{E} \times 1000 = 57.456$$

$$\therefore \frac{w}{151/6} \times 1000 = 57.456 \quad \left(\because E_{\text{NaBrO}_3} = \frac{M}{6} \right)$$

$$\therefore w = 1.446 \text{ g}$$

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

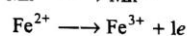
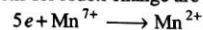
(ii) Similarly use valency factor 5 in place of 6 in this problem and get

$$w = 1.735 \text{ g}$$

$$\text{and } M = 0.1344 \text{ M}$$

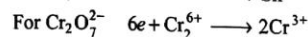
The term valency factor = No. of electrons lost or gained by one molecule of reductant or oxidant

4. The reactions for redox change are

Now Meq. of KMnO_4 = Meq. of FeSO_4

$$0.05 \times 5 \times v = \frac{2}{152/1} \times 1000 \quad \therefore \text{Meq.} = N \times V \text{ in mL}$$

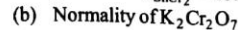
$$\therefore v = 52.63 \text{ mL} \quad \text{and Meq.} = \frac{\text{Mass}}{\text{Eq. mass}} \times 1000$$



$$\therefore \frac{w}{E} \times 1000 = 200$$

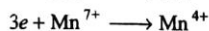
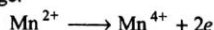
$$\therefore \frac{w}{189.7/2} \times 1000 = 200 \quad \left[\because E_{\text{SnCl}_2} = \frac{M_{\text{SnCl}_2}}{2} \right]$$

$$\therefore w_{\text{SnCl}_2} = 18.97 \text{ g}$$



$$= \frac{4.9}{M/6} \times \frac{1}{0.1} = \frac{4.9}{294/6 \times 0.1} = 1 \text{ N} \quad \left| \quad N = \frac{\text{Eq.}}{\text{litre}} \right.$$

6. For redox change:



$$\therefore \text{Meq. of KMnO}_4 = \text{Meq. of MnSO}_4$$

$$[\because N = M \times \text{valency factor}]$$

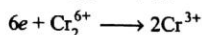
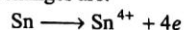
$$N \times 16 = 20 \times 0.2 \times 2$$

$$\therefore N = 0.5$$

$$\therefore M = \frac{0.5}{3} = 0.167$$

$$[\because \text{valency factor for KMnO}_4 = 3]$$

7. The redox changes are:



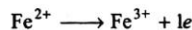
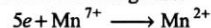
$$\therefore \text{Meq. of Sn} = \text{Meq. of K}_2\text{Cr}_2\text{O}_7$$

$$\text{or } \frac{1}{E_{\text{Sn}}} \times 1000 = \frac{1}{10} \times V$$

$$\text{or } \frac{1}{118.7} \times 1000 = \frac{1}{10} \times V \quad \left(\because \text{Eq. mass of Sn} = \frac{\text{At. mass}}{4} \right)$$

$$\text{or } V = 336.98 \text{ mL}$$

8. Reactions for redox change are:



It is to be noted here that only $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ will react with KMnO_4 to bring in redox change.

$$\therefore \text{Meq. of FeSO}_4 \cdot 7\text{H}_2\text{O} = \text{Meq. of KMnO}_4$$

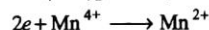
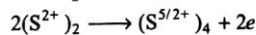
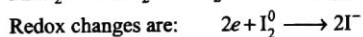
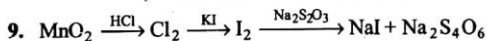
$$\frac{w}{E} \times 1000 = 5.4 \times 0.1 \quad \therefore \frac{w}{278} \times 1000 = 0.54$$

$$\therefore w = 0.150 \text{ g}$$

$$\therefore \text{Mass of Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} = 5.5 - 0.150 \text{ g} = 5.350 \text{ g}$$

$$\therefore \text{Mole of Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} = \frac{5.350}{562} = 9.5 \times 10^{-3} \text{ mol}$$

$$(\because \text{Molar mass of Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} = 562)$$



The reactions suggest that,

$$\text{Meq. of MnO}_2 = \text{Meq. of Cl}_2 \text{ formed}$$

$$= \text{Meq. of I}_2 \text{ liberated}$$

$$= \text{Meq. of Na}_2\text{S}_2\text{O}_3 \text{ used}$$

$$\therefore \frac{w}{M/2} \times 1000 = 0.1 \times 1 \times 30$$

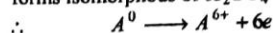
$$[\because N_{\text{Na}_2\text{S}_2\text{O}_3} = M_{\text{Na}_2\text{S}_2\text{O}_3} \text{ since valency factor} = 1, \text{ see redox changes for Na}_2\text{S}_2\text{O}_3]$$

$$\text{or } w = \frac{0.1 \times 1 \times 30 \times M}{2000} = \frac{0.1 \times 1 \times 30 \times 87}{2000} \quad (\because M_{\text{MnO}_2} = 87)$$

$$w_{\text{MnO}_2} = 0.1305$$

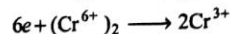
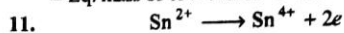
$$\therefore \text{Purity of MnO}_2 = \frac{0.1305}{0.5} \times 100 = 26.1\%$$

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
- .



$$\therefore \text{Atomic mass of A}$$

$$= \text{Eq. mass of A} \times \text{No. of 'e' lost} = 13.16 \times 6 = 78.96$$



Since, Sn^{2+} is oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$

$$\therefore \text{Meq. of Sn}^{2+} = \text{Meq. of K}_2\text{Cr}_2\text{O}_7 \text{ used for tin}$$

$$= N \times V_{\text{in mL}} \\ = \frac{2.5}{294.2} \times 10 = 1.0197$$

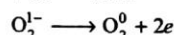
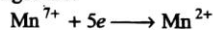
$$\left(\because N = \frac{2.5}{\frac{294.2}{6} \times 0.5} \right)$$

$$\therefore \frac{w_{\text{Sn}^{2+}}}{118/2} \times 1000 = 1.0197$$

$$\therefore w_{\text{Sn}^{2+}} = 0.06 \text{ g}$$

$$\therefore \% \text{ Sn} = \frac{0.06}{0.4} \times 100 = 15\%$$

12. Redox changes are:

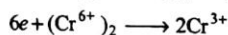
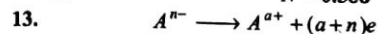


$$\therefore \text{Eq. mass of H}_2\text{O}_2 = \frac{34}{2}$$

$$\text{Now, Meq. of KMnO}_4 = \text{Meq. of H}_2\text{O}_2$$

$$N.(X) = \frac{X}{100 \times 34/2} \times 1000$$

$$\therefore N = 0.588$$

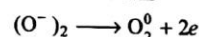
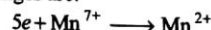


$$\therefore \text{Meq. of } A^{n-} = \text{Meq. of Cr}_2\text{O}_7^{2-}$$

$$\text{or } 3.26 \times 10^{-3} \times (a+n) = 1.68 \times 10^{-3} \times 6$$

$$\therefore a+n = 3 \quad \text{or} \quad a = 3 - n$$

14. Redox changes are:



$$(a) \therefore \text{Meq. of H}_2\text{O}_2 = \text{Meq. of KMnO}_4$$

$$\frac{w \times 1000}{34/2} = \frac{0.316}{M/5} \times 1000$$

$$\therefore \frac{w \times 2 \times 1000}{34} = \frac{0.316 \times 5 \times 1000}{158}$$

$$\therefore w_{\text{H}_2\text{O}_2} = 0.17 \text{ g}$$

$$\therefore 0.2 \text{ g impure sample of H}_2\text{O}_2 \text{ has } 0.17 \text{ g pure H}_2\text{O}_2$$

$$\therefore \% \text{ of H}_2\text{O}_2 = \frac{0.17 \times 100}{0.2} = 85\%$$

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

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

$$\therefore w_{O_2} = 0.16 \text{ g}$$

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

$$\therefore V_{O_2} = 124.79 \text{ mL}$$
15. Redox changes are: $5e + Mn^{7+} \longrightarrow Mn^{2+}$
 $(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$
- $\therefore$ Meq. of oxalate ion

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

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

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

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

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

$$\therefore \% \text{ of } C_2O_4^{2-} \text{ in sample} = \frac{0.198 \times 100}{0.3} = 66\%$$
16. Redox changes are: $2e + (O^-)_2 \longrightarrow 2O^{2-}$
 $2I^- \longrightarrow I_2 + 2e$
 $2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$
 and $2e + I_2^0 \longrightarrow 2I^{1-}$
- $$H_2O_2 \xrightarrow{KI} I_2 + H_2O \xrightarrow{Na_2S_2O_3} d \text{ Na}_2S_4O_6 + 2I^-$$
- $\therefore$ Meq. of H_2O_2 = Meq. of KI used = Meq. of I_2 liberated
 = Meq. of $Na_2S_2O_3$ used
- $\therefore$ Meq. of H_2O_2 = Meq. of $Na_2S_2O_3$ used
 $N \times 50 = 20 \times 0.1 \therefore N_{H_2O_2} = 0.04$
- $\therefore$ Strength of $H_2O_2 = N \times E = 0.04 \times \frac{34}{2} = 0.68 \text{ g litre}^{-1}$
17. Redox changes are:
 For $H_2C_2O_4$ $(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$
 For $KMnO_4$ $5e + Mn^{7+} \longrightarrow Mn^{2+}$
- 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 = $8.5 \times \frac{1}{10} \times \frac{200}{10}$
- $\therefore \frac{w}{E} \times 1000 = 17$
- Formula of oxalic acid is $H_2C_2O_4 \cdot 2H_2O$ $\therefore \frac{w}{126/2} \times 1000 = 17$
 $\therefore$ Molar mass = 126 $\therefore w_{H_2C_2O_4} = 1.071 \text{ g}$
- $\therefore$ % purity of oxalic acid = $\frac{1.071}{1.2} \times 100 = 89.25\%$
18. (a) The redox changes are
 $2e + (O^-)_2 \longrightarrow 2O^{2-}$
 $2I^- \longrightarrow I_2 + 2e$

- $$2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e$$
- $$I_2 + 2e \longrightarrow 2I^-$$
- Meq. of H_2O_2 = Meq. of I_2 = Meq. of $Na_2S_2O_3$
 $N \times 25 = 0.1 \times 20 \therefore N_{H_2O_2} = 0.08$
 Mass of H_2O_2 in one litre = $0.08 \times \frac{34}{2} = 1.36 \text{ g}$
 $\therefore$ % by mass = 0.136%
 Also concentration of H_2O_2 in terms of volume
 = 0.448 volume
- (b) Follow problem 18 (a)
 [Ans. 1.344]
19. The given reactions are:
 $MnO_2 + Na_2C_2O_4 + 2H_2SO_4 \longrightarrow MnSO_4 + 2CO_2 + Na_2SO_4 + 2H_2O$
 (ppt.) $\therefore$ Meq. of MnO_2 = Meq. of $Na_2C_2O_4 = 10 \times 0.2 \times 2 = 4$
 $\therefore Mn^{4+} + 2e \longrightarrow Mn^{2+}$
 $\therefore$ Valence factor of $MnO_2 = 2 \therefore$ mM of $MnO_2 = \frac{4}{2} = 2$
- Now, $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2O$
 (ppt.)
 Since, Eq. mass of MnO_2 is derived from $KMnO_4$ and $MnSO_4$ both, thus it is better to proceed by mole concept.
 $mM \text{ of } KMnO_4 = mM \text{ of } MnO_2 \times \frac{2}{5} = \frac{4}{5}$
- Also, $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$
 $\therefore mM \text{ of } H_2O_2 = mM \text{ of } KMnO_4 \times \frac{5}{2} = \frac{4}{5} \times \frac{5}{2} = 2$
 $\therefore M \times 20 = 2$
 $M_{H_2O_2} = 0.1$
20. Limestone $\xrightarrow{\text{oxalic acid}} CaCO_3 \xrightarrow{KMnO_4} \text{decolorizes}$
- $\therefore$ Redox changes are:
 For CaC_2O_4 $(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$
 For $KMnO_4$ $5e + Mn^{7+} \longrightarrow Mn^{2+}$
- $\therefore$ Meq. of $CaCO_3$ = Meq. of CaC_2O_4 = Meq. of $KMnO_4$
 $\therefore$ Meq. of $CaCO_3$ = Meq. of CaO
 (since CaO is present in $CaCO_3$)
- $\therefore$ Meq. of CaO = Meq. of $KMnO_4$

$$\frac{w}{56/2} \times 1000 = 45 \times 0.2$$
 Mass of $CaO = 0.252 \text{ g}$
 $\therefore$ % of CaO in limestone = $\frac{0.252}{0.56} \times 100 = 45\%$
21. The redox changes are:
 For $FeSO_4$ $Fe^{2+} \longrightarrow Fe^{3+} + 1e$
 For $KMnO_4$ $5e + Mn^{7+} \longrightarrow Mn^{2+}$
 $\therefore$ Meq. of $FeSO_4 \cdot 7H_2O$ in 25 mL solution
 = Meq. of $KMnO_4 = 20 \times \frac{1}{10}$

$$\therefore \text{Meq. of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O in 1 litre solution} \\ = 20 \times \frac{1}{10} \times \frac{1000}{25} = 80$$

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

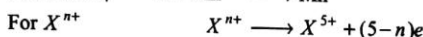
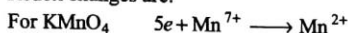
$$(\text{Molar mass of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278) \therefore \frac{w}{278} \times 1000 = 80$$

$$\therefore w = 22.24 \text{ g}$$

$$\therefore 25 \text{ g sample has } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 22.24 \text{ g}$$

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

22. Redox changes are:

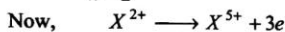


Now,

$$\begin{aligned} \text{Meq. of } X^{n+} &= \text{Meq. of } \text{KMnO}_4 \quad \therefore \text{Meq.} = \text{mole} \times \\ 2.68 \times 10^{-3} \times (5-n) \times 1000 & \quad \text{valency factor} \times 1000 \\ &= 1.61 \times 10^{-3} \times 5 \times 1000 \end{aligned}$$

$$\therefore n = 1.99$$

$$n = 2$$



If a is atomic mass of X ,

$$\therefore \text{Eq. mass of } \text{XCl}_2 = 56$$

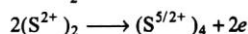
$$\therefore \text{Molar mass of } \text{XCl}_2 = 56 \times \text{valency factor} = 56 \times 3$$

$$\text{or } a + 71 = 56 \times 3$$

$$\therefore a = 97$$

23. Bleaching powder $\xrightarrow{\text{KI} + \text{HCl}} \text{I}_2 \xrightarrow{\text{Na}_2\text{S}_2\text{O}_3} \text{I}^- + \text{Na}_2\text{S}_4\text{O}_6$

The redox changes are: $2e + \text{I}_2 \longrightarrow 2\text{I}^-$



$$\begin{aligned} \text{Meq. of bleaching powder} &= \text{Meq. of available } \text{Cl}_2 \\ &= \text{Meq. of } \text{I}_2 \text{ liberated} \\ &= \text{Meq. of } \text{Na}_2\text{S}_2\text{O}_3 \text{ used} \end{aligned}$$

$$\therefore \text{Meq. of available } \text{Cl}_2 \text{ in 25 mL bleaching powder solution}$$

$$= \text{Meq. of } \text{Na}_2\text{S}_2\text{O}_3 \text{ used} = 24.35 \times \frac{1}{10}$$

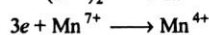
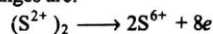
$$\therefore \text{Meq. of available } \text{Cl}_2 \text{ in 500 mL bleaching powder solution}$$

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

$$\therefore \frac{w}{71/2} \times 1000 = 48.7 \therefore w_{\text{Cl}_2} = 1.729 \text{ g}$$

$$\therefore \% \text{ of available } \text{Cl}_2 \text{ in bleaching powder} \\ = \frac{1.729}{5.7} \times 100 = 30.33\%$$

24. Redox changes are:



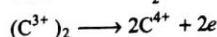
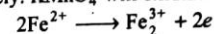
$$\therefore \text{Meq. of } \text{KMnO}_4 = \text{Meq. of } \text{S}_2\text{O}_3^{2-}$$

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

$$(\therefore \text{Molar mass of } \text{Na}_2\text{S}_2\text{O}_3 = 158)$$

$$V = 26.67 \text{ mL}$$

25. Let Meq. of $\text{Fe}_2(\text{SO}_4)_3$ and FeC_2O_4 are a and b respectively. KMnO_4 will oxidize only FeC_2O_4 as:



Note that valence factor for $\text{Fe}_2(\text{SO}_4)_3$ is 2 and for FeC_2O_4 is 3.

Meq. of FeC_2O_4 of valence factor 3

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

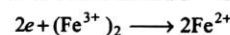
$$+ \text{Meq. of } \text{Ca}_2\text{O}_4^{2-} \text{ (v.f. = 2)}$$

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

$$b = \text{Meq. of } \text{KMnO}_4$$

$$b = 40 \times \frac{1}{16} = \frac{40}{16} \quad \dots(1)$$

Fe_2^{3+} from $\text{Fe}_2(\text{SO}_4)_3$ and Fe_2^{3+} obtained by oxidation of FeC_2O_4 will be converted to Fe^{2+} as,



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 $\text{Fe}_2(\text{SO}_4)_3$ reduction +

Meq. of Fe^{2+} of FeC_2O_4

$$= \text{Meq. of } \text{KMnO}_4$$

$$a + \frac{b}{3} = 60 \times \frac{1}{16} = \frac{60}{16} \quad \dots(2)$$

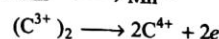
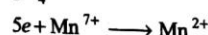
$$\text{By Eqs. (1) and (2), } a = \frac{140}{48}, \quad b = \frac{40}{16}$$

$$\therefore \frac{\text{Meq. of } \text{Fe}_2(\text{SO}_4)_3 \text{ of valence factor 2}}{\text{Meq. of } \text{FeC}_2\text{O}_4 \text{ of valence factor 3}} = \frac{140}{48} \times \frac{16}{40} = \frac{7}{6}$$

$$\therefore \text{Ratio of Meq. of } \text{Fe}_2(\text{SO}_4)_3 : \text{Meq. of } \text{FeC}_2\text{O}_4 = 7 : 6$$

26. Let a mole of Cu^{2+} and b mole of $\text{C}_2\text{O}_4^{2-}$ be present in solution.

Case I: The solution is oxidized by KMnO_4 which reacts with only $\text{C}_2\text{O}_4^{2-}$.

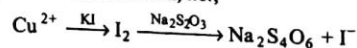


$$\therefore \text{Meq. of } \text{C}_2\text{O}_4^{2-} = \text{Meq. of } \text{KMnO}_4$$

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

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

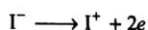
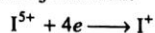
Case II: After oxidation of $\text{C}_2\text{O}_4^{2-}$, the resulting solution is neutralized by Na_2CO_3 , acidified with dilute CH_3COOH and then treated with excess of KI . The liberated I_2 required $\text{Na}_2\text{S}_2\text{O}_3$ for its neutralization, i.e.,



$$\begin{aligned}
 \therefore \text{Meq. of Cu}^{2+} &= \text{Meq. of I}_2 \text{ liberated} \\
 &= \text{Meq. of Na}_2\text{S}_2\text{O}_3 \text{ used} \\
 \therefore \text{Meq. of Cu}^{2+} &= \text{Meq. of Na}_2\text{S}_2\text{O}_3 \text{ used} \\
 a \times 1 \times 1000 &= 11.3 \times 0.05 \times 1 \\
 \therefore a &= 5.65 \times 10^{-4} \\
 \therefore \text{Molar ratio of} \\
 \frac{\text{Cu}^{2+}}{\text{C}_2\text{O}_4^{2-}} &= \frac{a}{b} = \frac{5.65 \times 10^{-4}}{1.13 \times 10^{-3}} = \frac{1}{2}
 \end{aligned}$$

Redox changes are:

$$\begin{aligned}
 2\text{Cu}^{2+} + 2e &\longrightarrow (\text{Cu}^+)_2 \\
 2\text{I}^- &\longrightarrow \text{I}_2 + 2e \\
 \text{and } 2e + \text{I}_2 &\longrightarrow 2\text{I}^- \\
 2(\text{S}^{2+})_2 &\longrightarrow (\text{S}^{5/2+})_4 + 2e
 \end{aligned}$$

27. For KI + KIO₃ reaction:

$\therefore$ valence factor of KI = 2 and valence factor of KIO₃ = 4

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

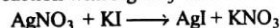
$$\therefore \text{Meq. of KI in 50 mL} = 12 \times \frac{50}{20} = 30$$

Now, Meq. of KI left after treatment with AgNO₃

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

$\therefore$ Meq. of KI (v.f. = 2) used by AgNO₃ = 30 - 20 = 10

But in its reaction with AgNO₃ valence factor of KI = 1



$$\therefore \text{Meq. of KI used by AgNO}_3 \text{ (v.f. = 1)} = \frac{10 \times 1}{2} = 5$$

$\therefore$ Meq. of AgNO₃ = 5

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

$$\therefore w = 0.85 \text{ g}$$

$$\therefore \% \text{ purity of AgNO}_3 \text{ in sample} = \frac{0.85 \times 100}{1} = 85\%$$

Alternative method:

milli mole of KIO₃ used by 20 mL of KI stock solution

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

$\therefore$ milli mole of KIO₃ used by 50 mL of KI stock solution

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

milli mole of KIO₃ used by KI left in 50 mL solution after reaction with

$$\text{AgNO}_3 = \frac{1}{10} \times 50 = 5$$

$\therefore$ Mole ratio of KIO₃ and KI is 1 : 2 in reaction

$\therefore$ milli mole of KI in 50 mL stock solution = 7.5 × 2 = 15

$\therefore$ milli mole of KI left in 50 mL solution after reaction with AgNO₃ = 5 × 2 = 10

$\therefore$ milli mole of KI used for AgNO₃ = 15 - 10 = 5

$\therefore$ m mole of AgNO₃ = 5

($\therefore$ mole ratio of KI and AgNO₃ reaction is 1 : 1)

Now for AgNO₃:

$$\frac{w}{M} \times 1000 = 5$$

$$\therefore \frac{w}{170} \times 1000 = 5$$

$$\therefore w_{\text{AgNO}_3} = 0.85$$

$$\therefore \% \text{ of AgNO}_3 = 0.85 \times \frac{100}{1} = 85\%$$

28. Meq. of MnO₂ = Meq. of oxalic acid added -

Meq. of oxalic acid left

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

$$= 18$$

$$\therefore \frac{w}{E} \times 1000 = 18 \quad \text{or} \quad w_{\text{MnO}_2} = \frac{18 \times 86.9}{2 \times 1000} = 0.7821 \text{ g}$$

$$\left(\therefore E = \frac{86.9}{2} \right)$$

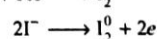
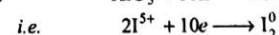
$$\therefore \% \text{ of MnO}_2 = \frac{0.7821}{1.6} \times 100 = 48.88\%$$

Also Meq. of MnO₂ = Meq. of O₂ = 18

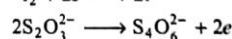
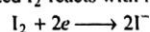
$$\therefore \frac{w}{8} \times 1000 = 18$$

$$w_{\text{O}_2} = 0.144 \text{ g}$$

$$\therefore \% \text{ of available O}_2 = \frac{0.144}{1.6} \times 100 = 9$$

29. $\text{KIO}_3 + 5\text{KI} \longrightarrow 3\text{K}_2\text{O} + 3\text{I}_2$ 

Now the liberated I₂ reacts with Na₂S₂O₃ to give



$\therefore$ millimole ratio is I₂ : S₂O₃ :: 1 : 2,

Thus, m. mole of I₂ liberated = m. mole of Na₂S₂O₃ used

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

(M is molarity of thiosulphate)

$$\text{Also m. mole of KIO}_3 = \frac{0.1}{214} \times 1000$$

Now, m. mole ratio is KIO₃ : I₂ :: 1 : 3

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

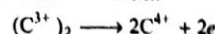
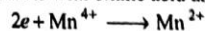
$$\therefore M = \frac{0.1 \times 1000 \times 3 \times 2}{214 \times 45}$$

$$M = 0.062$$

30. 1. Pyrolusite contains MnO₂.

2. Meq. of oxalic acid added to pyrolusite = 65 × 1 = 65

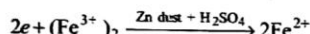
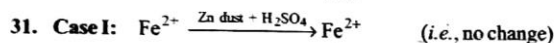
3. MnO₂ reacts with oxalic acid as,



4. Excess of oxalic acid is oxidized by KMnO₄

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

$$\begin{aligned}\therefore \text{Meq. of oxalic acid left in 500 mL} &= 5 \times \frac{500}{100} = 25 \\ \therefore \text{Meq. of oxalic acid used for MnO}_2 &= 65 - 25 = 40 \\ \therefore \text{Meq. of MnO}_2 &= 40 \\ \therefore \text{Molar mass of MnO}_2 = 87, \text{ Eq. mass} &= \frac{87}{2} \\ \therefore \frac{w}{87/2} \times 1000 &= 40 \quad \therefore w_{\text{MnO}_2} = 1.74 \text{ g} \\ \therefore \% \text{ of MnO}_2 \text{ in pyrolusite} &= \frac{1.74}{2.6} \times 100 = 66.92\%\end{aligned}$$



$\therefore$ Zn dust is used as reducing agent and thus,
 $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e$

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 $\text{Fe}^{3+} = a + b$

Now these are oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$

$\therefore$ Total Meq. of Fe^{2+} = Meq. of $\text{K}_2\text{Cr}_2\text{O}_7$

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

$$\therefore a + b = 3.425 \quad \dots(1)$$

Case II: If reduction is not made, the solution contains Fe^{2+} and Fe^{3+} of which only Fe^{2+} are oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$.

$\therefore$ Meq. of Fe^{2+} = Meq. of $\text{K}_2\text{Cr}_2\text{O}_7$

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

$$a = 2.245 \quad \dots(2)$$

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

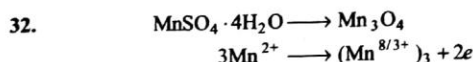
$\therefore$ Meq. of FeSO_4 (in 25 mL) = $a = 2.245$ Meq. of $\text{Fe}_2(\text{SO}_4)_3$ (in 25 mL) = $b = 1.18$

$$\therefore \frac{w}{M/1} \times 1000 = 2.245 \quad \therefore \frac{w}{M/2} \times 1000 = 1.18$$

$\therefore$ Molar mass of $\text{FeSO}_4 = 152$ Molar mass of $\text{Fe}_2(\text{SO}_4)_3 = 400$

$\therefore$ Mass of FeSO_4 in 25 mL = 0.341 g $\therefore$ Mass of $\text{Fe}_2(\text{SO}_4)_3$ in 25 mL = 0.236 g

$\therefore$ Strength of FeSO_4 = 13.64 g / litre $\therefore$ Strength of $\text{Fe}_2(\text{SO}_4)_3$ = 9.45 g / litre



The residue Mn_3O_4 is dissolved in FeSO_4 which is reduced from $\text{Mn}^{8/3+}$ to Mn^{2+} . $(\text{Mn}^{8/3+})_3 + 2e \longrightarrow 3\text{Mn}^{2+}$. 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 = Meq. of FeSO_4

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

Now Meq. of FeSO_4 added to $\text{Mn}_3\text{O}_4 = 100 \times 0.1 = 10$
 Meq. of FeSO_4 left after reaction with Mn_3O_4
 $= \text{Meq. of KMnO}_4$ used
 $= 50 \times \frac{3}{25} = 6$

$\therefore$ Meq. of FeSO_4 used for $\text{Mn}_3\text{O}_4 = 10 - 6 = 4$

$\therefore$ Meq. of $\text{Mn}_3\text{O}_4 = 4$

$\therefore$ Meq. of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O} = 4$

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

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

$$\therefore \frac{w \times 2}{3 \times 223} \times 1000 = 4 \quad \therefore w = 1.338 \text{ g}$$

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

Meq. of H_2SO_4 + Meq. of $\text{H}_2\text{C}_2\text{O}_4$ = Meq. of NaOH

$$a + b = 35.5 \times \frac{1}{10} = 3.55 \quad \dots(1)$$

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

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

$\therefore$ Meq. of $\text{H}_2\text{SO}_4 = a$ and Meq. of oxalic acid (in 25 mL) = $b = 2.345$

$$= 3.55 - 2.345 = 1.205 \quad N_{\text{H}_2\text{C}_2\text{O}_4} = \frac{2.345}{25} = 0.0938$$

$$\begin{aligned}\therefore N_{\text{H}_2\text{SO}_4} &= \frac{1.205}{25} = 0.0482 \\ \text{and Strength} &= N \times E = 0.0482 \times 49 = 2.362 \text{ g litre}^{-1} \\ \text{Strength} &= N \times E = 0.0938 \times 63 = 5.909 \text{ g litre}^{-1}\end{aligned}$$

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

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

Now Meq. of MnO_2 = Meq. of HCl

$$= \text{Meq. of Cl}_2 \text{ formed} = \frac{1.78}{11.2} \times 1000 = 158.93$$

($\therefore$ Eq. mass of $\text{Cl}_2 = M/2$; $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2e$)

$\therefore$ Meq. of $\text{HCl} = 158.93$

$$N \times V = 158.93$$

$$\therefore V = \frac{158.93}{1.315} = 120.85 \text{ mL}$$

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

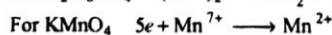
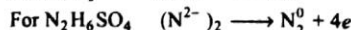
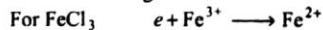
$$= 2 \times 120.85 = 241.7 \text{ mL}$$

Also Meq. of $\text{MnO}_2 = 158.93$

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

$\therefore$ Mass of $\text{MnO}_2 = 6.9134 \text{ g}$

35. The redox changes are:



Meq. of $N_2H_6SO_4$ in 10 mL solution
 = Meq. of $FeCl_3$ reacting with $N_2H_6SO_4$
 = Meq. of Fe^{2+} formed = Meq. of $KMnO_4$
 $\therefore$ Meq. of $N_2H_6SO_4$ in 10 mL solution = $20 \times \frac{1}{50} \times 5 = 2$
 $\therefore \frac{w}{M/4} \times 1000 = 2$
 $(\because \text{Molar mass of } N_2H_6SO_4 = 130)$

$\therefore w = \frac{2 \times 130}{4000} = 0.065$
 $\therefore$ Mass of $N_2H_6SO_4$ in 10 mL = 0.065 g
 $\therefore$ 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
 $2e + (Fe^{3+})_2 \longrightarrow 2Fe^{2+}$
 $Fe^{2+} \longrightarrow Fe^{3+} + e$
 Oxidant + ne $\longrightarrow$ Reductant

Meq. of Fe_2O_3 in 25 mL
 = Meq. of Fe^{3+} in Fe_2O_3 = Meq. of Fe^{2+} formed
 = 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 = $17 \times 0.0167 \times n \times \frac{100}{25}$

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

$\therefore$ Molar mass of $Fe_2O_3 = 160$
 $\therefore \frac{1 \times 55.2 \times 2 \times 1000}{100 \times 160 \times 17 \times 0.0167 \times 4} = 6$

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

37. Redox changes are:

For $CuFeS_2$ $e + Fe^{3+} \longrightarrow Fe^{2+}$
 For $K_2Cr_2O_7$ $6e + (Cr^{6+})_2 \longrightarrow 2Cr^{3+}$
 $Fe^{2+} \longrightarrow Fe^{3+} + e$

$\therefore$ Meq. of $CuFeS_2$ = Meq. of Fe^{2+} = Meq. of $K_2Cr_2O_7$
 = $42 \times 0.01 \times 6 = 2.52$

$\therefore \frac{w}{183.5/1} \times 1000 = 2.52$
 $(\because \text{Molar mass of } CuFeS_2 = 183.5)$

$\therefore$ Mass of $CuFeS_2 = 0.4624$ g
 $\therefore$ % of $CuFeS_2 = \frac{0.4624 \times 100}{0.5} = 92.48\%$

38. Let mass of $H_2C_2O_4 = a$ g in 1 litre
 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
 = 3×0.1

$\therefore$ Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in one litre
 = $3 \times 0.1 \times 100 = 30$

$$\therefore \frac{a}{45} \times 1000 + \frac{b}{112/1} \times \frac{1}{1000} = 30$$

$$\therefore \frac{1000a}{45} + \frac{1000b}{112} = 30 \dots (1)$$

$$\begin{aligned} \text{E of } H_2C_2O_4 &= \frac{M}{2} \\ &= \frac{90}{2} = 45 \\ \text{E of } NaHC_2O_4 &= \frac{M}{1} \\ &\quad (\text{as acid salt}) \\ &= \frac{112}{1} = 112 \end{aligned}$$

For redox change: $C_2^{3+} \longrightarrow 2C^{4+} + 2e$
 $5e + Mn^{7+} \longrightarrow Mn^{2+}$

Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in 10 mL = 4×0.1
 $\therefore$ Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in 1 litre
 = $4 \times 0.1 \times 100 = 40$

$$\therefore \frac{a}{45} \times 1000 + \frac{b}{112/2} \times \frac{1}{1000} = 40$$

$$\therefore \frac{1000a}{45} + \frac{2000b}{112} = 40 \dots (2)$$

$$\therefore \text{Eq. mass of } H_2C_2O_4 = \frac{M}{2}$$

$$\text{and Eq. mass of } NaHC_2O_4 \text{ (as reductant)} = \frac{M}{2}$$

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

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

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

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 $n_1e + Mn^{7+} \longrightarrow Mn^{2+} \therefore n_1 = 7 - a$

Neutral medium $n_2e + Mn^{7+} \longrightarrow Mn^{4+} \therefore n_2 = 7 - b$

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

$\therefore$ Meq. of reducing agent = Meq. of $KMnO_4$ in acid
 = Meq. of $KMnO_4$ in neutral
 = Meq. of $KMnO_4$ in alkali
 $= 1 \times n_1 \times 20 = 1 \times n_2 \times 33.3 = 1 \times n_3 \times 100$
 $n_1 = 1.665 \quad n_2 = 5n_3$

$\therefore n_1, n_2, n_3$ are integers and $n_1 \geq 7, \therefore n_3 = 1$

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

Therefore, different oxidation states of Mn are:

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

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

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

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

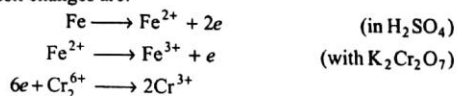
Meq. of reducing agent = Meq. of $K_2Cr_2O_7$

$20 \times 5 = 1 \times 6 \times V \therefore 6e + Cr_2^{6+} \longrightarrow 2Cr^{3+}$

$\therefore V = \frac{100}{6} = 16.67 \text{ mL} \therefore N = M \times \text{Valence factor}$

Note: The conditions are valid only when Mn in each medium exist as monomeric atom, i.e., not as Mn_2 .

40. Redox changes are:



$$\begin{aligned} \text{Meq. of Fe}^{2+} \text{ in 20 mL} &= \text{Meq. of } \text{K}_2\text{Cr}_2\text{O}_7 \\ &= 30 \times \frac{1}{30} = 1 \end{aligned}$$

$$\therefore \text{Meq. of Fe}^{2+} \text{ of valence factor one in 100 mL} = \frac{1 \times 100}{20} = 5$$

$$\therefore \text{Meq. of Fe}^{2+} \text{ of valence factor two in 100 mL} = 5 \times 2 = 10$$

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

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

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

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

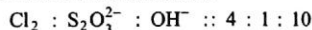
$$\therefore \% \text{ of Fe in wire} = \frac{0.28}{0.2828} \times 100 = 99.0\%$$

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



Mole	0.15	0.01	0.30	0	0	0
before reaction						
Mole (0.15 - 4 × 0.01)	0	(0.3 - 0.01 × 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

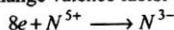


$\therefore [\text{OH}^-] \text{ left after reaction is 0.2 mole.}$

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 $\text{NH}_3 = 1$. (an acid-base reaction)

In redox change valence factor of NH_3 is 8;



Thus, Meq. of NH_3 for valence factor 8 = 8×4.29

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

$$\therefore N_{\text{NO}_3} = \frac{34.32}{25} = 1.37 \quad (N \times V \text{ in mL} = \text{Meq.})$$

$$\text{Also, } M_{\text{NO}_3} = \frac{1.37}{8} = 0.1716 \quad (N = M \times V \text{ factor})$$

- 43.
- $2\text{NaClO}_2 + \text{Cl}_2 \longrightarrow 2\text{NaCl} + 2\text{ClO}_2$

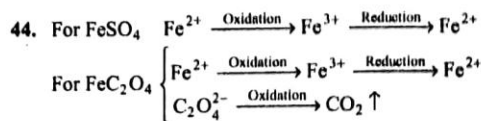
$$\text{Thus, mole ratio of } \frac{\text{NaClO}_2}{\text{ClO}_2} = \frac{2}{2}$$

Also mole of $\text{NaClO}_2 = 2 \times 3.78$ (Mole = $M \times V_{\text{in L}}$)

$$\therefore \text{Mole of } \text{ClO}_2 = 2 \times 3.78$$

Further % yield of the reaction = 97%

$$\begin{aligned} \therefore \text{Mole of } \text{ClO}_2 \text{ actually formed} &= \frac{2 \times 3.78 \times 97}{100} \\ &= 7.33 \text{ mol} \end{aligned}$$



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

$$\begin{aligned} \therefore \text{Meq. of } \text{Fe}^{2+} + \text{Meq. of } \text{Fe}^{2+} + \text{Meq. of } \text{C}_2\text{O}_4^{2-} &= \text{Meq. of } \text{KMnO}_4 \text{ used} \\ \text{in } \text{FeSO}_4 \quad \text{in } \text{FeC}_2\text{O}_4 \quad \text{in } \text{FeC}_2\text{O}_4 \quad \text{KMnO}_4 \text{ used} \\ a \times 1 + b \times 1 + b \times 2 &= 40 \times \frac{1}{15} = \frac{8}{3} \end{aligned}$$

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

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

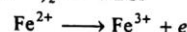
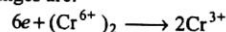
$$\begin{aligned} \therefore \text{Meq. of } \text{Fe}^{2+} \text{ of } \text{FeSO}_4 + \text{Meq. of } \text{Fe}^{2+} \text{ of } \text{FeC}_2\text{O}_4 &= \text{Meq. of } \text{KMnO}_4 \text{ used} \\ a \times 1 + b \times 1 &= 25 \times \frac{1}{15} = \frac{5}{3} \end{aligned}$$

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

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

$$\therefore \text{Ratio of Fe in } \text{FeSO}_4 \text{ and } \text{FeC}_2\text{O}_4 = \frac{a}{b} = \frac{7}{3}$$

45. Redox changes are:



$$\begin{aligned} \text{Meq. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ in 1 mL} &= \text{Meq. of Fe} \\ &= \frac{0.006}{56} \times 1000 = \frac{6}{56} \end{aligned}$$

$$\begin{aligned} \therefore \text{Meq. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ in 15.05 mL} &= \frac{6}{56} \times 15.05 = 1.612 \end{aligned}$$

$$\therefore \text{Meq. of } \text{Fe}^{2+} \text{ left unused} = \text{Meq. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ used} = 1.612$$

$$\begin{aligned} \text{Now Meq. of ferrous ammonium sulphate added} &= 50 \times 0.12 = 6 \\ \text{Meq. of ferrous ammonium sulphate left unused} &= 1.612 \end{aligned}$$

$$\begin{aligned} \therefore \text{Meq. of ferrous ammonium sulphate used for sample} &= 6 - 1.612 = 4.388 \end{aligned}$$

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

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

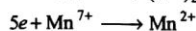
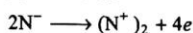
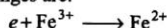
$$\therefore \% \text{ Cr} = \frac{0.0761}{0.5} \times 100 = 15.20\%$$

$$\text{Also Meq. of } \text{Cr}_2\text{O}_3 = 4.388 \text{ or } \frac{w}{E} \times 1000 = 4.388$$

$$w_{\text{Cr}_2\text{O}_3} = \frac{4.388 \times 152}{6 \times 1000} = 0.1112 \text{ g } \left(\because E_{\text{Cr}_2\text{O}_3} = \frac{152}{6} \right)$$

$$\therefore \% \text{ Cr}_2\text{O}_3 = \frac{0.1112}{0.5} \times 100 = 22.23\%$$

46. Redox changes are:

Meq. of Fe^{2+} formed by NH_2OH in 50 mL dilute solution

$$= \text{Meq. of } \text{KMnO}_4 \text{ used} = 12 \times 0.02 \times 5 = 1.2$$

 $\therefore$ 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

$$= \text{Meq. of } \text{NH}_2\text{OH} \text{ in } 1000 \text{ mL dilute solution} = 24$$

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

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

$$w_{\text{NH}_2\text{OH}} = 0.396 \text{ g}$$

 $\therefore$ Mass of NH_2OH in 10 mL original solution = 0.396 g $\therefore$ Mass of NH_2OH in 1 litre original solution

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

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

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

[Eq. mass of $\text{NaIO}_3 = M/6$; because $\text{I}^{5+} + 6e \longrightarrow \text{I}^-$]

$$\text{Meq. of } \text{NaHSO}_3 = 175.76$$

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

$$\therefore w_{\text{NaHSO}_3} = \frac{175.76 \times 104}{2000} = 9.14 \text{ g}$$

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

$$\therefore N \times V = \frac{175.76}{6}$$

$$\text{or } \frac{5.8}{198/5} \times V = \frac{175.76}{6} \therefore V_{\text{NaIO}_3} = 200 \text{ mL}$$

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

$$= 27 \times 0.12$$

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

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

 $(\because Y \text{ is replaceable H-atom } \therefore E_{\text{salt}} = M/Y)$

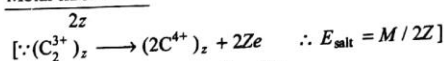
Also Meq. of oxalate salt as reductant in 30 mL

$$= \text{Meq. of } \text{KMnO}_4 \text{ used} = 36 \times 0.12$$

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

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

$$\text{or } \frac{9.15}{\text{Molar mass of salt}} \times 1000 = \frac{36 \times 0.12 \times 1000}{30} \quad \dots (2)$$

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

$$4Y = 6Z \quad \dots (3)$$

Also, Total cationic charge = total anionic charge

$$\therefore X + Y = 2Z \quad \dots (4)$$

By Eqs. (3) and (4), $X : Y : Z :: 1 : 3 : 2$

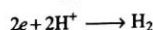
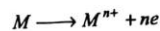
These are in simplest ratio.

 $\therefore$ Molecular formula is $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$.

$$\text{Now Molar mass of salt} = 39 + 3 + 176 + 18n = 218 + 18n$$

 $\dots (5)$ By Eq. (1) and putting, $Y = 3$

$$M = 254.16 \quad \dots (6)$$

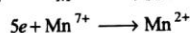
 $\therefore$ By Eqs. (5) and (6), $n = 2$ $\therefore$ Oxalate salt is $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ 49. Metal is M  $\therefore$ Meq. of metal or Meq. of M^{n+} = Meq. of H_2

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

 $(\because 11200 \text{ mL } \text{H}_2 = 1 \text{ equivalent})$

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

$$\therefore n = 2$$

Now $M^{2+} \longrightarrow M^{a+} + (a-2)e$  $\therefore$ Meq. of M^{2+} = Meq. of KMnO_4

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

 $\therefore$ Different oxidation states of metal are 2 and 5.50. For the reaction: $\text{Fe} + \text{Fe}_2(\text{SO}_4)_3 \longrightarrow 3\text{FeSO}_4$ $\therefore 964 \text{ g } \text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ gives 3

$$\times 152 \text{ g } \text{FeSO}_4$$

 $\therefore 1.25 \text{ g } \text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ gives

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

$$= 0.5913 \text{ g } \text{FeSO}_4$$

 FeSO_4 formed is now oxidized by KMnO_4 $\therefore$ Meq. of FeSO_4 = Meq. of KMnO_4

$$\frac{0.5913}{152/1} \times 1000 = 0.107 \times V \therefore V = 36.36 \text{ mL}$$

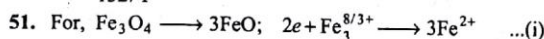
Similarly, if Cu is used

 $\therefore 964 \text{ g salt gives} = 2 \times 152 \text{ g } \text{FeSO}_4$

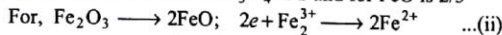
$$\therefore 1.25 \text{ g salt gives} = \frac{2 \times 152 \times 1.25}{964} \text{ g} = 0.3942 \text{ g } \text{FeSO}_4$$

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

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



Thus, valence factor for Fe_3O_4 is 2 and for FeO is 2/3



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.

$$\therefore \text{Meq. of } \text{Fe}_3\text{O}_4 + \text{Meq. of } \text{Fe}_2\text{O}_3$$

$$= \text{Meq. of } \text{I}_2 \text{ liberated} = \text{Meq. of hypo used}$$

$$a + b = \frac{11 \times 0.5 \times 100}{20} = 27.5 \quad \dots \text{(iii)}$$

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

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

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

$$\text{Meq. of } \text{Fe}^{2+} \text{ (from } \text{Fe}_2\text{O}_3) =$$

$$= \text{Meq. of } \text{KMnO}_4 \text{ used}$$

$$\left[\begin{array}{l} \text{If valence factor for } \text{Fe}^{2+} \text{ is } 2/3 \text{ from Eq. (1),} \\ \text{then Meq. of } \text{Fe}^{2+} \text{ (from } \text{Fe}_3\text{O}_4) = a \\ \text{If valence factor for } \text{Fe}^{2+} \text{ is 1 then Meq. of } \text{Fe}^{2+} \\ \text{(from } \text{Fe}_2\text{O}_3) = 3a/2 \\ \text{Similarly, from Eq. (ii), Meq. of } \text{Fe}^{2+} \text{ from } \text{Fe}_2\text{O}_3 = b \end{array} \right]$$

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

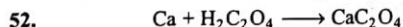
$$\text{or } 3a + 2b = 64 \quad \dots \text{(iv)}$$

From Eqs. (iii) and (iv),

$$\begin{array}{l} \text{Meq. of } \text{Fe}_3\text{O}_4 = a = 9 \\ \text{and Meq. of } \text{Fe}_2\text{O}_3 = b = 18.5 \\ \therefore w_{\text{Fe}_3\text{O}_4} = \frac{9 \times 232}{2 \times 1000} = 1.044 \text{ g} \\ w_{\text{Fe}_2\text{O}_3} = \frac{18.5 \times 160}{2 \times 1000} = 1.48 \text{ g} \end{array}$$

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

$$\text{and } \% \text{ of } \text{Fe}_2\text{O}_3 = \frac{1.48 \times 100}{3} = 49.33$$



The Meq. of $\text{H}_2\text{C}_2\text{O}_4$ solution added to precipitate Ca as CaC_2O_4 is derived as:

25 mL of $\text{H}_2\text{C}_2\text{O}_4$ is diluted 4 folds, i.e., to 100 mL

Now Meq. of dil. $\text{H}_2\text{C}_2\text{O}_4$ in 25 mL

$$= \text{Meq. of } \text{KMnO}_4 \text{ used} \\ = 24.1 \times 0.1025 = 2.47025$$

$$\therefore \text{Meq. of } \text{H}_2\text{C}_2\text{O}_4 \text{ in 100 mL dilute solution} \\ = \frac{2.47025 \times 100}{25} = 9.881$$

$$\therefore \text{Meq. of } \text{H}_2\text{C}_2\text{O}_4 \text{ in 25 mL conc. solution} = 9.881$$

Meq. of $\text{H}_2\text{C}_2\text{O}_4$ left after precipitation of $\text{Ca}_2\text{C}_2\text{O}_4$ in one fourth filtrate

$$= \text{Meq. of } \text{KMnO}_4 \text{ used} = 5 \times 0.1025$$

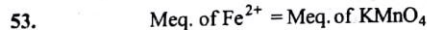
$$\therefore \text{Total Meq. of } \text{H}_2\text{C}_2\text{O}_4 \text{ left} = 5 \times 0.1025 \times 4 = 2.05$$

$$\therefore \text{Meq. of } \text{H}_2\text{C}_2\text{O}_4 \text{ used for Ca} = 9.881 - 2.05 = 7.831$$

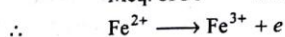
$$\therefore \text{Meq. of Ca} = 7.831$$

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

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

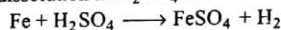


$$\text{Meq. of } \text{Fe}^{2+} = 47.2 \times 0.112 = 5.2864$$



$$\therefore \text{Meq. of } \text{Fe}^{2+} = 5.2864 \quad (\text{valence factor} = 1)$$

Fe ore on dissolution in H_2SO_4 show valence factor 2

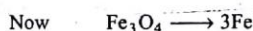


$$\therefore \text{Meq. of } \text{Fe}^{2+} \text{ of valence factor 2} = 5.2864 \times 2$$

$$\therefore \text{Meq. of Fe} = 5.2864 \times 2$$

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

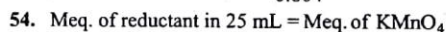
$$\therefore \% \text{ purity of Fe} = \frac{0.296 \times 100}{0.804} = 36.82\%$$



3 × 56 g Fe is obtained from 232 g Fe_3O_4

$$\therefore 0.296 \text{ g Fe is obtained} = \frac{232 \times 0.296}{56 \times 3} = 0.409 \text{ g } \text{Fe}_3\text{O}_4$$

$$\therefore \% \text{ of } \text{Fe}_3\text{O}_4 = \frac{0.409}{0.804} \times 100 = 50.87\%$$



$$= 20 \times 0.01 \times 5$$

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

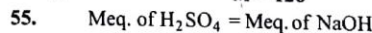
Reductant shows the change $A_2^{+a} \longrightarrow 2A^{+b} + 2e$

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

$$\therefore \text{Meq. of reductant} = 40$$

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

$$\therefore M = 126$$



$$N \times 10.27 = 10.35 \times 0.1297 \therefore N_{\text{H}_2\text{SO}_4} = 0.1307$$

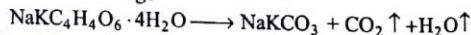
$$V_{\text{H}_2\text{SO}_4} \text{ used for } \text{KNaCO}_3 = 41.72 - 1.91 \text{ mL}$$

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

$$- \text{Meq. of } \text{H}_2\text{SO}_4 \text{ used by NaOH}$$

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

Also for the change



Now Meq. of NaKCO_3 using valency factor 2 during its neutralization with H_2SO_4 = 5.2050

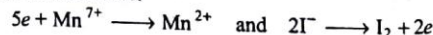
$$\therefore \text{Mass of } \text{NaKCO}_3 = \frac{5.2050 \times 122}{2 \times 1000} = 0.3175 \text{ g}$$

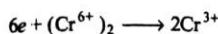
$\therefore$ For 1:1 mole ratio of conversion, mass of Rochelle salt

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

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

56. The reactions are:





Let mass of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ be a and b g respectively.

$\therefore$ Meq. of KMnO_4 + Meq. of $\text{K}_2\text{Cr}_2\text{O}_7$ = Meq. of I_2
= Meq. of hypo = 60×0.1

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

Also given $a + b = 0.24 \quad \dots(ii)$

$$\therefore \begin{aligned} a &= 0.098 \text{ g} & \text{i.e., mass of } \text{KMnO}_4 \\ b &= 0.142 \text{ g} & \text{i.e., mass of } \text{K}_2\text{Cr}_2\text{O}_7 \end{aligned}$$

$$\text{Also, mass of Mn in } 0.098 \text{ g } \text{KMnO}_4 = \frac{55 \times 0.098}{158}$$

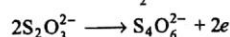
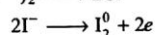
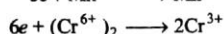
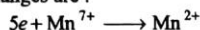
$$= 0.034 \text{ g}$$

$$\text{Mass of Cr in } 0.142 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{52 \times 2 \times 0.142}{294} = 0.050 \text{ g}$$

$$\therefore \% \text{ of Mn in sample} = \frac{0.034 \times 100}{0.24} = 14.17\%$$

$$\therefore \% \text{ of Cr in sample} = \frac{0.050 \times 100}{0.24} = 20.83\%$$

57. The redox changes are :



Let $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 be a and b g respectively

$$\therefore a + b = 0.5 \quad \dots(1)$$

Further Meq. of KMnO_4 + Meq. of $\text{K}_2\text{Cr}_2\text{O}_7$

= Meq. of KI = Meq. of I_2 liberated = Meq. of $\text{Na}_2\text{S}_2\text{O}_3$

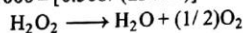
$$\frac{a}{294/6} \times 1000 + \frac{b}{158/5} \times 1000 = 100 \times 0.15 \dots(2)$$

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

$\therefore$ % of $\text{K}_2\text{Cr}_2\text{O}_7$ = 14.6% and % of KMnO_4 = 85.4%

58. Meq. of H_2O_2 = Meq. of I_2

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



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

$\therefore$ 0.068 g gives $(11.2 \times 0.068) / 34 = 22.4 \text{ mL } \text{O}_2$

$\therefore$ Volume strength of H_2O_2 = $22.4 / 5 = 4.48\%$

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

$$\therefore m = a + 16 \quad \dots(1)$$

$$\text{and } n = 2a + 48 \quad \dots(2)$$

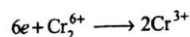
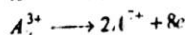
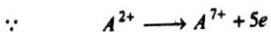
where a is Atomic mass of A .

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

$$\text{Then } X + Y = 2.198 \quad \dots(3)$$

Also Meq. of AO + Meq. of A_2O_3 = Meq. of $\text{K}_2\text{Cr}_2\text{O}_7$

$$\frac{X}{(a+16)/5} \times 1000 + \frac{Y}{(2a+48)/8} \times 1000 = 0.015 \times 6 \times 1000 \quad \dots(4)$$



$$\therefore \text{By Eq. (4), } \frac{5X}{a+16} + \frac{8Y}{2a+48} = 0.09 \quad \dots(5)$$

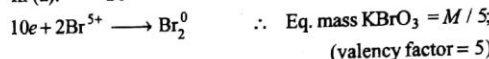
Also, mole AO_4^- by AO + mole of AO_4^- by A_2O_3 = 0.0187

$$\frac{X}{a+16} + \frac{2Y}{2a+48} = 0.0187 \quad \dots(6)$$

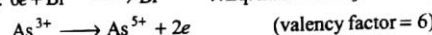
$\therefore$ Mole ratio of $\text{AO} : \text{AO}_4^- :: 1 : 1$, $\text{A}_2\text{O}_3 : \text{AO}_4^- :: 1 : 2$

Solving Eqs. (3), (5) and (6) $a = 100$

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



In (b): $6e + \text{Br}^{5+} \longrightarrow \text{Br}^{1-} \quad \therefore \text{Eq. mass } \text{KBrO}_3 = M/6;$



Let Meq. of BrO_3^- of valency factor 6 = Meq. of AsO_2^-

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

Meq. of BrO_3^- of valency factor 5 added

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

$$\text{Left Meq. of } \text{BrO}_3^- \text{ of valency factor } 5 = \frac{0.408 \times 5}{6} = 0.34$$

$$\therefore \text{Meq. of } \text{BrO}_3^- \text{ used for } \text{SeO}_3^{2-} = 1.67 - 0.34 = 1.33$$

$$\therefore \text{Meq. of } \text{SeO}_3^{2-} = 1.33 \quad \text{or } \frac{w}{127/2} \times 1000 = 1.33$$

$$\therefore w_{\text{SeO}_3^{2-}} = 0.084 \text{ g}$$

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

$$\text{or } a = 1.005 \quad \dots(1)$$

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

$$\text{or } a + b = \frac{1.1113}{248} \times 1000 \quad \text{or } a + b = 4.481 \quad \dots(2)$$

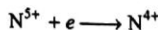
By Eqs. (1) and (2), $b = 4.481 - 1.005 = 3.476$

$$\therefore \text{Mass of } \text{As}_2\text{O}_3 = \frac{\text{Meq.} \times \text{Eq. mass}}{1000} = \frac{1.005 \times 198}{4 \times 1000} = 0.0497 \text{ g}$$

$$\text{and Mass of } \text{As}_2\text{O}_5 = \frac{3.476 \times 230}{4 \times 1000} = 0.1999 \text{ g}$$

$$\therefore \text{Mass of mixture} = 0.0497 + 0.1999 = 0.2496 \text{ g}$$

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



- $\therefore \text{Eq. of Cu} = \text{Eq. of NO}_2$

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

$$\left(\because \text{mole of NO}_2 = \text{Eq. of NO}_2 = \frac{PV}{RT} \right)$$

$$\therefore w_{\text{Cu}} = 1.35 \text{ g}$$

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

$$\therefore \% \text{ of Cu} = \frac{1.35}{1.5} \times 100 = 90\%$$

$$\therefore \% \text{ of Zn} = \frac{0.15}{1.5} \times 100 = 10\%$$
- (b) Thus, 1 g brass contains 0.9 g Cu and 0.1 g Zn
- | | |
|--|--|
| $\therefore \text{Meq. of HNO}_3$
$= \text{Meq. of Zn}$
or
$3 \times 8 \times V_1 = \frac{0.1}{65/2} \times 1000$
$\therefore V_1 = 0.128 \text{ mL}$
$(\because \text{N}^{5+} + 8e \rightarrow \text{N}^{3+})$ | and Meq. of HNO_3
$= \text{Meq. of Cu}$
or
$3 \times V_2 = \frac{0.9}{63.6/2} \times 1000$
$\therefore V_2 = 9.43 \text{ mL}$ |
|--|--|
- $\therefore \text{Total volume of HNO}_3 \text{ used} = 0.128 + 9.43 = 9.558 \text{ mL}$
63. Meq. of alkali added = $30 \times 0.04 = 1.2$
 Meq. of alkali left = $22.48 \times 0.024 = 0.54$
 $\therefore \text{Meq. of alkali used for SO}_2 \text{ and H}_2\text{O}_2$
 $= 1.2 - 0.54 = 0.66$
 $\therefore \text{Mass of alkali used} = \frac{0.66 \times 40}{1000} = 0.0264 \text{ g}$
 $\therefore 80 \text{ g NaOH reacts with } 64 \text{ g SO}_2$
 $\therefore 0.0264 \text{ g NaOH reacts} = \frac{64 \times 0.0264}{80} = 0.021 \text{ g SO}_2$
 Now $\therefore 64 \text{ g SO}_2 \text{ required} = 32 \text{ g S}$
 $\therefore 0.021 \text{ g SO}_2 \text{ required} = \frac{32 \times 0.021}{64} = 0.0105 \text{ g}$
 $\therefore \% \text{ of S} = \frac{0.0105}{5.6} \times 100 = 0.1875\%$
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
 $= \text{Meq. of iron sulphate oxidized}$
 $= \text{Meq. of ferric sulphate used by Cu}$
 $= \text{Meq. of Cu}$
 $\therefore \text{Meq. of Cu} = \text{Meq. of KMnO}_4 \text{ used}$

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

 $\therefore n = 2 \text{ (integer)}$
 It is thus, clear that during reduction of Fe^{3+} , Cu is oxidized to Cu^{2+} . Thus reaction is:

$$\text{Cu} + \text{Fe}_2(\text{SO}_4)_3 \longrightarrow \text{CuSO}_4 + 2\text{FeSO}_4$$
65. The reactions are

$$\text{H}_2\text{O} + 2\text{KI} + \text{O}_3 \longrightarrow 2\text{KOH} + \text{I}_2 + \text{O}_2$$

 Also $2e + \text{I}_2 \longrightarrow 2\text{I}^-$
 and $2(\text{S}^{2+})_2 \longrightarrow (\text{S}^{5/2+})_4 + 2e$

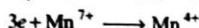
- $\therefore \text{Meq. of I}_2 = \text{Meq. of Na}_2\text{S}_2\text{O}_3 = 1.5 \times 0.01 = 1.5 \times 10^{-2}$
 or $\text{mM of I}_2 = \frac{1.5 \times 10^{-2}}{2} = 7.5 \times 10^{-3}$
 $\therefore \text{mM of O}_3 = \text{mM of I}_2 = 7.5 \times 10^{-3}$
 $(\because \text{Mole ratio of O}_3 : \text{I}_2 :: 1:1)$
 $\therefore P'_{\text{O}_3} = \frac{nRT}{V} = \frac{7.5 \times 10^{-6} \times 0.0821 \times 300}{10}$
 $= 184.725 \times 10^{-7} \text{ atm}$
 $\therefore \text{Vol. \% of O}_3 = 184.725 \times 10^{-7} \times 100 = 1.847 \times 10^{-3}\%$
66.
$$\text{O}_3 + 2\text{KI} + \text{H}_2\text{O} \longrightarrow 2\text{KOH} + \text{I}_2 + \text{O}_2$$

$$\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$$

 $\therefore \text{Millimole of O}_3 = \text{Millimole of I}_2$
 $= \frac{1}{2} \times \text{mM of Na}_2\text{S}_2\text{O}_3$
 $(\text{mM} = M \times V_{\text{in mL}})$
 $= \frac{1}{2} \times 40 \times \frac{1}{10} = 2 \text{ mM} = 0.002 \text{ mole}$
 Total millimole of O_2 and O_3 in mixture are calculated from
 $PV = nRT$
 $1 \times 1 = n \times 0.0821 \times 273 \therefore n = 0.044 \text{ mole}$
 $\therefore \text{Mole of O}_2 = 0.044 - 0.002 = 0.042$
 Now $\text{mass of O}_2 = 0.042 \times 32 \text{ g} = 1.344 \text{ g}$
 $\text{mass of O}_3 = 0.002 \times 48 \text{ g} = 0.096 \text{ g}$
 $\therefore \% \text{ of O}_3 = \frac{0.096}{1.44} \times 100 = 6.7\%$
 No. of photon or molecules of ozone
 $= \frac{0.096 \times 6.023 \times 10^{23}}{48} = 1.2 \times 10^{21}$
67. Meq. of MnO_4^- added = $200 \times 0.75 \times 5 = 750$
 $\therefore \text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+} \therefore N = M \times 5$
 Meq. of MnO_4^- left unused = Meq. of Fe^{2+} used
 $= 175 \times 1 \times 1 = 175$
 $\therefore \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e \therefore N = M \times 1$
 Now Meq. of MnO_4^- used = $750 - 175 = 575$
 MnO_4^- is used for Cu_2S and CuS to give.
 For Cu_2S : $\text{Cu}_2^{+} \longrightarrow 2\text{Cu}^{2+} + 2e$
 $\text{S}^{2-} \longrightarrow \text{S}^{4+} + 6e$
 $\text{Cu}_2\text{S} \longrightarrow 2\text{Cu}^{2+} + \text{S}^{4+} + 8e$
 For CuS : $\text{S}^{2-} \longrightarrow \text{S}^{4+} + 6e$
 Let Cu_2S and CuS be a and b g respectively
 $\therefore a + b = 10 \dots (1)$
 $\therefore \text{Meq. of MnO}_4^- \text{ used} = \text{Meq. of Cu}_2\text{S} + \text{Meq. of CuS}$

$$575 = \frac{a}{159.2/8} \times 1000 + \frac{b}{95.6/6} \times 1000 \dots (2)$$

 $\therefore \text{Solving Eqs. (1) and (2), } a = 4.206 \text{ g}$
 $b = 5.794 \text{ g}$
 $\therefore \% \text{ of CuS in mixture} = \frac{5.794}{10} \times 100 = 57.94\%$

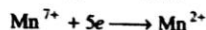
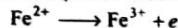


$$\text{Meq. of KMnO}_4 \text{ added} = 50 \times 0.33 \times 3 = 49.5$$

$$(\text{v.f. of KMnO}_4 = 3)$$

Meq. of KMnO_4 (v.f. = 5) left after reaction with NaCN

$$= \text{Meq. of FeSO}_4 \text{ used} = 500 \times 0.06 \times 1 = 30$$



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

$$\therefore \text{Meq. of NaCN in sample} = 49.5 - 18 = 31.5$$

$$\frac{w}{49/2} \times 1000 = 31.5$$

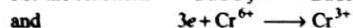
$$\therefore w = 0.7718 \text{ g}$$

$$\therefore \% \text{ of NaCN} = 77.18$$

69. Suppose mass of BaCO_3 , CaCO_3 and CaO are a , b , c be respectively.

$$a + b + c = 1.249 \quad \dots(1)$$

For the reactions $\text{BaCO}_3 \longrightarrow \text{BaCrO}_4$



$$\text{Meq. of BaCO}_3 = \text{Meq. of BaCrO}_4 = \text{Meq. of I}_2$$

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

$$\therefore a = 0.657 \text{ g} \quad \dots(2)$$

The Eq. mass of BaCrO_4 is $M/3$ and thus for BaCO_3 it should be $M/3$.

Also for acid-base reaction

$$\text{Meq. of BaCO}_3 + \text{Meq. of CaCO}_3 = \text{Meq. of CO}_2$$

$$\frac{a}{197/2} \times 1000 + \frac{b}{100/2} \times 1000 = \frac{168 \times 44}{22400 \times 22} \times 1000$$

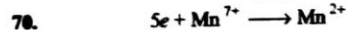
$$\therefore 200a + 394b = 295.5 \quad \dots(3)$$

$$\text{By Eqs. (2) and (3)} \quad b = 0.416 \text{ g}$$

$$\therefore \text{By Eq. (1)} \quad 0.657 + 0.416 + c = 1.249$$

$$\therefore c = 0.176$$

$$\text{or } \% \text{ of CaO} = \frac{0.176 \times 100}{1.249} = 14.09\%$$



$$\text{Thus, Meq. of KMnO}_4 = \frac{100 \times 5 \times 1000}{158} = 3164.56$$

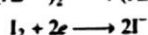
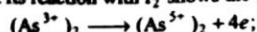
$$\text{Meq. of P}_4\text{O}_6 = \frac{100 \times 8 \times 1000}{219.9} = 3638.02$$

$$\therefore \text{Meq. of P}_4\text{O}_6 \text{ in excess} = 473.46$$

$$\therefore \frac{w \times 8 \times 1000}{219.9} = 473.46 \quad \therefore w_{\text{P}_4\text{O}_6} \text{ in excess} = 13.01 \text{ g}$$

71. As_2O_3 sample = 12.0 g. It reacts with NaHCO_3 to give

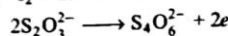
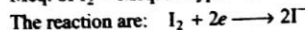
Na_3AsO_3 . Its reaction with I_2 shows the changes:



$$\text{Meq. of As}_2\text{O}_3 \text{ in 25 mL} = \text{Meq. of I}_2 = 22.4 \times N \quad \dots(1)$$

Also N of I_2 can be evaluated as:

$$\text{Meq. of I}_2 = \text{Meq. of hypo} = N \times V$$



$$N \times 25 = \frac{24.8}{248 \times 1} \times 25$$

$$\therefore N_{\text{I}_2} = \frac{N}{10}$$

$$\therefore \text{Meq. of As}_2\text{O}_3 \text{ in 25 mL} = 22.4 \times \frac{1}{10} = 2.24$$

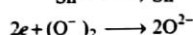
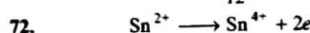
$$\text{or Meq. of As}_2\text{O}_3 \text{ in 250 mL} = 2.24 \times \frac{250}{25} = 22.4$$

$$\text{or } \frac{w}{E} \times 1000 = 22.4$$

$$\frac{w}{\frac{198}{4}} \times 1000 = 22.4$$

$$\therefore w_{\text{As}_2\text{O}_3} = \frac{22.4 \times 198}{4 \times 1000} = 1.1088$$

$$\therefore \% \text{ of As}_2\text{O}_3 = \frac{1.1088}{12} \times 100 = 9.24\%$$

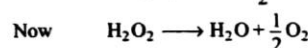


$$\text{Meq. of H}_2\text{O}_2 \text{ used} = \text{Meq. of Sn}^{2+} = 100 \times 2 \times 2 = 400$$

$$\therefore \text{Meq. of H}_2\text{O}_2 \text{ taken} = \frac{200 \times 10 \times 2 \times 1000}{100 \times 34} = 1176.47$$

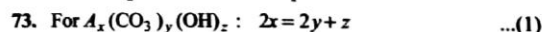
$$\therefore \text{Meq. of H}_2\text{O}_2 \text{ left} = 1176.47 - 400 = 776.47$$

$$m \text{ mole of H}_2\text{O}_2 \text{ left} = \frac{776.47}{2}$$



$$\text{or } m \text{ mole of O}_2 \text{ formed} = \frac{776.47}{2 \times 2} = 194.12$$

$$\therefore V = \frac{nRT}{P} = \frac{194.12 \times 10^{-3} \times 0.0821 \times 293}{1} = 4.67 \text{ litre}$$



The reaction of salt with H_2SO_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.

$$\text{Meq. of H}_2\text{SO}_4 = \frac{1}{2} \text{ Meq. of salt for carbonate} +$$

$$\frac{10 \times 1 \times 100}{50} = \frac{1}{2} \times \frac{1.7225 \times 1000}{\frac{M}{2y}} + \frac{1.7225 \times 1000}{\frac{M}{z}}$$

$$\text{or } 20 = \frac{1722.5y}{M} + \frac{1722.5z}{M} \quad \dots(2)$$

In case of methyl orange : Salt is completely neutralized.

$$\frac{15 \times 1 \times 100}{50} = \frac{1.7225 \times 1000}{\frac{M}{2y}} + \frac{1.7225 \times 1000}{\frac{M}{z}}$$

$$\text{or } 30 = \frac{3445y}{M} + \frac{1722.5z}{M} \quad \dots(3)$$

By subtracting Eq. (2) from Eq. (3).

$$10 = \frac{1722.5y}{M} \quad \dots(4)$$

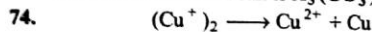
$$\text{By Eqs. (2) and (4), } 10 = \frac{1722.5z}{M} \quad \dots(5)$$

$$\therefore \text{ By Eqs. (4) and (5), } y = z \quad \dots(6)$$

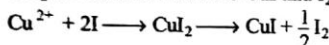
Also from Eqs. (1) and (6), $x = 1.5y$

Thus for simplest ratio $x : y : z :: 1.5 : 1 : 1$ or $3 : 2 : 2$

Therefore formula of salt is $A_3(\text{CO}_3)_2(\text{OH})_2$

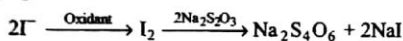


The solution after dissolution of Cu_2O in dil. H_2SO_4 contains Cu^{2+} and Cu ions. Cu^{2+} ions react with KI to give CuI_2 which is converted to CuI and I_2 .



$$\text{Millimole of KI taken} = \frac{8.3}{166} \times 1000 = 50$$

Now, KI left unused reacts with oxidizing agent to liberate I_2 again.



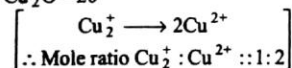
$$\therefore \text{ Millimole of KI left} = \text{Millimole of Na}_2\text{S}_2\text{O}_3 \text{ used}$$

$$(\text{mole ratio of I}^- \text{ to Na}_2\text{S}_2\text{O}_3 \text{ is } 1:1)$$

$$= 10 \times 1.0 = 10$$

Therefore, millimole of KI used for $\text{Cu}^{2+} = 50 - 10 = 40$

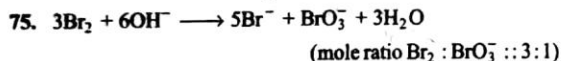
$$\therefore \text{ Millimole of Cu}_2\text{O} = 20$$



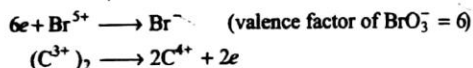
$$\text{or } \frac{w}{M} \times 1000 = 20$$

$$\frac{w \times 1000}{142} = 20 \quad \therefore w_{\text{Cu}_2\text{O}} = 2.84$$

$$\therefore \% \text{ of Cu}_2\text{O} = \frac{2.84 \times 100}{3} = 94.67$$



BrO_3^- and $\text{C}_2\text{O}_4^{2-}$ reacts to give redox change as:



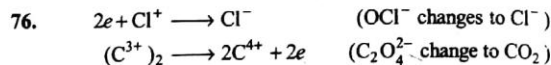
Millimole of Br_2 taken $= 10 \times 1.0 = 10$

$$\therefore \text{ Millimole of BrO}_3^- \text{ formed} = \frac{10}{3}$$

$$\text{Also, Meq. of CaC}_2\text{O}_4 = \text{Meq. of BrO}_3^- = \frac{10}{3} \times 6 = 20$$

$$\text{or } \frac{w \times 1000}{128/2} = 20 \quad \therefore w_{\text{CaC}_2\text{O}_4} = 1.28 \text{ g}$$

$$\therefore \% \text{ of CaC}_2\text{O}_4 = \frac{1.28}{1.5} \times 100 = 85.33$$



Let a and b millimole of NaOCl and CaOCl_2 be present in mixture.

$$\text{Meq. of NaOCl} + \text{Meq. of CaOCl}_2 = \text{Meq. of Na}_2\text{C}_2\text{O}_4$$

$$2a + 2b = 10 \times 0.15 \times 2 \times \frac{100}{10} = 30$$

$$\therefore 2a + 2b = 30 \quad \dots(1)$$

$$\text{Also millimole of Cl}^- \text{ from NaOCl} +$$

$$\text{millimole of Cl}^- \text{ from CaOCl}_2$$

$$= \text{millimole of AgCl}$$

$$\text{or } a + 2b = \frac{0.287}{143.5} \times 1000 \times \frac{100}{10} = 20$$

$$a + 2b = 20 \quad \dots(2)$$

$$\text{By Eqs. (1) and (2), } a = 10, b = 5$$

$$\therefore \% \text{ of NaOCl} = 10 \times 74.5 \times 10^{-3} \times \frac{100}{2} = 37.25$$

$$\% \text{ of CaOCl}_2 = 5 \times 127 \times 10^{-3} \times \frac{100}{2} = 31.75$$

77. Equivalent of $\text{KMnO}_4 = \frac{6.32}{31.6} = 0.2$

$$\text{Equivalent of KCl} = \left[\frac{4}{74.5} \right] = 0.0537$$

$$\text{Equivalent of KBr} = \left[\frac{m}{119} \right]$$

$$\therefore 0.2 = 0.0537 + \frac{m}{119} \quad \therefore m = 17.41 \text{ g}$$

78. Let mM of Cl^- and ClO_3^- be a and b respectively

$$\therefore a + b = \text{mM of AgCl} = \frac{0.1435}{143.5} \times 1000 = 1$$

Also, Meq. of $\text{KClO}_3 = 6a \quad \therefore 6e + \text{Cl}^{5+} \longrightarrow \text{Cl}^-$

and Meq. of FeSO_4 used for KClO_3

$$= 30 \times 0.2 - 37.5 \times 0.08 = 6 - 3 = 3$$

$$\therefore 6a = 3$$

$$\therefore a = \frac{1}{2} \text{ and } b = \frac{1}{2}$$

$$\text{i.e., } 5 \times 10^{-3} \text{ mole each, (1:1)}$$

79. Meq. of $\text{KMnO}_4 = \text{Meq. of ReO}_4^{1-} = \text{Meq. of Re}$

$$1145 \times 0.05 = \text{Meq. of ReO}_4^{1-} = \text{Meq. of Re}$$

$$\therefore \text{ Meq. of Re from Re}^{n+} \text{ to ReO}_4^{1-} = 0.5725$$

$$\text{or } \frac{26.83 \times 10^{-3}}{186.2/(7-n)} \times 1000 = 0.5725$$

$$\therefore 7 - n = \frac{0.5725 \times 186.2}{26.83 \times 10^{-3} \times 1000} = 4 \quad \therefore n = 3$$

$\therefore$ Oxidation state is Re^{3+} .

● SINGLE INTEGER ANSWER PROBLEMS ●

- 'n' factor of FeC_2O_4 during its oxidation by acidified KMnO_4 is
- An element A in a compound has oxidation state A^{n-} . If 1.68×10^{-3} mole of $\text{K}_2\text{Cr}_2\text{O}_7$ are required for complete oxidation of 3.26×10^{-3} mole of ABD for oxidation to A^{n-} to elemental state. The value of n is
- 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 :
- 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 0.0167M solution of an oxidant for titration. The number of electrons taken up by oxidant in the above titration is
- 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 $\frac{N}{30} \text{ K}_2\text{Cr}_2\text{O}_7$ solution for exact oxidation. The % purity (in closest value) of Fe in wire is :
- The reaction $\text{Cl}_2(\text{g}) + \text{S}_2\text{O}_3^{2-} \longrightarrow \text{SO}_4^{2-} + \text{Cl}^-$ to be carried out in basic medium. 1.5 mole of Cl_2 are allowed to react can with 0.1 mole of $\text{S}_2\text{O}_3^{2-}$ in presence of 3.0 mole of OH^- . Mole of OH^- left after the reaction is
- Equivalent mass of O_3 in the reaction : $2\text{O}_3 \longrightarrow 3\text{O}_2$ is
- 'n' factor for H_2S during its oxidation to SO_2 is
- 'n' factor for Cu_2S in the reaction

$$\text{Cu}_2\text{S} + \text{KMnO}_4 \longrightarrow \text{Cu}^{2+} + \text{SO}_2 + \text{Mn}^{2+}$$
is:
- 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
- 80 mL of $M/24 \text{ K}_2\text{Cr}_2\text{O}_7$ solution oxidises 22.4 mL H_2O_2 solution. The volume strength of H_2O_2 solution is
- 10 mL of 0.2 M solution of $\text{K}_2\text{H}(\text{C}_2\text{O}_4)_x$ requires 8 mL of 0.2 M acidified KMnO_4 solution. The value of x is
- 'n' factor for SO_2 in $\text{FeS}_2 + \text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$ is
- 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
- 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
- 'n' factor for S in SO_2 is 4 and in SO_3 is 6. The 'n' factor of S in $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3$ is
- 'n' factor of $\text{C}_2\text{H}_5\text{OH}$ in the reactions is....

$$\text{C}_2\text{H}_5\text{OH} \longrightarrow \text{CH}_3\text{CHO}$$
- 4 mole each of Hg^{2+} and I^- will form how much mole of $[\text{HgI}_4]^{2-}$
- 2.5 mole of $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ requires how much mole of KMnO_4 for its complete oxidation in acidic medium?
- 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.....
- The number of mole of $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ oxidised by 4 mole of acidified KMnO_4 is.....
- CrO_5 reacts with H_2SO_4 to give $\text{Cr}_2(\text{SO}_4)_3$, 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 .
- 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.....
- Number of H_2O_2 mole needed to convert two mole of $\text{Cr}(\text{OH})_3$ in alkaline medium to sodium chromate is.....
- 6×10^{-3} mole $\text{K}_2\text{Cr}_2\text{O}_7$ reacts completely with 9×10^{-3} mole X^{n+} to give XO_3^- and Cr^{3+} . The value of n is
- Mole of KMnO_4 required to oxidise a mixture of 2 mole each of FeSO_4 , FeC_2O_4 and $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ in acid medium.
- Mole of $\text{K}_2\text{Cr}_2\text{O}_7$ required to oxidise one mole of $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ in acid medium.
- Equivalent mass of nitrogen in the reaction :

$$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$$
is $\frac{M}{X}$. The value of X is
- 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 $\text{Na}_2\text{S}_2\text{O}_3$ solution for titration. The % of copper by mass in sample is
- 9.824 g of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x \text{H}_2\text{O}$ 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 4 mL 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.
- $$2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$$
- 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 :
- $$\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}^{2+} + \text{NO}_2(g) + \text{H}_2\text{O}$$
- $$\text{Zn} + \text{HNO}_3 \longrightarrow \text{Zn}^{2+} + \text{NH}_4^+ + \text{H}_2\text{O}$$
- The liberated $\text{NO}_2(g)$ 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 : $2\text{Mn}_2\text{O}_7 \longrightarrow 4\text{MnO}_2 + 3\text{O}_2$ 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 : $\text{As}_2\text{S}_3 + \text{HNO}_3 \longrightarrow \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4 + \text{NO}$
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]

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)

- 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
- Number of mole of $\text{K}_2\text{Cr}_2\text{O}_7$ 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
- Equivalent mass of As_2S_5 in $\text{As}_2\text{S}_5 + \text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}_2 + \text{H}_3\text{AsO}_4 + \text{H}_2\text{O}$ is :
 (a) $M/20$ (b) $M/40$
 (c) $M/10$ (d) $M/5$
- 4 mole of FeC_2O_4 are oxidised separately by acidified KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$. The mole ratio of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ is :
 (a) 6/5 (b) 5/6
 (c) 24/5 (d) 5/2n
- Which of the following is not disproportionation reaction?
 (a) $\begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array} \xrightarrow{\text{OH}^-} \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COOH} \end{array} + \begin{array}{c} \text{COO}^- \\ | \\ \text{COO}^- \end{array}$
 (b) $\text{KO}_2 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{KHCO}_3 + \text{O}_2$
 (c) $\text{KClO}_3 \longrightarrow \text{KClO}_4 + \text{KCl}$
 (d) $\text{PbO}_2 + \text{H}_2\text{O} \longrightarrow \text{PbO} + \text{H}_2\text{O}_2$
- Which of the following is intermolecular redox change?
 (a) $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
 (b) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
 (c) $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
 (d) $\text{PbO}_2 + \text{H}_2\text{O} \longrightarrow \text{PbO} + \text{H}_2\text{O}_2$
- For the reaction : $4\text{CrO}_5 + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{Cr}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} + 7\text{O}_2$, 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
- In which of the reaction oxygen is not an oxidant :
 (a) $\text{N}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{N}_2\text{O}$ (b) $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$
 (c) $\text{F}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{F}_2\text{O}$ (d) $\text{C} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}$
- The equilibrium : $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{CrO}_4^{2-} + 2\text{H}^+$ exist at $\text{pH} = 4$. The concentration of $[\text{CrO}_4^{2-}]$ at equilibrium is :
 (a) $4 \times K_c \times [\text{Cr}_2\text{O}_7^{2-}]$ (b) $2 \times \sqrt{K_c \cdot [\text{Cr}_2\text{O}_7^{2-}]}$
 (c) $10^4 \times \sqrt{K_c \times [\text{Cr}_2\text{O}_7^{2-}]}$ (d) $10^{-8} \times K_c \times [\text{Cr}_2\text{O}_7^{2-}]$
- 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
- 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 = $5.6 \times \text{molarity}$
- 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
- Titration of I_2 produced from 0.1045 g of primary standard KIO_3 required 30.72 mL of sodium thiosulphate as shown below:

$$\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$$

$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$
 The molarity of sodium thiosulphate ion is :
 (a) 0.095 (b) 0.079
 (c) 0.084 (d) 0.064
- The mass of 1 g-equivalent of V_2O_5 used in the reaction $\text{Zn} + \text{V}_2\text{O}_5 \longrightarrow \text{ZnO} + \text{V}$ is : (atomic mass of V = A)
 (a) $\frac{A}{5}$ (b) $\frac{A+80}{5}$
 (c) $\frac{2A+80}{5}$ (d) $\frac{2A+80}{10}$
- 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
- Equivalent mass of Fe_3O_4 and Fe_2O_3 in the change $\text{Fe}_3\text{O}_4 \longrightarrow \text{Fe}_2\text{O}_3$ 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) $M_1, \frac{3M_2}{2}$
- 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 to 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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ is completely oxidised by 5.5 mL of 0.1 M KMnO_4 in acid medium. The % of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 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 $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$ 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 $\text{K}_2\text{Cr}_2\text{O}_7$ 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) $\frac{5M}{3}$ (b) $\frac{3M}{5}$
 (c) $\frac{4M}{6}$ (d) $\frac{5M}{8}$
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 $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ 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) $\frac{2N_A}{10}$ (d) $\frac{5N_A}{10}$
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. 10 g 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 $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ 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) $\frac{3}{5}$ (b) $\frac{2}{5}$
 (c) $\frac{4}{5}$ (d) 1
36. 9×10^{-3} mole of X^{n+} are oxidised to $X\text{O}_3^-$ by 6×10^{-3} mole of $\text{K}_2\text{Cr}_2\text{O}_7$. If atomic mass of X is A , then equivalent mass of X^{n+} will be :
 (a) A (b) $\frac{A}{2}$
 (c) $\frac{A}{3}$ (d) $\frac{A}{4}$
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 : $\text{H}_3\text{PO}_2 \longrightarrow \text{PH}_3 + \text{H}_3\text{PO}_3$; the n factor of H_3PO_2 is :
 (a) $\frac{3}{4}$ (b) $\frac{4}{3}$
 (c) $\frac{2}{3}$ (d) $\frac{3}{2}$
39. Number of mole of KMnO_4 required for 1 mole of Hg_2S in the reaction :
 $\text{Hg}_2\text{S} + \text{MnO}_4^- + \text{H}^+ \longrightarrow \text{Hg}^{2+} + \text{SO}_4^{2-} + \text{Mn}^{2+} + \text{H}_2\text{O}$
 are same as required for the change 5 mole of :
 (a) N_2 to NO_2 (b) $\text{C}_2\text{H}_5\text{OH}$ to CH_3CHO
 (c) NO to HNO_3 (d) NH_3 to NO
40. Photosynthesis is a redox reaction *i.e.*,
 $\text{XCO}_2 + \text{XH}_2\text{O} \xrightarrow[\text{Chlorophyll}]{h\nu} (\text{CH}_2\text{O})_n + \text{XO}_2$; 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 $\text{Na}_2\text{S}_2\text{O}_3$ using $\text{K}_2\text{Cr}_2\text{O}_7$ by iodometry, the equivalent mass of $\text{K}_2\text{Cr}_2\text{O}_7$ 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) $2e + \text{Cl}_2 \longrightarrow 2\text{Cl}^- \times 3$
 (The lowest oxidation state of Cl is -1)
 $\text{Cl}_2 \longrightarrow 2\text{Cl}^{3-} + 6e$
 $4\text{Cl}_2 \longrightarrow 6\text{Cl}^- + 2\text{Cl}^{3+}$
2. (a) $6\text{Cu}_3\text{P} + 124\text{H}^+ + 11\text{Cr}_2\text{O}_7^{2-} \longrightarrow 18\text{Cu}^{2+} + 6\text{H}_3\text{PO}_4 + 22\text{Cr}^{3+} + 53\text{H}_2\text{O}$
3. (b) $(\text{As}^{5+})_2 \longrightarrow 2\text{As}^{5+}$, No redox
 $(\text{S}^{2-})_5 \longrightarrow 5\text{S}^{6+} + 40e$, $E_{\text{As}_2\text{S}_5} = M/40$
4. (a) $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e$ $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$
 $(\text{C}^{3+})_2 \longrightarrow 2\text{C}^{4+} + 2e$ $(\text{Cr}^{6+})_2 + 6e \longrightarrow 2\text{Cr}^{3+}$
 $\text{FeC}_2\text{O}_4 \longrightarrow \text{Fe}^{3+} + 2\text{C}^{4+} + 3e$
 $\therefore 4 \text{ mole FeC}_2\text{O}_4 \equiv \frac{12}{5} \text{ mole KMnO}_4$
 $\equiv 2 \text{ mole K}_2\text{Cr}_2\text{O}_7$
5. (d) It is intermolecular redox change.
6. (d) —do—
7. (a) $3e + \text{Cr}^{6+} \longrightarrow \text{Cr}^{3+}$
 $\text{O}^{-1} \longrightarrow \text{O}_2^0 + 2e$
8. (c) F_2 is oxidant and O_2 is reductant (0 to +2)
9. (c) $K_c = \frac{[\text{CrO}_4^{2-}]^2 [\text{H}^+]^2}{[\text{Cr}_2\text{O}_7^{2-}]}$
 $\therefore [\text{CrO}_4^{2-}] = \sqrt{10^8 \times [\text{Cr}_2\text{O}_7^{2-}] \times K_c}$
10. (c) $\text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} \longrightarrow \text{Fe}^{3+} + 2\text{CO}_2 + 3e$
 $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$
 $\text{Fe}^{2+} + \text{SC}_2\text{O}_4^{2-} \longrightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + e$
 Meq. of FeC_2O_4 = Meq. of KMnO_4 ,
 $1 \times 3 \times 1000 = 1 \times 5 \times V_1$
 Meq. of FeSO_4 = Meq. of KMnO_4 ,
 $1 \times 1 \times 1000 = 1 \times 5 \times V_2$
 $\therefore \frac{V_1}{V_2} = 3$
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 = $\frac{17}{56} \times \text{vol. strength}$
 volume strength = $5.6 \times N = 11.2 \times M$
12. (c) Meq. of H_2S = Meq. of S^{2-} = Meq. of AgNO_3
 $= 16.50 \times 0.02 = 0.33$
 $\frac{w}{17} \times 1000 = 0.33 \therefore w_{\text{H}_2\text{S}} = 5.6 \times 10^{-3}$
 $\therefore \text{ppm of H}_2\text{S} = \frac{5.6 \times 10^{-3} \times 10^6}{10^2} = 56$
13. (a) $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$
 $3\text{I}_2 + 6\text{S}_2\text{O}_3^{2-} \longrightarrow 6\text{I}^- + 3\text{S}_4\text{O}_6^{2-}$
 $\text{IO}_3^- + 6\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ \longrightarrow \text{I}^- + 3\text{S}_4\text{O}_6^{2-}$
 Mole of KIO_3 = 6 mole of $\text{S}_2\text{O}_3^{2-}$
 Mole of $\text{KIO}_3 = \frac{0.1045}{214} = 4.88 \times 10^{-4}$
 $\therefore$ Mole of $\text{S}_2\text{O}_3^{2-}$ used = $4.88 \times 10^{-4} \times 6$
 Mole of $\text{S}_2\text{O}_3^{2-} = 2.93 \times 10^{-3}$
 $\frac{M \times 30.72}{1000} = 2.93 \times 10^{-3}$
 $\therefore M = 0.095$
14. (d) $10e + (\text{V}^{5+})_2 \longrightarrow 2\text{V}^0$
 $E = \frac{M}{10} = \frac{2A + 80}{10}$
15. (a) $A \longrightarrow \text{oxide of } A \xrightarrow{\text{KOH}}$ Isomorph of K_2SO_4 , i.e., K_2AO_4
 $A^0 \longrightarrow A^{6+} + 6e$
 $\therefore$ atomic mass = eq. mass $\times$ v. f. = $13 \times 6 = 78$
16. (a) $2(\text{Fe}^{8/3+})_3 \longrightarrow 3(\text{Fe}^{3+})_2 + 2e$
 $\therefore E_{\text{Fe}_3\text{O}_4} = \frac{M}{1}$ and $E_{\text{Fe}_2\text{O}_3} = \frac{M}{2/3}$
17. (b) $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$ (Acid med.)
 $\text{Mn}^{7+} + 3e \longrightarrow \text{Mn}^{4+}$ (Neutral med.)
 $\therefore$ Meq. of KMnO_4 in acid medium
 $=$ Meq. of KMnO_4 in neutral medium.
 $1 \times 5 \times 20 = 1 \times 3 \times V$
 $\therefore V = 33.3 \text{ mL}$
18. (a) Meq. of KMnO_4 = Meq. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
 $5.5 \times 0.1 \times 5 = \frac{w}{278} \times 1000$ ($\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$)
 $\therefore w = 0.7645$ ($\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + 1e$)
 $\therefore \% \text{ of FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{0.7645}{5} \times 100 = 15.29$
19. (a) $\text{S}^{4+} \longrightarrow \text{S}^{6+} + 2e \times 5$
 $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+} \times 2$
20. (c) $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+} \times 2$
 $(\text{O}^{-1})_2 \longrightarrow \text{O}_2^0 + 2e \times 5$
21. (d) Let mole of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$ be a, b respectively, then $a + b = 2$ and $a = b$ (equimolar)
 Eq. of $\text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4 = V_1 \times 0.1 \times 5$
 ($\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$)
 $2a + 2b = 0.5V_1$ ($\therefore a = b$) ... (i)
 $\therefore V_1 = 8 \text{ L}$
 Eq. of $\text{H}_2\text{C}_2\text{O}_4 = V_2 \times 0.1 \times 1$
 $2b = 0.1V_2$

- $\therefore \frac{V_2}{V_1} = \frac{20}{8} = \frac{5}{2}$
 $\therefore \frac{V_1}{V_2} = \frac{8}{20} = \frac{2}{5}$
22. (d) Meq. of $\text{NaHC}_2\text{O}_4 = \text{Meq. of KMnO}_4$
 $\frac{a \times 2}{M} \times 1000 = 100 \times 0.02 \times 5 = 10$
 Also Meq. of $\text{NaHC}_2\text{O}_4 = \text{Meq. of NaOH}$
 $\frac{b \times 1 \times 1000}{M} = 100 \times 0.2 = 20$
 $\therefore \frac{2a}{b} = \frac{10}{20}$
 or $b = 4a$
23. (a) $6e + (\text{Cr}^{6+})_2 \longrightarrow 2\text{Cr}^{3+}$
 $5e + \text{Mn}^{3+} \longrightarrow \text{Mn}^{2+}$
 $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e$
 One mole of $\text{K}_2\text{Cr}_2\text{O}_7$ will oxidise 6 mole Fe^{2+}
 One mole of KMnO_4 will oxidise 5 mole Fe^{2+}
24. (b) $10e + 2\text{Br}^{5+} \longrightarrow (\text{Br}^0)_2$
 $2\text{Br}^- \longrightarrow (\text{Br}^0)_2 + 2a$
 $2\text{Br}^{5+} + 10\text{Br}^- \longrightarrow 6\text{Br}_2$
 $6 \text{ mole of Br}_2 = 2 \text{ mole Br}^{5+}$
 $= 10 \text{ eq. Br}^{5+}$
 $= 10 \text{ eq. Br}_2$
 $\therefore 1 \text{ mole Br}_2 = \frac{10}{6} \text{ eq. Br}_2 = \frac{5}{3} \text{ eq. Br}_2$
 $\therefore n = \frac{5}{3}$
 $E_{\text{Br}_2} = \frac{M}{5/3} = \frac{3M}{5}$
25. (c) HNO_3 will also oxidise Fe^{2+}
26. (a) KMnO_4 will oxidise Fe^{2+} to Fe^{3+} and $\text{C}_2\text{O}_4^{2-}$ to CO_2
 $(\text{C}_2^{3+})_3 \longrightarrow 6\text{C}^{4+} + 6e$
 $(\text{C}_2^{3+}) \longrightarrow 2\text{C}^{4+} + 2e$
 and $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e$
 Meq. of $\text{C}_2\text{O}_4^{2-}$ in $\text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{Meq. of FeC}_2\text{O}_4$
 $= \text{Meq. of KMnO}_4$
 $= X \cdot 5$ (Total mole of $\text{FeC}_2\text{O}_4 = 0.5$
 and mole of $\text{Fe}_2(\text{C}_2\text{O}_4)_3 = 0.5$)
 $0.5 \times 6 + 0.5 \times 3 = X \cdot 5$
 $\therefore X = 0.9$
27. (a) Eq. of $\text{KMnO}_4 = 5 \times 1 = 5$
 $\therefore \text{mole of KMnO}_4 = 1$ (mole $\times$ V.f. = Eq.)
28. (a) $10e + 2\text{I}^{5+} \longrightarrow (\text{I}^0)_2$
 $2\text{I}^- \longrightarrow (\text{I}^0)_2 + 2e$
 Meq. of $\text{KIO}_3 = \text{Meq. of I}^-$
 $50 \times M \times 5 = 10 \times 0.1 \times 1$
 $\therefore \text{Molarity} = \frac{1}{250} = 4 \times 10^{-3} \text{ M}$
29. (b) Meq. of Fe^{2+} in $\text{Fe}_3\text{O}_4 = 50 \times 0.1 \times 5 = 25 = \text{Meq. of FeO}$
 mm of Fe^{2+} in $\text{Fe}_3\text{O}_4 = 25 = \text{mm of FeO}$
 $\therefore w_{\text{FeO}} = \frac{25 \times 72}{1000} = 1.8 \text{ g}$
 $\therefore w_{\text{Fe}_2\text{O}_3} = 10 - 1.8 = 8.2 \text{ g}$
30. (b) $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+}$
 $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e$
 $(\text{C}^{3+})_2 \longrightarrow 2\text{C}^{4+} + 2e$
 $[(\text{C}^{3+})_2]_3 \longrightarrow 6\text{C}^{4+} + 6e$
 Eq. of $\text{KMnO}_4 = \text{Eq. of FeSO}_4 + \text{Eq. of FeC}_2\text{O}_4 + \text{Eq. of Fe}_2(\text{C}_2\text{O}_4)_3$
 $= 1 \times 1 + 1 \times 3 + 1 \times 6$
 $M \times 5 = 10$
 $M = 2$
31. (b) $8e + \text{N}^{5+} \longrightarrow \text{N}^{3-}$
 $\therefore E_{\text{NO}_3^-} = \frac{62}{8} = 7.75$
32. (a) $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{ClO}_3^- + \text{Cl}^-$
33. (a) $\text{Mn}^{7+} + e \longrightarrow \text{Mn}^{6+}$
 $\therefore E = \frac{M}{1}$
34. (b) $\text{Mn}^{2+} \longrightarrow \text{Mn}^{4+} + 2e$
 $\therefore E = \frac{M}{2}$
35. (a) $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e$
 $(\text{C}^{3+})_2 \longrightarrow 2\text{C}^{4+} + 2e$
 $\text{FeC}_2\text{O}_4 \longrightarrow \text{Fe}^{3+} + 2\text{C}^{4+} + 3e \times 5$
 $\text{Mn}^{7+} + 5e \longrightarrow \text{Mn}^{2+} \times 3$
 or 5 mole $\text{FeC}_2\text{O}_4 \equiv 3 \text{ mole KMnO}_4$
36. (d) $6e + (\text{Cr}^{6+})_2 \longrightarrow 2\text{Cr}^{3+}$
 $X^{n+} \longrightarrow X^{5+} + (5-n)e$
 $\therefore \text{Meq. of K}_2\text{Cr}_2\text{O}_7 = \text{Meq. of } X^{n+}$
 $6 \times 6 \times 10^{-3} = 9 \times 10^{-3} \times (5-n)$
 $\therefore n = 1$
 $\therefore X^{1+} \longrightarrow X^{5+} + 4e$
 $\therefore E \text{ of } X^{n+} = \frac{A}{4}$
37. (b) $\text{As}^{3+} \longrightarrow \text{As}^{5+} + 2e$
 $\therefore \text{Eq. mass} = \frac{\text{molar mass}}{2} = \frac{228.5}{2} = 114.25$
38. (b) $4e + \text{P}^{+1} \longrightarrow \text{P}^{-3}$
 $\text{P}^{+1} \longrightarrow \text{P}^{+3} + 2e$
 $3\text{P}^{+1} \longrightarrow \text{P}^{-3} + 2\text{P}^{+3}$
 $3\text{H}_3\text{PO}_2 \longrightarrow \text{PH}_3 + 2\text{H}_3\text{PO}_3$
 3 mole $\text{H}_3\text{PO}_2 = 1 \text{ mole PH}_3$
 $= 4 \text{ eq. PH}_3 = 4 \text{ eq. H}_3\text{PO}_2$

$$\therefore 1 \text{ mole } \text{H}_3\text{PO}_2 = \frac{4}{3} \text{ eq. } \text{H}_3\text{PO}_2$$

$$\text{or } n \text{ factor} = \frac{4}{3}$$

39. (b) $\text{Hg}^{+1}_2 \longrightarrow 2\text{Hg}^{2+} + 2e^-$
 $\text{S}^{-2} \longrightarrow \text{S}^{6+} + 8e^-$
 $\text{Hg}_2\text{S} \longrightarrow 2\text{Hg}^{2+} + \text{S}^{6+} + 10e^-$
 for (b) $(\text{C}^{-2})_2 \longrightarrow (2\text{C}^{-1}) + 2e^-$
 $\therefore 5\text{C}_2\text{H}_5\text{OH} \longrightarrow 10\text{CH}_3\text{CHO}$
 $5e^- + \text{Mn}^{7+} \longrightarrow \text{Mn}^{2+}$
40. (d) $4e^- + \text{C}^{4+} \longrightarrow \text{C}^0$
 $2(\text{O}^{-2}) \longrightarrow \text{O}_2 + 4e^-$
 (of H_2O)

$$\therefore \text{Equivalent mass of } \text{CO}_2 = \frac{44}{4} = 11$$

$$\text{and Equivalent mass of } \text{H}_2\text{O} = \frac{18}{2} = 9$$

41. (b) $6e^- + (\text{Cr}^{6+})_2 \longrightarrow 2\text{Cr}^{3+}$
 $\therefore E = M/6$
42. (a) $2\text{MnO}_4^- + \text{I}^- + \text{H}_2\text{O} \longrightarrow \text{IO}_3^- + 2\text{MnO}_2 + 2\text{OH}^-$
43. (d) $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^- \times 6$
 $6e^- + (\text{Cr}^{6+})_2 \longrightarrow 2\text{Cr}^{3+}$
44. (c) $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \longrightarrow \text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$

Redox Titrations

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OBJECTIVE PROBLEMS (More Than One Answer Correct)

- 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 $\frac{V_1}{V_2} = 5:1$
 (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
- A mixture of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$ 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 $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4 = 4:1$
 (b) Equivalent ratio of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4 = 4:1$
 (c) Mole of $\text{C}_2\text{O}_4^{2-}$ in mixture = 25×10^{-3}
 (d) Mole ratio of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4 = 1:4$
- 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
- Which are correct about the reaction?
 $\text{FeS}_2 + \text{O}_2 \longrightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$
 (a) Eq. mass of FeS_2 is $M/11$
 (b) Eq. mass of $\text{SO}_2 = M/5$
 (c) 1 mole of FeS_2 requires $7/4$ mole of O_2
 (d) S has -2 oxidation state in FeS_2
- Which of the following are primary standards?
 (a) As_2O_3 (b) $\text{H}_2\text{C}_2\text{O}_4$
 (c) NaOH (d) Na_2CO_3
- Which of the followings are not valid reactions for iodometric titrations?
 (a) $\text{O}_3 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{O}_2 + \text{I}_2 + \text{H}_2\text{O}$
 (b) $8\text{HNO}_3 + 6\text{I}^- \longrightarrow 6\text{NO}_3^- + 2\text{NO} + 2\text{I}_2 + 4\text{H}_2\text{O}$
 (c) $\text{CuSO}_4 + 2\text{KI} \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2 + \text{K}_2\text{SO}_4$
 (d) $\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$
- In which of the following reactions O_2 is oxidant?
 (a) $\text{F}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{F}_2\text{O}$ (b) $3\text{O}_3 \longrightarrow 2\text{O}_2$
 (c) $\text{CO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2$ (d) $\text{N}_2 + \text{O}_2 \longrightarrow 2\text{NO}$
- Reduction of the metal centre in aqueous permanganate ion involves :
 (a) 3 electrons in neutral medium
 (b) 5 electrons in neutral medium
 (c) 3 electrons in alkaline medium
 (d) 5 electrons in acidic medium

(IIT 2011)

SOLUTIONS (More Than One Answer Correct)

1. (b, c) Meq. of $\text{NaHC}_2\text{O}_4 = 100 \times 0.1 = 10$

Meq. of NaOH required $= 10 = V_1 \times 0.1 \times 1$

(v.f. of $\text{NaOH} = 1$)

$V_1 = 100 \text{ mL}$

Meq. of KMnO_4 required $= 10 = V_2 \times a \times 5$

(v.f. of $\text{KMnO}_4 = 5$)

$\therefore V_2 = \frac{10}{5a} \therefore \frac{V_1}{V_2} = \frac{100 \times 5a}{10}$

if $M_{\text{KMnO}_4} = 0.1M$, then $10 = V_2 \times 0.1 \times 5$

$\therefore V_2 = 20 \text{ mL}$

2. (a, b, c) Meq. of $\text{KMnO}_4 = 100 \times 0.1 \times 5 = 50$

$= \text{Meq. of } \text{Na}_2\text{C}_2\text{O}_4 + \text{Meq. of } \text{H}_2\text{C}_2\text{O}_4$

$\therefore a + b = 50$

Meq. of $\text{NaOH} = 50 \times 0.2 = 10 = \text{Meq. of } \text{H}_2\text{C}_2\text{O}_4$

$\therefore b = 10$

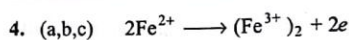
$\therefore a = 40$

milli mole of $\text{Na}_2\text{C}_2\text{O}_4 = \frac{a}{2}$

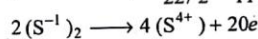
$\therefore \text{milli mole of } \text{C}_2\text{O}_4 = \frac{a}{2} + \frac{b}{2} = \frac{a+b}{2} = \frac{40+10}{2} = 25$

milli mole of $\text{H}_2\text{C}_2\text{O}_4 = \frac{b}{2}$

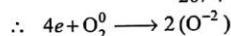
3. (a) HNO_3 also oxidises Fe^{2+} whereas KMnO_4 oxidises HCl .



Eq. mass of $\text{FeS}_2 = \frac{M}{22/2} = \frac{M}{11}$



Eq. mass of $\text{SO}_2 = \frac{M}{20/4} = \frac{M}{5}$



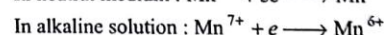
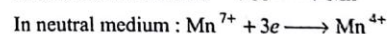
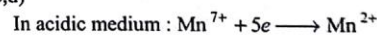
S has -1 oxidation state.

5. (a, b) Primary standard solutions are those whose solution of exact normality can be prepared by weighing desired amount of its pure sample.

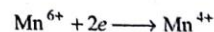
6. (b) In strong acidic medium either I^- produced in reaction tend to be oxidised to I_2 or starch used to detect end point is decomposed and hydrolysed.

7. (c, d) In the reaction of F_2 and O_2 , F_2 is oxidant.

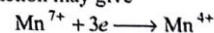
8. (a, c, d)



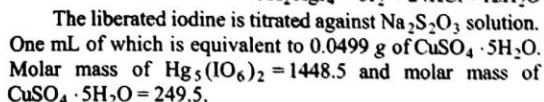
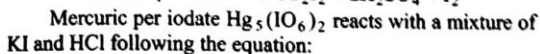
Note that in **alkaline medium**, Mn^{6+} is further reduced to Mn^{4+}



Thus over all reaction may give

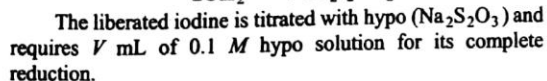


Comprehension 1: Estimation of CuSO_4 is made by iodometric titrations. In a given titration CuSO_4 reacts with KI in acidic medium to liberate I_2 .



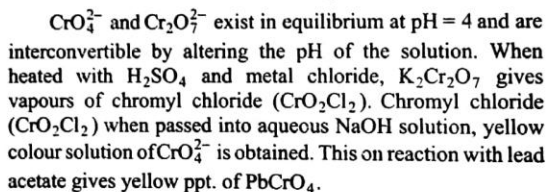
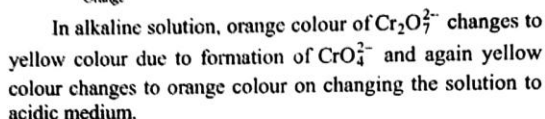
- (a) 40 mL (b) 10 mL
(c) 20 mL (d) 30 mL

Comprehension 2: 2.5 g sample of copper is dissolved in excess of H_2SO_4 to prepare 100 mL of 0.02 M $\text{CuSO}_4(aq.)$. 10 mL of 0.02 M solution of $\text{CuSO}_4(aq.)$ is mixed with excess of KI to show the following changes.

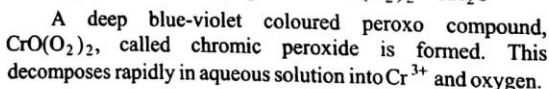


- [1] The volume (V) of hypo required is :
(a) 2 mL (b) 20 mL
(c) 1 mL (d) 10 mL
- [2] Percentage of purity of sample is :
(a) 10.16 (b) 5.08
(c) 2.54 (d) 1.27
- [3] The mass of I_2 liberated in the reaction of 10 mL of 0.02 M solution with KI_{excess} is :
(a) 0.051 g (b) 0.0254 g
(c) 0.102 g (d) 0.204 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

- Comprehension 3:** $K_2Cr_2O_7$ acts as a good oxidizing agent in acidic medium.



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 .



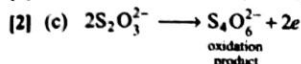
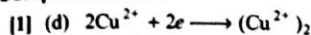
- [1] What happens when a solution of potassium chromate is treated with an excess of dilute nitric acid?
- (a) Cr^{3+} and $\text{Cr}_2\text{O}_7^{2-}$ are formed
- (b) $\text{Cr}_2\text{O}_7^{2-}$ and H_2O are formed
- (c) CrO_4^{2-} is reduced to +3 state of Cr
- (d) CrO_4^{2-} is reduced to 0 state of Cr
- [2] Which of the following statement is wrong when a mixture of NaCl and $\text{K}_2\text{Cr}_2\text{O}_7$ 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) $\text{CrO}_2\text{Cl}_2, \text{CrO}_4^{2-}$ (b) $\text{Cr(OH)}_2, \text{CrO}_4^{2-}$
 (c) $\text{Cl}_2, \text{Cr}_2\text{O}_7^{2-}$ (d) $\text{Cl}_2, \text{Cr(OH)}_3$
- [4] Number of mole of $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $\text{Ba} = 137.34$ and $\text{Cr} = 52$)
 (a) 137.34 (b) 85.78
 (c) 114.45 (d) 68.67
- [6] The equivalent mass of KIO_3 in the reaction
 $2\text{Cr(OH)}_3 + \text{OH}^- + \text{KIO}_3 \longrightarrow 2\text{CrO}_4^{2-} + \text{KI} + 5\text{H}_2\text{O}$
 (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 $\text{K}_2\text{Cr}_2\text{O}_7$, 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 $\text{CrO(O}_2)_2$ and no redox change
 (c) a deep blue-violet coloured compound $\text{CrO(O}_2)_2$ due to reduction of Cr
 (d) solution gives green ppt. $\text{CrO(O}_2)_2$ due to oxidation of Cr
- [8] The colour of $\text{Cu}_2\text{Cr}_2\text{O}_7$ 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 $[\text{CrO}_4^{2-}]$ ions at equilibrium for the reaction
 $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{CrO}_4^{2-} + 2\text{H}^+$ at $\text{pH} = 4$ is :
 (a) $10^{-4} [\text{Cr}_2\text{O}_7^{2-}] \cdot K_C$
 (b) $10^{-8} [\text{Cr}_2\text{O}_7^{2-}] \cdot K_C$
 (c) $10^{-4} [(\text{Cr}_2\text{O}_7^{2-}) \cdot K_C]^{1/2}$
 (d) $10^{-4} [\text{Cr}_2\text{O}_7^{2-}]^{1/2} \cdot K_C$
- 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 :

$$E_{\text{red/oxi}} = \frac{\text{Molar mass of reductant or oxidant}}{\text{Number of electron lost or gained by 1 molecule of reductant or oxidant}}$$
- [1] The equivalent mass of cyanogen $(\text{CN})_2$ in the redox change is :
 $(\text{CN})_2 + \text{H}_2\text{O} \longrightarrow \text{HCN} + \text{HOCN}$
 (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 :
 $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
 (a) $\frac{M}{6}$ (b) $\frac{M}{2}$
 (c) $\frac{M}{3}$ (d) $\frac{M}{5}$
- [3] The equivalent mass of $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ in the redox reaction is :
 $5\text{Fe}_2(\text{C}_2\text{O}_4)_3 + 6\text{KMnO}_4 + 24\text{H}_2\text{SO}_4 \longrightarrow 5\text{Fe}_2(\text{SO}_4)_3 + 6\text{MnSO}_4 + 30\text{CO}_2 + 24\text{H}_2\text{O}$
 (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 $\text{Na}_2\text{S}_2\text{O}_3$ 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

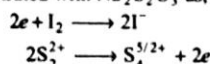
Comprehension 1

[3] (a) $\therefore$ 1 mole $\text{Hg}_5(\text{IO}_6)_2$ or 1448.5 g gives = 8 mole I_2

$$\therefore 0.7245 \text{ g Hg}_5(\text{IO}_6)_2 \text{ will give}$$

$$= \frac{8 \times 0.7245}{1448.5} \text{ mole I}_2$$

$$= 4.0 \times 10^{-3} \text{ mole I}_2$$

This I_2 is titrated with $\text{Na}_2\text{S}_2\text{O}_3$ as,

Meq. of $\text{Na}_2\text{S}_2\text{O}_3$ = Meq. of $\text{I}_2 = 4 \times 10^{-3} \times 10^3 \times 2 = 8$

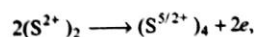
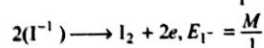
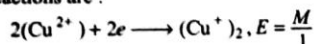
$$\text{Meq. of Na}_2\text{S}_2\text{O}_3 \text{ in one mL} = \text{Meq. of CuSO}_4$$

$$= \frac{0.0499}{249/1} \times 1000 = 0.20$$

$$\therefore 0.20 \times V = 8 \quad \therefore V = 40 \text{ mL}$$

Comprehension 2

[1] (a) The reactions are :



$$E_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{M}{1}$$

$$\text{Meq. of CuSO}_4 = \text{Meq. of Na}_2\text{S}_2\text{O}_3$$

$$= \text{Meq. of I}_2 \text{ liberated}$$

$$10 \times 0.02 \times 1 = V \times 0.1 \times 1$$

$$\therefore V = 2 \text{ mL}$$

[2] (b) Meq. of CuSO_4 in 100 mL = $100 \times 0.02 = 2$

$$\therefore w_{\text{CuSO}_4} = \frac{2 \times 249.6}{1000} = 0.499 \text{ g}$$

$$\therefore w_{\text{Cu}} = \frac{0.499 \times 63.6}{249.6} = 0.127 \text{ g}$$

$$\therefore \% \text{ of Cu} = \frac{0.127}{2.5} \times 100 = 5.08$$

[3] (b) Eq. of I_2 = Eq. of CuSO_4

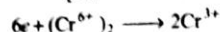
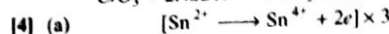
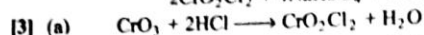
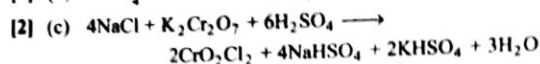
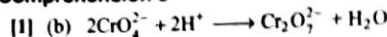
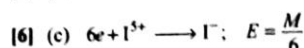
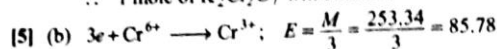
$$= \frac{10 \times 0.02}{1000} = 2 \times 10^{-4}$$

$$\therefore \frac{w}{254/2} = 2 \times 10^{-4}$$

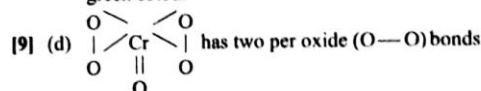
$$\therefore w_{\text{I}_2} = 0.0254 \text{ g}$$

[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

 $\therefore$ 1 mole of $\text{K}_2\text{Cr}_2\text{O}_7$ will oxidise 3 mole of Sn^{2+} 

(Not a redox change)

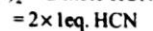
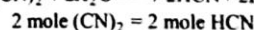
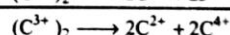
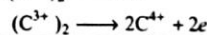
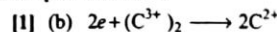
[8] (a) Cu^{2+} ions are blue and $\text{Cr}_2\text{O}_7^{2-}$ ions are orange to give green colour

[10] (c)
$$K_C = \frac{[\text{CrO}_4^{2-}]^2 [\text{H}^+]^2}{[\text{Cr}_2\text{O}_7^{2-}]}$$

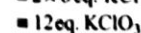
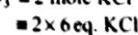
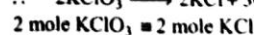
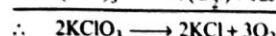
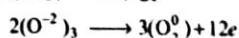
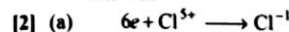
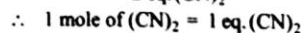
$$\therefore [\text{CrO}_4^{2-}]^2 = \frac{[\text{Cr}_2\text{O}_7^{2-}] \times K_C}{[\text{H}^+]^2} = \frac{K_C [\text{Cr}_2\text{O}_7^{2-}]}{(10^{-4})^2}$$

$$= 10^4 [K_C \cdot \text{Cr}_2\text{O}_7^{2-}]^{1/2}$$

Comprehension 4



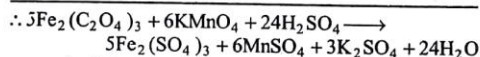
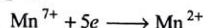
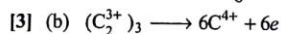
(V.f. for HCN = 1)



$\therefore$ 1 mole $\text{KClO}_3 \equiv 6 \text{ eq. KClO}_3$

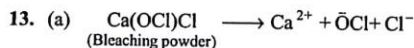
$\therefore$ v.f. for $\text{KClO}_3 \equiv 6$

$$\therefore E_{\text{KClO}_3} = \frac{M}{6}$$



v.f. of $\text{Fe}_2(\text{C}_2\text{O}_4)_3 = 6$

Comprehension 5

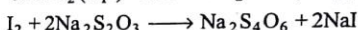
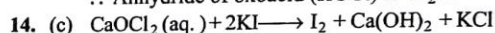


Thus bleaching powder contains OCl^- i.e., part of oxoacid HOCl and Cl^- i.e., part of HCl .

Oxidation no. of Cl in oxoacid = +1.

Thus, oxide of Cl with same ox. no. is Cl_2O

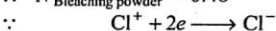
$\therefore$ Anhydride of oxoacid (HOCl) is Cl_2O .



Thus Meq. of $\text{Na}_2\text{S}_2\text{O}_3$ used = Meq. of I_2 formed
= Meq. of bleaching powder

or $48 \times 0.25 = \text{Meq. of bleaching powder} = N \times 25$

$$\therefore N_{\text{Bleaching powder}} = 0.48$$



Thus, n -factor for bleaching powder = 2

$$\therefore M_{\text{Bleaching powder}} = \frac{0.48}{2} = 0.24$$

Redox Titrations



STATEMENT EXPLANATION PROBLEMS



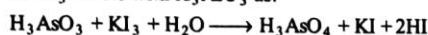
Read the statements (S) and explanations (E) given below. Choose the correct choices a, b, c and d from the options

- (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 $M/2$

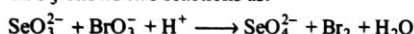
E: The reaction is: $\text{C}^{2+} \longrightarrow \text{C}^{4+} + 2e$

2. S: The I_3^- reacts with H_3AsO_3 as:



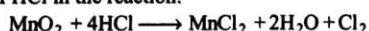
E: Equivalent mass of $\text{KI}_3 = 210$.

3. S: BrO_3^- shows two reactions as:



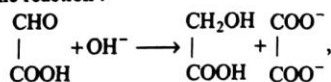
E: The ratio of equivalent mass of BrO_3^- in two reactions is $5/6$.

4. S: One equivalent of MnO_2 reacts with 2 equivalent of HCl in the reaction:



E: One equivalent of MnO_2 reacts with one equivalent of HCl .

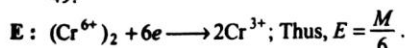
5. S: The reaction:



is Cannizzaro's reaction.

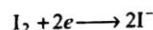
E: This is an example of disproportionation reaction.

6. S: In acidic medium, equivalent mass of $\text{K}_2\text{Cr}_2\text{O}_7$ is 49.



7. S: Iodometric titration are redox titrations.

E: The iodine solution acts as an oxidant to reduce the reductant.



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.

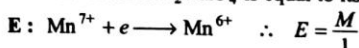
9. S: KMnO_4 acts as oxidant as well as self indicator in its titration with ferrous ammonium sulphate solution in acidic medium.

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.

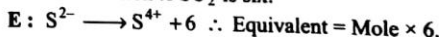
10. S: The equivalence point refers the condition where equivalents of one species react with same number of equivalent of other species.

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.



12. S: The number of equivalent per mole of H_2S used in its oxidation to SO_2 is six.



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) $E_{\text{BrO}_3^-} = \frac{M}{5}$
 (ii) $E_{\text{BrO}_3^-} = \frac{M}{6}$
 $10e + 2\text{Br}^{5+} \longrightarrow \text{Br}^0$;
 $6e + \text{Br}^{5+} \longrightarrow \text{Br}^{-1}$
 $\therefore \text{Ratio} = \frac{6}{5}$
4. (a) 1 mole $\text{MnO}_2 \equiv 4$ mole HCl
 2 eq. $\text{MnO}_2 \equiv 4$ eq. HCl
5. (c) Both are facts.
6. (c) One mole of $\text{K}_2\text{Cr}_2\text{O}_7$ 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) $2\text{KI} + \text{CuSO}_4 \longrightarrow \text{CuI}_2 + \text{K}_2\text{SO}_4$
 $2\text{CuI}_2 \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$
 $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$
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 $\times$ 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) $5e + \text{Mn}^{7+} \longrightarrow \text{Mn}^{2+}$ (Acidic)
 $3e + \text{Mn}^{7+} \longrightarrow \text{Mn}^{4+}$ (Alkaline or neutral)
 $1e + \text{Mn}^{7+} \longrightarrow \text{Mn}^{6+}$ (Neutral or alkaline)

MATCHING TYPE PROBLEMS

Type I : Only one match is possible

- | 1. Half Reactions | <i>n</i> -factor of reactant |
|--|------------------------------|
| A. $\text{Bi}_2\text{S}_3 \rightarrow \text{Bi}^{5+} + \text{S}$ | (a) 6 |
| B. $\text{FeS}_2 \rightarrow \text{Fe}^{3+} + 2\text{SO}_2$ | (b) 10 |
| C. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + \text{Cr}_2\text{O}_3$ | (c) 11 |
| D. $\text{Al}_2(\text{Cr}_2\text{O}_7)_3 \rightarrow \text{Al}^{3+} + \text{Cr}^{3+}$ | (d) 18 |
-
- | 2. Reaction | <i>n</i> -factor of reactant |
|--|------------------------------|
| A. $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$ | (a) 4/3 |
| B. $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ | (b) 2/3 |
| C. $\text{P}_2\text{H}_4 \rightarrow \text{PH}_3 + \text{P}_4\text{H}_2$ | (c) 1 |
| D. $\text{H}_3\text{PO}_2 \rightarrow \text{PH}_3 + \text{H}_3\text{PO}_3$ | (d) 5/3 |
| E. $\text{I}_2 \rightarrow \text{I}^- + \text{IO}_3^-$ | (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) $\text{H}_2\text{C}_2\text{O}_4$ vs. KMnO_4 |
| E. Precipitation | (e) $\text{H}_2\text{C}_2\text{O}_4$ vs. NaOH |

- | 4. Reaction | Equivalent mass of reactant |
|---|-----------------------------|
| A. $\text{Fe}(\text{SCN})_2 \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{CO}_3^{2-} + \text{NO}_3^-$ | (a) $\frac{M}{28}$ |
| B. $\text{As}_2\text{S}_3 \rightarrow \text{As}^{5+} + \text{SO}_4^{2-}$ | (b) $\frac{M}{33}$ |
| C. $\text{CrI}_3 \rightarrow \text{Cr}_2^{6+} + \text{I}^{5+}$ | (c) $\frac{M}{27}$ |
| D. $\text{CrI}_3 \rightarrow \text{Cr}_2^{6+} + \text{I}^{7+}$ | (d) $\frac{M}{21}$ |
| E. $\text{CrI}_3 \rightarrow \text{Cr}^{6+} + \text{I}^{7+}$ | |

Type III : Only one match from each list

- | 5. List A | List B | List C |
|--------------------------------|------------------|---|
| A. CH_4 | (i) $E = M/8$ | (a) $\text{C}^{2+} \rightarrow \text{C}^{4+}$ |
| B. CO | (ii) $E = M/2$ | (b) $\text{C}^{4-} \rightarrow \text{C}^{4+}$ |
| C. $\text{C}_2\text{O}_4^{2-}$ | (iii) $E = M/12$ | (c) $\text{C}^{3+} \rightarrow \text{C}^{4+}$ |
| D. C_2H_4 | | (d) $\text{C}^{2-} \rightarrow \text{C}^{4+}$ |
-
- | 6. Redox change | Equivalent mass | Number of electrons involved in change |
|--|-------------------------------|--|
| A. $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$ | i. $E_{\text{MnO}_2} = M/2$ | (a) 4 |
| B. $\text{MnO}_2 \rightarrow \text{MnSO}_4$ | ii. $E_{\text{MnO}_2} = M/4$ | (b) 2 |
| C. $\text{MnO}_2 \rightarrow \text{Mn}$ | iii. $E_{\text{MnO}_2} = M/1$ | (c) 3 |
| D. $\text{KMnO}_4 \rightarrow \text{Mn}_2\text{O}_3$ | iv. $E_{\text{MnO}_4} = M/4$ | (d) 8 |
| E. $\text{KMnO}_4 \rightarrow \text{MnO}_2$ | v. $E_{\text{MnO}_4} = M/3$ | |

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