CHAPTER 1

Some Basic Concepts of Chemistry

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. The modern atomic mass unit is based on .... *(1980)*
2. The total number of electrons present in 18 ml of water is .... *(1980)*
3. 3 g of a salt of molecular weight 30 is dissolved in 250 g of water. The molality of the solution is .... *(1983 - 1 Mark)*
4. The weight of 1×10^{22} molecules of $CuSO_4.5H_2O$ is .... *(1991 - 1 Mark)*
5. The compound $YBa_2Cu_3O_7$, which shows super-conductivity, has copper in oxidation state..................., assume that the rare earth element yttrium is in its usual + 3 oxidation state. *(1994 - 1 Mark)*

C MCQs with One Correct Answer

1. 27 g of Al will react completely with how many grams of oxygen? *(1978)*
(a) 8 g (b) 16 g
(c) 32 g (d) 24 g
2. A compound was found to contain nitrogen and oxygen in the ratio 28 gm and 80 gm respectively. The formula of compound is *(1978)*
(a) NO (b) N_2O_3
(c) N_2O_5 (d) N_2O_4
3. The largest number of molecules is in *(1979)*
(a) 36 g of water
(b) 28 g of carbon monoxide
(c) 46 g of ethyl alcohol
(d) 54 g of nitrogen pentoxide
4. The total number of electrons in one molecule of carbon dioxide is *(1979)*
(a) 22 (b) 44
(c) 66 (d) 88
5. A gaseous mixture contains oxygen and nitrogen in the ratio of 1 : 4 by weight. Therefore the ratio of their number of molecules is *(1979)*
(a) 1 : 4 (b) 1 : 8
(c) 7 : 32 (d) 3 : 16
6. 2.76 g of silver carbonate on being strongly heated yields a residue weighing *(1979)*
(a) 2.16 g (b) 2.48 g
(c) 2.32 g (d) 2.64 g
7. M is molecular weight of $KMnO_4$. The equivalent weight of $KMnO_4$ when it is converted into K_2MnO_4 is *(1980)*
(a) M (b) M/3
(c) M/5 (d) M/7
8. If 0.50 mole of $BaCl_2$ is mixed with 0.20 mol of Na_3PO_4, the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is *(1981 - 1 Mark)*
(a) 0.70 (b) 0.50
(c) 0.20 (d) 0.10
9. One mole of N_2H_4 loses ten moles of electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y? (There is no change in the oxidation state of hydrogen). *(1981 - 1 Mark)*
(a) –1 (b) –3
(c) +3 (d) +5
10. The oxidation number of carbon in CH_2O is *(1982 - 1 Mark)*
(a) – 2 (b) + 2
(c) 0 (d) + 4
11. A molal solution is one that contains one mole of a solute in: *(1986 - 1 Mark)*
(a) 1000 g of the solvent
(b) one litre of the solvent
(c) one litre of the solution
(d) 22.4 litres of the solution
12. The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)]SO_4$. The oxidation state of iron is : *(1987 - 1 Mark)*
(a) 1 (b) 2
(c) 3 (d) 0
13. The equivalent weight of $MnSO_4$ is half of its molecular weight when it is converted to : *(1988 - 1 Mark)*
(a) Mn_2O_3 (b) MnO_2
(c) MnO_4^- (d) MnO_4^{2-}
14. In which mode of expression, the concentration of a solution remains independent of temperature? *(1988 - 1 Mark)*
(a) Molarity (b) Normality
(c) Formality (d) Molality

15. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is : *(1990 - 1 Mark)*

(a) +3
(b) +2
(c) +1
(d) –1

16. The oxidation states of the most electronegative element in the products of the reaction, BaO_2 with dil. H_2SO_4 is *(1991 - 1 Mark)*

(a) 0 and –1
(b) –1 and –2
(c) –2 and 0
(d) –2 and –1

17. For the redox reaction : *(1992 - 1 Mark)*

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are *(1992 - 1 Mark)*

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

18. The normality of 0.3 *M* phosphorous acid (H_3PO_3) is, *(1999 - 2 Marks)*

(a) 0.1
(b) 0.9
(c) 0.3
(d) 0.6

19. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are *(1999 - 2 Marks)*

(a) 0, +1 and –2
(b) +2, +1 and –2
(c) 0, +1 and +2
(d) –2, +1 and –2

20. Amongst the following identify the species with an atom in +6 oxidation state *(2000S)*

(a) MnO_4^-
(b) $Cr(CN)_6^{3-}$
(c) NiF_6^{2-}
(d) CrO_2Cl_2

21. The reaction, $3ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$, is an example of *(2001S)*

(a) oxidation reaction
(b) reduction reaction
(c) disproportionation reaction
(d) decomposition reaction

22. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is *(2001S)*

(a) 40 ml
(b) 20 ml
(c) 10 ml
(d) 4 ml

23. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is *(2001S)*

(a) (molecular weight)/2
(b) (molecular weight)/6
(c) (molecular weight)/3
(d) same as molecular weight

24. How many moles of electron weigh one kilogram? *(2002S)*

(a) 6.023×10^{23}
(b) $\frac{1}{9.108} \times 10^{31}$
(c) $\frac{6.023}{9.108} \times 10^{54}$
(d) $\frac{1}{9.108 \times 6.023} \times 10^{8}$

25. Which has maximum number of atoms? *(2003S)*

(a) 24g of C (12)
(b) 56g of Fe (56)
(c) 27g of Al (27)
(d) 108g of Ag (108)

26. Mixture *X* = 0.02 mol of $[Co(NH_3)_5SO_4]Br$ and 0.02 mol of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 litre of solution. *(2003S)*

1 litre of mixture X + excess $AgNO_3 \longrightarrow Y$.

1 litre of mixture X + excess $BaCl_2 \longrightarrow Z$

No. of moles of *Y* and *Z* are

(a) 0.01, 0.01
(b) 0.02, 0.01
(c) 0.01, 0.02
(d) 0.02, 0.02

27. The pair of the compounds in which both the metals are in the highest possible oxidation state is *(2004S)*

(a) $[Fe(CN)_6]^{3-}, [Co(CN)_6]^{3-}$
(b) CrO_2Cl_2, MnO_4^-
(c) TiO_3, MnO_2
(d) $[Co(CN)_6]^{3-}, MnO_3$

28. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is *(2007)*

(a) 3
(b) 4
(c) 5
(d) 6

E Subjective Problems

1. What weight of AgCl will be precipitated when a solution containing 4.77 g of NaCl is added to a solution of 5.77 g of $AgNO_3$? *(1978)*

2. One gram of an alloy of aluminium and magnesium when treated with excess of dil. HCl forms magnesium chloride, aluminium chloride and hydrogen. The evolved hydrogen, collected over mercury at 0°C has a volume of 1.20 litres at 0.92 atm. pressure. Calculate the composition of the alloy. [H = 1, Mg = 24, Al = 27] *(1978)*

3. Igniting MnO_2 converts it quantitatively to Mn_3O_4. A sample of pyrolusite is of the following composition : MnO_2 80%, SiO_2 and other inert constituents 15%, rest being water. The sample is ignited in air to constant weight. What is the percentage of Mn in the ignited sample? *(1978)* [O = 16, Mn = 54.9]

4. 4.215 g of a metallic carbonate was heated in a hard glass tube and the CO_2 evolved was found to measure 1336 ml at 27°C and 700 mm pressure. What is the equivalent weight of the metal? *(1979)*

5. (a) 5.5 g of a mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ requires 5.4 ml of 0.1 N $KMnO_4$ solution for complete oxidation. Calculate the number of gram mole of hydrated ferric sulphate in the mixture.

(b) The vapour density (hydrogen = 1) of a mixture consisting of NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 g of the mixture. ***(1979)***

6. 5 ml of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 ml) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 ml. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 ml of the residual gas being pure oxygen. All volumes have been reduced to N.T.P. Calculate the molecular formula of the hydrocarbon gas. ***(1979)***

7. In the analysis of 0.500 g sample of feldspar, a mixture of chlorides of sodium and potassium is obtained which weighs 0.1180g. Subsequent treatment of mixed chlorides with silver nitrate gives 0.2451g of silver chloride. What is the percentage of sodium oxide and potassium oxide in feldspar. ***(1979)***

8. A compound contains 28 percent of nitrogen and 72 percent of metal by weight. 3 atoms of metal combine with 2 atoms of N. Find the atomic weight of metal. ***(1980)***

9. (i) A sample of $MnSO_4.4H_2O$ is strongly heated in air. The residue is Mn_3O_4.

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

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

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

Find the amount of $MnSO_4.4H_2O$ present in the sample. ***(1980)***

10. (a) One litre of a sample of hard water contains 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$. Find the total hardness in terms of parts of $CaCO_3$ per 10^6 parts of water by weight.

(b) A sample of hard water contains 20 mg of Ca^{++} ions per litre. How many milli-equivalent of Na_2CO_3 would be required to soften 1 litre of the sample?

(c) 1 gm of Mg is burnt in a closed vessel which contains 0.5 gm of O_2.

(i) Which reactant is left in excess?

(ii) Find the weight of the excess reactants?

(iii) How may milliliters of 0.5 N H_2SO_4 will dissolve the residue in the vessel. ***(1980)***

11. A hydrocarbon contains 10.5g of carbon per gram of hydrogen. 1 litre of the vapour of the hydrocarbon at 127°C and 1 atmosphere pressure weighs 2.8g. Find the molecular formula. ***(1980)***

12. Find ***(1980)***

(i) The total number of neutrons and

(ii) The total mass of neutron in 7 mg of ^{14}C.

(Assume that mass of neutron = mass of hydrogen atom)

13. A mixture contains NaCl and unknown chloride MCl.

(i) 1 g of this is dissolved in water. Excess of acidified $AgNO_3$ solution is added to it. 2.567 g of white ppt. is formed.

(ii) 1 g of original mixture is heated to 300°C. Some vapours come out which are absorbed in acidified $AgNO_3$ solution, 1.341 g of white precipitate was obtained.

Find the molecular weight of unknown chloride. ***(1980)***

14. A 1.00 gm sample of H_2O_2 solution containing *X* per cent H_2O_2 by weight requires *X* ml of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of the $KMnO_4$ solution. ***(1981 - 3 Marks)***

15. Balance the following equations.

(i) $Cu_2O + H^+ + NO_3^- \rightarrow Cu^{2+} + NO + H_2O$

(1981 - 1 Mark)

(ii) $K_4[Fe(CN)_6] + H_2SO_4 + H_2O$
$\rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO$

(1981 - 1 Mark)

(iii) $C_2H_5OH + I_2 + OH^- \rightarrow CHI_3 + HCO_3^- + I^- + H_2O$

(1981 - 1 Mark)

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

$2NH_2OH + 4\,Fe^{3+} \rightarrow N_2O(g)\uparrow + H_2O + 4\,Fe^{2+} + 4H^+$

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

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

A 10 ml. sample of hydroxylamine solution was diluted to 1 litre. 50 ml. of this diluted solution was boiled with an excess of iron (III) solution. The resulting solution required 12 ml. of 0.02 M $KMnO_4$ solution for complete oxidation of iron (II). Calculate the weight of hydroxylamine in one litre of the original solution. (H = 1, N = 14, O = 16, K = 39, Mn = 55, Fe = 56) ***(1982 - 4 Marks)***

17. The density of a 3 M sodium thiosulphate solution ($Na_2S_2O_3$) is 1.25 g per ml. Calculate (i) the percentage by weight of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate and (iii) the molalities of Na^+ and $S_2O_3^{2-}$ ions. ***(1983 - 5 Marks)***

18. 4.08 g of a mixture of BaO and an unknown carbonate MCO_3 was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 ml of 1 N HCl. The excess acid required 16 ml of 2.5 N NaOH solution for complete neutralization. Identify the metal M. ***(1983 - 4 Marks)***

(At. wt. H = 1, C = 12, O = 16, Cl = 35.5, Ba = 138)

19. Complete and balance the following reactions :

(i) $Zn + NO_3^- \rightarrow Zn^{2+} + NH_4^+$ ***(1983 - 1 Mark)***

(ii) $Cr_2O_7^{2-} + C_2H_4O \rightarrow C_2H_4O_2 + Cr^{3+}$ ***(1983 - 1 Mark)***

(iii) $HNO_3 + HCl \rightarrow NO + Cl_2$ ***(1983 - 1 Mark)***

(iv) $Ce^{3+} + S_2O_8^{2-} \rightarrow SO_4^{2-} + Ce^{4+}$ ***(1983 - 1 Mark)***

(v) $Cl_2 + OH^- \rightarrow Cl^- + ClO^-$ ***(1983 - 1 Mark)***

(vi) $Mn^{2+} + PbO_2 \rightarrow MnO_4^- + H_2O$ ***(1986 - 1 Mark)***

(vii) $S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$ ***(1986 - 1 Mark)***

(viii) $ClO_3^- + I^- + H_2SO_4 \rightarrow Cl^- + HSO_4^-$ ***(1986 - 1 Mark)***

(ix) $Ag^+ + AsH_3 \rightarrow H_3AsO_3 + H^+$ ***(1986 - 1 Mark)***

20. 2.68×10^{-3} moles of a solution containing an ion A^{n+} require 1.61×10^{-3} moles of MnO_4^- for the oxidation of A^{n+} to AO_3^- in acid medium. What is the value of n? ***(1984 - 2 Marks)***

21. Five ml of 8N nitric acid, 4.8 ml of 5N hydrochloric acid and a certain volume of 17M sulphuric acid are mixed together and made upto 2litre. Thirty ml. of this acid mixture exactly neutralise 42.9 ml of sodium carbonate solution containing one gram of $Na_2CO_3.10H_2O$ in 100 ml. of water. Calculate the amount in gram of the sulphate ions in solution. ***(1985 - 4 Marks)***

22. Arrange the following in increasing oxidation number of iodine. ***(1986 - 1 Mark)***

I_2, HI, HIO_4, ICl

23. (i) What is the weight of sodium bromate and molarity of solution necessary to prepare 85.5 ml of 0.672 N solution when the half-cell reaction is

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

(ii) What would be the weight as well as molarity if the half-cell reaction is :

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

(1987 - 5 Marks)

24. A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate : (i) molal concentration and (ii) mole fraction of sugar in the syrup. ***(1988 - 2 Marks)***

25. A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 ml. of water, 10 ml of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 ml. of M/50 potassium permanganate solution. Estimate the amount of hydrazine sulphate in one litre of the solution. ***(1988 - 3 Marks)***

Reaction :

$$4Fe^{3+} + N_2H_4 \rightarrow N_2 + 4Fe^{2+} + 4H^+$$

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

26. An equal volume of a reducing agent is titrated separately with 1M $KMnO_4$ in acid neutral and alkaline media. The volumes of $KMnO_4$ required are 20 ml. in acid, 33.4 ml. neutral and 100 ml. in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half reactions. Find out the volume of 1M $K_2Cr_2O_7$ consumed; if the same volume of the reducing agent is titrated in acid medium. ***(1989 - 5 Marks)***

27. A mixture of $H_2C_2O_4$ (oxalic acid) and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and solution made upto one litre. Ten millilitres of the solution required 3.0 ml. of 0.1 N sodium hydroxide solution for complete neutralization. In another experiment, 10.0 ml. of the same solution, in hot dilute sulphuric acid medium. require 4.0 ml. of 0.1 N potassium permanganate solution for complete reaction. Calculate the amount of $H_2C_2O_4$ and $NaHC_2O_4$ in the mixture. ***(1990 - 5 Marks)***

28. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the weight of the residue was constant. If the loss in weight is 28.0 per cent, find the amount of lead nitrate and sodium nitrate in the mixture. ***(1990 - 4 Marks)***

29. Calculate the molality of 1 litre solution of 93% H_2SO_4 (weight/volume). The density of the solution is 1.84 g/ml. ***(1990 - 1 Marks)***

30. A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 ml. of the oxidant. The resultant solution is neutralized with Na_2CO_3, acidified with dil. acetic acid and treated with excess KI. The liberated iodine requires 11.3 ml of 0.05 M $Na_2S_2O_3$ solution for complete reduction.

Find out the molar ratio of Cu^{2+} to $C_2O_4^{2-}$ in the compound. Write down the balanced redox reactions involved in the above titrations. ***(1991 - 5 Marks)***

31. A 1.0 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 100.0 ml. An aliquot of 25.0 ml of this solution requires 17.0 ml of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. ***(1991 - 4 Marks)***

32. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 ml. A 1.5g of the same sample requires 150 ml. of (M/10) HCl for complete neutralisation. Calculate the % composition of the components of the mixture. ***(1992 - 5 Marks)***

33. One gram of commercial $AgNO_3$ is dissolved in 50 ml. of water. It is treated with 50 ml. of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filterate is titrated with (M/10) KIO_3 solution in presence of 6M HCl till all I^- ions are 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 the percentage of $AgNO_3$ in the sample.

(Reaction : $KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$)

(1992 - 4 Marks)

34. Upon mixing 45.0 ml. of 0.25 M lead nitrate solution with 25.0 ml of 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also, calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. *(1993 - 3 Marks)*

35. The composition of a sample of Wustite is $Fe_{0.93}O_{1.00}$. What percentage of the iron is present in the form of Fe (III)? *(1994 - 2 Marks)*

36. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate the molarity, molality and mole fraction of Na_2SO_4 in the solution. *(1994 - 3 Marks)*

37. A 3.00 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance, is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the diluted solution requires 11.0 ml of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 ml of the diluted solution, after complete extraction of the 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 percentages of Fe_2O_3 and Fe_3O_4 in the original sample.

(1996 - 5 Marks)

38. An aqueous solution containing 0.10 g KIO_3 (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution. *(1998 - 5 Marks)*

39. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper(II) carbonate? *(1999 - 3 Marks)*

40. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be a single particle, find its molar mass. *(1999 - 3 Marks)*

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

(2001 - 5 Marks)

42. Calculate the molarity of water if its density is 1000 kg/m^3.

(2003 - 2 Marks)

H Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below :

STATEMENT(S) : In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of the acid required using phenolphthalein indicator.

EXPLANATION(E) : Two moles of HCl are required for the complete neutralization of one mole of Na_2CO_3.

(1991 - 2 Marks)

(a) Both S and E are true, and E is the correct explanation of S.

(b) Both S and E are true, but E is not the correct explanation of S.

(c) S is true but E is false.

(d) S is false but E is true.

I Integer Value Correct Type

1. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is

(2010)

2. Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3}. The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is : *(2010)*

3. The difference in the oxidation numbers of the two types of sulphur atoms in $Na_2S_4O_6$ is *(2011)*

4. If the value of Avogadro number is 6.023×10^{23} mol^{-1} and the value of Boltzmann constant is 1.380×10^{-23} J K^{-1}, then the number of significant digits in the calculated value of the universal gas constant is *(JEE Adv. 2014)*

Section-B JEE Main / AIEEE

1. In a compound C, H and N atoms are present in 9 : 1 : 3.5 by weight. Molecular weight of compound is 108. Molecular formula of compound is **[2002]**

(a) $C_2H_6N_2$ (b) C_3H_4N (c) $C_6H_8N_2$ (d) $C_9H_{12}N_3$.

2. With increase of temperature, which of these changes? **[2002]**

(a) molality (b) weight fraction of solute

(c) molarity (d) mole fraction.

3. Number of atoms in 558.5 gram Fe (at. wt. of Fe = 55.85 g mol^{-1}) is

(a) twice that in 60 g carbon **[2002]**

(b) 6.023×10^{22}

(c) half that in 8 g He

(d) $558.5 \times 6.023 \times 10^{23}$

4. What volume of hydrogen gas, at 273 K and 1 atm. pressure will be consumed in obtaining 21.6 g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen ? **[2003]**

(a) 67.2 L (b) 44.8 L (c) 22.4 L (d) 89.6 L

5. 25ml of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a litre value of 35ml. The molarity of barium hydroxide solution was **[2003]**

(a) 0.14 (b) 0.28 (c) 0.35 (d) 0.07

6. 6.02×10^{20} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is **[2004]**

(a) 0.02 M (b) 0.01 M (c) 0.001 M (d) 0.1 M

(Avogadro constant, $N_A = 6.02 \times 10^{23}\ mol^{-1}$)

7. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the value of 0.1 M aqueous KOH solution required is **[2004]**

(a) 40mL (b) 20mL (c) 10mL (d) 60mL

8. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is **[2004]**

(a) urea (b) benzamide

(c) acetamide (d) thiourea

9. Two solutions of a substance (non electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 ml of 1.2 M second solution. What is the molarity of the final mixture? **[2005]**

(a) 2.70 M (b) 1.344 M (c) 1.50 M (d) 1.20 M

10. If we consider that 1/6, in place of 1/12, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of the substance will **[2005]**

(a) be a function of the molecular mass of the substance

(b) remain unchanged

(c) increase two fold

(d) decrease twice

11. How many moles of magnesium phosphate, $Mg_3(PO_4)_2$ will contain 0.25 mole of oxygen atoms? **[2006]**

(a) 1.25×10^{-2} (b) 2.5×10^{-2}

(c) 0.02 (d) 3.125×10^{-2}

12. Density of a 2.05M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is **[2006]**

(a) 2.28 mol kg^{-1} (b) 0.44 mol kg^{-1}

(c) 1.14 mol kg^{-1} (d) 3.28 mol kg^{-1}

13. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be

(a) 1.45 (b) 1.64 **[2007]**

(c) 1.88 (d) 1.22

14. In the reaction, **[2007]**

$$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq) + 3H_2(g)$$

(a) 11.2 L H_2(g) at STP is produced for every mole HCl(aq) consumed

(b) 6 L HCl(aq) is consumed for every 3 L H_2(g) produced

(c) 33.6 L H_2(g) is produced regardless of temperature and pressure for every mole A*l* that reacts

(d) 67.2 H_2(g) at STP is produced for every mole A*l* that reacts.

15. Consider the following reaction :

$$xMnO_4^{-} + yC_2O_4^{2-} + zH^{+} \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$$

The value's of x, y and z in the reaction are, respectively : **[JEE M 2013]**

(a) 5, 2 and 16

(b) 2, 5 and 8

(c) 2, 5 and 16

(d) 5, 2 and 8

16. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is : **[JEE M 2013]**

(a) C_2H_4 (b) C_3H_4 (c) C_6H_5 (d) C_7H_8

17. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be : **[JEE M 2013]**

(a) 7.01% (b) 4.08% (c) 6.05% (d) 5.08%

Solutions & Explanations

1 Some Basic Concepts of Chemistry

Section-A : JEE Advanced/ IIT-JEE

A **1.** Carbon-12. **2.** 6.02×10^{24} **3.** 0.4m **4.** 4.14 g **5.** $+\frac{7}{3}$

C **1.** (d) **2.** (c) **3.** (a) **4.** (a) **5.** (c) **6.** (a) **7.** (a)
8. (d) **9.** (c) **10.** (c) **11.** (a) **12.** (b) **13.** (b) **14.** (d)
15. (c) **16.** (b) **17.** (a) **18.** (d) **19.** (a) **20.** (d) **21.** (c)
22. (a) **23.** (b) **24.** (d) **25.** (a) **26.** (a) **27.** (b) **28.** (d)

E **1.** 4.87 g **2.** Al 54.87%, Mg 45.13% **3.** 59.33% **4.** 8.38
5. (a) 9.5×10^{-3} gram mole, (b) 0.437 moles **6.** CH_4 **7.** $Na_2O = 3.58\%$, $K_2O = 10.62\%$
8. 24 **9.** 1.338 gm
10. (a) 1.95 parts; (b) 1 milli equivalents; (c) (i) Mg, (ii) 0.25g, (iii) 62.5 ml **11.** C_7H_8
12. 3.5×10^{-3} g **13.** 53.53 **14.** 0.588N **16.** 39.6 g l^{-1}
17. (i) 37.92; (ii) 0.065; (iii) 7.74 m, 3.87 m **18.** Ca **20.** 2
21. 6.3648 g **22.** $HI < I_2 < ICl < HIO_4$ **23.** (i) 1.446 gm, 0.112 M; (ii) 1.7532 g, 0.1344 M
24. (i) 0.56; (ii) 0.0999 **25.** 6.5 g **26.** +2, +4, +6, 16.66 ml
27. 1.12 g, 0.90 g **28.** 3.324 g, 1.676 g **29.** 10.43 m **30.** 1 : 2
31. 6 **32.** Na_2CO_3-26.5%, Na_2SO_4-31.5% **33.** 85%
34. 0.0075 M, $Pb^{2+} = 0.05357$ M, $NO_3^- = 0.3214$ M, $Cr^{3+} = 0.0714$ M **35.** 15.05%
36. 0.25 M, 0.24 m, 4.3×10^{-3} **37.** 49.33%, 34.8% **38.** 0.062
39. 8.097 ml **40.** 7.09×10^7 **41.** 0.1 **42.** 55.55 M

H **1.** (b)

I **1.** 3 **2.** 7 **3.** 5 **4.** 4

Section-B : JEE Main/ AIEEE

1. (c) **2.** (c) **3.** (a) **4.** (a) **5.** (d) **6.** (b) **7.** (a) **8.** (a)
9. (b) **10.** (d) **11.** (d) **12.** (a) **13.** (d) **14.** (a) **15.** (c) **16.** (d)
17. (b)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **Carbon (C – 12)**

2. **6.02×10^{24}**

18 ml $H_2O = 18$ g H_2O ($\because$ density of water = 1 g/cc)
$= 1$ mole of H_2O.

1 Mole of $H_2O = 10 \times 6.02 \times 10^{23}$ electrons
($\because$ Number of electrons present in one molecule of water $= 2 + 8 = 10$)
$= 6.02 \times 10^{24}$ electrons

3. **TIPS/Formulae :** Molality $= \dfrac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$

$$= \frac{\text{wt. of solute in gram / M.wt. of solute}}{\text{Mass of solvent in kg}}$$

$$\text{Molality} = \frac{3/30}{250/1000} = \mathbf{0.4m}$$

4. **TIPS/Formulae :**

1 Mole $= 6.023 \times 10^{23}$ molecules $=$ Molecular weight in gms.

Weight of 6.023×10^{23} (Avogadro's number) molecules of $CuSO_4.5H_2O =$ Molecular wt. of $CuSO_4.5H_2O = 249$ g.

$\therefore$ Weight of 1×10^{22} molecules of $CuSO_4.5H_2O$

$$= \frac{249 \times 1 \times 10^{22}}{6.023 \times 10^{23}} = \mathbf{4.14\ g}$$

5. **NOTE :** Sum of oxidation states of all atoms (elements) in a neutral compound is zero.

TIPS/Formulae : As $YBa_2Cu_3O_7$ is neutral.

$$(+3) + 2(+2) + 3(x) + 7(-2) = 0$$

or $\quad 3 + 4 + 3x - 14 = 0$

$\Rightarrow \quad 3x + 7 - 14 = 0 \qquad$ or $\qquad x = +\dfrac{7}{3}$

C. MCQs with ONE Correct Answer

1. **(d)** $4\,Al + 3O_2 \longrightarrow 2\,Al_2O_3$

At. wt. of Al $= 27$

Thus 4×27 g of Al reacts with oxygen $= 3 \times 32$ g

$\therefore$ 27 g of Al reacts with oxygen $= \dfrac{3 \times 32}{4 \times 27} \times 27$ g

$= 24$ g

2. **(c)** No. of nitrogen atoms $= \dfrac{\text{Mass in grams}}{\text{Atomic wt.}} = \dfrac{28}{14} = 2$

No. of oxygen atoms $= \dfrac{\text{Mass in grams}}{\text{Atomic wt.}} = \dfrac{80}{16} = 5$

$\therefore$ Formula of compound is N_2O_5.

3. **(a)** (a) 18 g of $H_2O = 6.02 \times 10^{23}$ molecules of H_2O

$\therefore$ 36 g of $H_2O = 2 \times 6.02 \times 10^{23}$ molecules of H_2O

$= 12.04 \times 10^{23}$ molecules of H_2O

(b) 28 g of CO $= 6.02 \times 10^{23}$ molecules of CO

(c) 46 g of $C_2H_5OH = 6.02 \times 10^{23}$ molecules of C_2H_5OH

(d) 108 g of $N_2O_5 = 6.02 \times 10^{23}$ molecules of N_2O_5

$\therefore$ 54 g of $N_2O_5 = \dfrac{1}{2} \times 6.02 \times 10^{23}$ molecules of N_2O_5

$= 3.01 \times 10^{23}$ molecules of N_2O_5

$\therefore$ 36 g of water has highest number of molecules.

4. **(a)** No. of e^- in C $= 6$ and in O $= 8$

$\therefore$ Total no. of e^- in $CO_2 = 6 + 8 \times 2 = 22$

5. **(c)** Let mass of oxygen $=$ 1g, Then mass of nitrogen $=$ 4g

Mol. wt. of $N_2 = 28$g, Mol. wt. of $O_2 = 32$g

28 g of N_2 has $= 6.02 \times 10^{23}$ molecules of nitrogen

4 g of N_2 has $= \dfrac{6.02 \times 10^{23}}{28} \times 4$ molecules of nitrogen

$= \dfrac{6.02 \times 10^{23}}{7}$ molecules of nitrogen

32 g of O_2 has $= 6.02 \times 10^{23}$ molecules of oxygen

$\therefore \quad$ 1g of O_2 has $= \dfrac{6.02 \times 10^{23}}{32} \times 1 = \dfrac{6.02 \times 10^{23}}{32}$ molecules of oxygen

Thus, ratio of molecules of oxygen : nitrogen

$$= \frac{6.02 \times 10^{23}/32}{6.02 \times 10^{23}/7} = 7 : 32$$

6. **(a)**

$$\begin{array}{ccc} \underset{2.76}{Ag_2CO_3} & \xrightarrow{\Delta} & Ag_2O + CO_2 \\ & & \big\downarrow \Delta \\ & & \underset{\text{(residue)}}{2Ag + \frac{1}{2}O_2} \end{array}$$

NOTE : Ag_2O is thermally unstable and decompose on heating liberating oxygen]

Mol. wt. of $Ag_2CO_3 = 108 \times 2 + 12 + 16 \times 3 = 276$ g

$\therefore$ 276 g of Ag_2CO_3 on heating gives residue

$= 2 \times 108 = 216$ g of Ag

$\therefore$ 2.76 g of Ag_2CO_3 on heating gives $= \dfrac{216}{276} \times 2.76$

$= 2.16$g of Ag

7. **(a)** The change involved is $MnO_4{}^- + e^- \longrightarrow MnO_4^{2-}$

i.e. it involves only one electron

$$\text{Eq.wt} = \frac{\text{Mol.wt}}{\text{No.of } e^- \text{ involved}} = \frac{M}{1} = M \ [\because \text{Mol. wt.} = M]$$

8. **(d)** **TIPS/Formulae :**

(i) Write balanced chemical equation for chemical change.

(ii) Find limiting reagent.

(iii) Amount of product formed will be determined by amount of limiting reagent.

The balanced equation is :

$$\begin{array}{lcccc} & 3BaCl_2 & + \ 2Na_3PO_4 & \rightarrow Ba_3(PO_4)_2 & + \ 6NaCl \\ \text{No. of} & 0.5 & 0.2 & & \\ \text{moles :} & 3\,\text{mole} & 2\,\text{mole} & 1\,\text{mole} & \end{array}$$

Limiting reagent is Na_3PO_4 (0.2 mol), $BaCl_2$ is in excess.

From the above equation :

2.0 moles of Na_3PO_4 yields $Ba_3(PO_4)_2 = 1$ mole

$\therefore$ 0.2 moles of Na_3PO_4 will yield $Ba_3(PO_4)_2 = \dfrac{1}{2} \times 0.2$

$= \mathbf{0.1\ mol.}$

9. **(c)** **TIPS/Formulae :**

(i) Find oxidation state of N in N_2H_4.

(ii) Find change in oxidation number with the help of number of electrons given out during formation of compound Y.

$N_2H_4 \rightarrow Y + 10\,e^-$, Calculation of O.S. of N in N_2H_4 :

$2x + 4 = 0 \Rightarrow x = -2$

The two nitrogen atoms will balance the charge of 10 e. Hence oxidation state of N will increase by +5, i.e. from –2 to +3.

10. (c) NOTE:
The sum of oxidation states of all atoms in compound is zero. Calculation of O.S. of C in CH_2O.
$x+2+(-2)=0 \Rightarrow x=0$

11. (a) TIPS/Formulae :

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

A molal solution is one which contains one mole of solute per 1000 g of solvent. $\left\{\because 1\text{m} = \frac{1\,\text{mole}}{1\,\text{kg}}\right\}$

12. (b) TIPS/Formulae :
Sum of oxidation state of all atoms in neutral compound is zero. Let the oxidation state of iron in the complex ion $[Fe(H_2O)_5(NO)]^{2+}.SO_4^{2-}$ be x; then
$x+5\times 0+0=+2. \quad \therefore \quad x=+2$

13. (b) For equivalent weight of $MnSO_4$ to be half of its molecular weight, change in oxidation state must be equal to 2. It is possible only when oxidation state of Mn in product is + 4. Since oxidation state of Mn in $MnSO_4$ is + 2. So, MnO_2 is correct answer.
In MnO_2, O.S. of Mn = +4
$\therefore$ Change in O.S. of Mn = +4 – (+2) = +2

14. (d) TIPS/Formulae :
(i) Volume of substance changes with temperature and mass is not effected by change in temperature.
(ii) Find expression which does not have volume term in it.
(a) Molarity – Moles of solute/volume of solution in L
(b) Normality – gm equivalents of solute/volume of solution in L.
(c) Formality – gm formula wt./volume of solution in L.
(d) Molality – Moles of solute/mass of solvent in kg
$\because$ Molality does not involve volume term.
$\therefore$ It is independent of temperature.

15. (c) $2+2(2+x-4)=0$ [$\because$ $Ba(H_2PO_2)_2$ is neutral molecule]
or $2x-2=0 \Rightarrow x=+1$

16. (b) TIPS/Formulae :
(i) Write balance chemical equation for given change.
(ii) Identify most electronegative element and find its oxidation state.
$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$
Oxygen is the most electronegative element in the reaction and has the oxidation states of –1 (in H_2O_2) and –2 (in $BaSO_4$). In H_2O_2, peroxo ion is present.

17. (a) TIPS/Formulae :
Balance the reaction by ion electron method.

Oxidation reaction : $C_2O_4^{-2} \rightarrow 2CO_2 + 2e^-] \times 5$

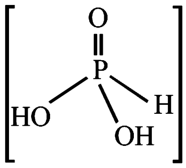
Reduction reaction :

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

Net reaction :

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

18. (d) TIPS/Formulae :
(i) H_3PO_3 is dibasic acid as it contains two –OH groups.



(ii) Normality = Molarity × basicity of acid.
(iii) Basicity of $H_3PO_3 = 2$
$\therefore$ Normality = 0.3 × 2 = 0.6

19. (a) TIPS/Formulae :
(i) Oxidation state of element in its free state is zero.
(ii) Sum of oxidation states of all atoms in compound is zero.
O.N. of S in $S_8 = 0$; O.N. of S in $S_2F_2 = +1$;
O.N. of S in $H_2S = -2$;

20. (d) TIPS/Formulae :
(i) In an ion sum of oxidation states of all atoms is equal to charge on ion and in a compound sum of oxidation states of all atoms is always zero.
Oxidation state of Mn in $MnO_4^- = +7$
Oxidation state of Cr in $Cr(CN)_6^{3-} = +3$
Oxidation state of Ni in $NiF_6^{2-} = +4$
Oxidation state of Cr in $CrO_2Cl_2 = +6$

21. (c) TIPS/Formulae :
(i) In a disproportionation reaction same element undergoes oxidation as well as reduction during the reaction.
(ii) In decomposition reaction a molecule breaks down to more than one atoms or molecules

$$3\overset{+1}{Cl}O^-_{(aq)} \rightarrow \overset{+5}{Cl}O_3^- + 2\overset{-1}{Cl}{}^-_{(aq)}$$

It is disproportionation reaction because Cl is both oxidised (+ 1 to + 5) and reduced (+ 1 to – 1) during reaction.

22. (a) TIPS/Formulae :
Equivalents of $H_2C_2O_4.2H_2O$ = Equivalents of NaOH
(At equivalence point)

$$\text{Strength of } H_2C_2O_4 \,.\, 2H_2O \text{ (in g/L)} = \frac{6.3}{250/1000}$$
$$= 25.2 \text{ g/L}$$

$$\text{Normality of } H_2C_2O_4 \,.\, 2H_2O = \frac{\text{Strength}}{\text{Eq. wt}}$$

$$= \frac{25.2}{63} = 0.4\text{N}$$

$$\left\{\text{Eq. wt. of oxalic acid} = \frac{\text{Mol. wt}}{2} = \frac{126}{2} = 63\right\}$$

Using normality equation :
$N_1V_1 \;=\; N_2V_2$
$(H_2C_2O_4.2H_2O)$ (NaOH)

$$0.4 \times 10 \quad = 0.1 \times V_2 \text{ or } V_2 = \frac{0.4 \times 10}{0.1} = 40 \text{ ml.}$$

23. (b) TIPS/Formulae :

(i) Find change in oxidation number of Cr atom.

(ii) $\text{Eq. wt.} = \dfrac{\text{Molecular wt.}}{\text{change in O.N.}}$

In iodometry, $K_2Cr_2O_7$ liberates I_2 from iodides (NaI or KI). Thus it is titrated with $Na_2S_2O_3$ solution.

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

O.N. of Cr changes from + 6 (in $K_2Cr_2O_7$) to +3. i.e. +3 change for each Cr atom

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

Thus, one mole of $K_2Cr_2O_7$ accepts 6 mole of electrons.

$$\therefore \text{ Equivalent weight} = \frac{\text{Molecular weight}}{6}$$

24. (d) TIPS/Formulae :

(i) Mass of one electron = 9.108×10^{-31} kg

(ii) 1 mole of electron = 6.023×10^{23} electrons

Weight of 1 mole of electron

= Mass of one electron × Avogadro Number

$= 9.108 \times 10^{-31} \times 6.023 \times 10^{23}$ kg

∴ No. of moles of electrons in 1 kg

$$= \frac{1}{9.108 \times 10^{-31} \times 6.023 \times 10^{23}} = \frac{1}{9.108 \times 6.023} \times 10^8$$

25. (a) TIPS/Formulae :

Atomic weight in gms = 6.023×10^{23} atoms = 1 Mole atoms

(i) Number of atoms in 24 g of C

$$= \frac{24}{12} \times 6.023 \times 10^{23} = 2 \times 6.023 \times 10^{23} \text{ atom}$$

= 2 mole atoms

(ii) Number of atoms in 56 g of Fe

$$= \frac{56}{56} \times 6.023 \times 10^{23} = 6.023 \times 10^{23} \text{ atom}$$

= 1 mole atoms

(iii) Number of atoms in 27 g of Al

$$= \frac{27}{27} \times 6.023 \times 10^{23} = 6.023 \times 10^{23} \text{ atom}$$

= 1 mole atoms

(iv) Number of atoms in 108 g of Ag

$$= \frac{108}{108} \times 6.023 \times 10^{23} = 6.023 \times 10^{23} \text{ atom}$$

= 1 mole atoms

∴ 24 g of C has maximum number of atoms.

26. (a) TIPS/Formulae :

Write the reaction for chemical change during reaction and equate moles of products formed.

$[Co(NH_3)_5SO_4]$ Br has ionisable Br^- ions & $[Co(NH_3)_5 Br]$ SO_4 has ionisable SO_4^{--} ion.

Given mixture $X = 0.02$ mol of $[Co(NH_3)_5SO_4]$ Br and 0.02 mol of $[Co(NH_3)_5Br]$ SO_4

Volume = 2 L

∴ Mixture X has 0.02 mol. of $[Co(NH_3)_5SO_4]$ Br and 0.02 mol of $[Co(NH_3)_5Br]$ SO_4 in 2 L of solution

∴ Conc. of $[Co(NH_3)_5SO_4]$ Br and $[Co(NH_3)_5Br]SO_4$ = 0.01 mol/L for each of them.

(i) 1 L mixture of X + excess $AgNO_3 \to Y$

$$\underset{\text{0.01 mol/L soluble}}{[Co(NH_3)_5SO_4]\,Br} + \underset{\text{excess}}{AgNO_3} \longrightarrow [Co(NH_3)_5SO_4]NO_3 + \underset{\substack{(Y)\\ 0.01\,\text{mol}}}{AgBr}$$

$$\left[Ag^+ + Br^- \to AgBr\right]$$

∴ No. of moles of $Y = 0.01$

(ii) Also 1 L mixture of X + excess $BaCl_2 \to Z$

$$\underset{\text{0.01 mol/L soluble}}{[Co(NH_3)_5Br]SO_4} + \underset{\text{excess}}{BaCl_2} \longrightarrow [Co(NH_3)_5Br]Cl_2 + \underset{\substack{(Z)\\ 0.01\,\text{mol}}}{BaSO_4}$$

$$\left[Ba^{++} + SO_4^{=} \to BaSO_4\right]$$

∴ moles of $Z = 0.01$.

27. (b) TIPS/Formulae :

The highest O.S. of an element is equal to the number of its valence electrons

(i) $[Fe(CN)_6]^{3-}$, O.N. of Fe = + 3,
$[Co(CN)_6]^{3-}$, O.N. of Co = + 3

(ii) CrO_2Cl_2, O.N. of Cr = +6, (Highest O.S. of Cr)
$[MnO_4]^-$ O.N of Mn = + 7 (Highest O.S. of Mn)

(iii) TiO_3, O.N. of Ti = + 6, MnO_2 O.N. of Mn = + 4

(iv) $[Co(CN)_6]^{3-}$, O.N. of Co = + 3,
MnO_3, O.N. of Mn = + 6

28. (d) The following reaction occurs:

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

From the above equation, we find that Mohr's salt ($FeSO_4.(NH_4)_2SO_4.6H_2O$) and dichromate reacts in 6 : 1 molar ratio.

E. Subjective Problems

1. TIPS/Formulae :

Write the balance chemical equation and use mole concept for limiting reagent.

$$\underset{170\text{ g}}{AgNO_3} + \underset{58.5\text{ g}}{NaCl} \longrightarrow NaNO_3 + \underset{143.5\text{ g}}{AgCl}$$

From the given data, we find $AgNO_3$ is limiting reagent as NaCl is in excess.

$\because$ 170.0 g of $AgNO_3$ precipitates AgCl = 143.5 g

$\therefore$ 5.77 g of $AgNO_3$ precipitates AgCl

$$= \frac{143.5}{170.0} \times 5.77 = \mathbf{4.87\ g}$$

2. **TIPS/Formulae :**

(i) Find volume of H_2 at N.T.P.

(ii) Total amount of H_2 liberated = H_2 liberated by Mg & HCl + H_2 liberated by Al & HCl.

Conversion of volume of H_2 to N.T.P

Given conditions	N.T.P conditions
$P_1 = 0.92$ atm.	$P_2 = 1$ atm.
$V_1 = 1.20$ litres	$V_2 = ?$
$T_1 = 0 + 273 = 273$ K	$T_2 = 273$ K

Applying ideal gas equation, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{0.92 \times 1.20}{273} = \frac{1 \times V_2}{273},\ V_2 = \frac{0.92 \times 1.20 \times 273}{273 \times 1} \text{ litres}$$

= 1.104 litres = 1104 ml

The relevant chemical equations are

$$\text{(i)}\quad \begin{array}{llll} 2\,Al & + \ 6HCl \longrightarrow & 2AlCl_3 \ + & 3H_2 \\ 2 \times 27 & & & 3 \times 22400 \\ = 54\ g & & & = 67200 \text{ ml at NTP} \end{array}$$

$$\text{(ii)}\quad \begin{array}{llll} Mg & + \ 2HCl \longrightarrow & MgCl_2 \ + & H_2 \\ 24\ g & & & 22400 \text{ ml at NTP} \end{array}$$

Wt. of alloy = 1 g

Let the wt. of aluminium in alloy = x g

$\therefore$ Wt. of magnesium in alloy = $(1 - x)$ g

According to equation (i)

54 g of Al = 67200 ml of H_2 at N.T.P

$$\therefore x \text{ g of Al} = \frac{67200}{54} \times x = 1244.4\,x \text{ ml of } H_2 \text{ at N.T.P}$$

Similarly, from equation (ii)

24 g of Mg = 22400 ml of H_2 at N.T.P

$$(1 - x) \text{ g of Mg} = \frac{22400}{24} \times (1 - x) = 933.3\,(1 - x) \text{ ml of } H_2$$

Hence total vol. of H_2 collected at N.T.P

$= 1244.4\,x + 933.3\,(1 - x)$ ml

But total vol. of H_2 as calculated above = 1104 ml

$\therefore$ $1244.4\,x + 933.3\,(1 - x) = 1104$ ml

$1244.4\,x - 933.3\,x = 1104 - 933.3$

$311.1\,x = 170.7, x = 0.5487$

Hence 1 g of alloy contains Al = 0.5487 g

$$\therefore \text{ Percentage of Al in alloy} = \frac{0.5487 \times 100}{1} = \mathbf{54.87\%}$$

% of Mg in alloy = 100 – 54.87 = **45.13%**

3.

$$\begin{array}{lcl} 3\,MnO_2 & \longrightarrow & Mn_3O_4 \ + \ O_2 \\ 3\,(54.9 + 32) & & (3 \times 54.9 + 64) \\ = 260.7\ g & & = 228.7\ g \end{array}$$

Let the amount of pyrolusite ignited = 100.00 g

$\therefore$ Wt. of MnO_2 = 80 g (80% of 100 g = 80 g)

Wt. of SiO_2 and other inert substances = 15 g

Wt. of water = 100 – (80 + 15) = 5 g

According to equation,

260.7 g of MnO_2 gives = 228.7 g of Mn_3O_4

$$\therefore 80 \text{ g of } MnO_2 \text{ gives} = \frac{228.7}{260.7} \times 80 = 70.2 \text{ g of } Mn_3O_4$$

NOTE:

During ignition, H_2O present in pyrolusite is removed while silica and other inert substances remain as such.

$\therefore$ Total wt. of the residue = 70.2 + 15 = 85.2 g

Calculation of % of Mn in ignited Mn_3O_4

$$\begin{array}{ccc} 3\,Mn & = & Mn_3O_4 \\ 3 \times 54.9 = 164.7\ g & & 3 \times 54.9 + 64 = 228.7g \end{array}$$

Since, 228.7 g of Mn_3O_4 contains 164.7 g of Mn

$$70.2 \text{ g of } Mn_3O_4 \text{ contains} = \frac{164.7}{228.7} \times 70.2 = 50.55 \text{ g of Mn}$$

Weight of residue = 85.2 g

Hence, percentage of Mn is the ignited sample

$$= \frac{50.55}{85.2} \times 100 = \mathbf{59.33\%}$$

4. **TIPS/Formulae :**

(i) Find the volume of CO_2 at NTP

(ii) Find molecular wt. of metal carbonate

(iii) Find the wt. of metal

(iv) Calculate equivalent weight of metal

Given $P_1 = 700$ mm, $P_2 = 760$ mm, $V_1 = 1336$ ml, $V_2 = ?$

$T_1 = 300$ K, $T_2 = 273$ K

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}, \text{ or } V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{700 \times 1336 \times 273}{760 \times 300}$$

= 1119.78 ml = 1.12 L at NTP

$\because$ 1.12 L of CO_2 is given by carbonate = 4.215 g

$$\text{Molecular weight of metal carbonate} = \frac{4.215}{1.12} \times 22.4$$

$= 84.3$

Metal carbonate is MCO_3 = M + 12 + 48 = M + 60

Atomic weight of M = 84.3 – 60 = 24.3

$$\text{Eq. wt. of metal} = \frac{1}{2} \times \text{M. wt.} = \frac{1}{2} \times 24.3 = 12.15$$

5. (a) Equivalents of $KMnO_4$ = Equivalents of $FeSO_4 \cdot 7H_2O$

$$5.4 \text{ ml } 0.1\text{ N } KMnO_4 = \frac{5.4 \times 0.1}{1000} = 5.4 \times 10^{-4} \text{ equivalents}$$

Amount of $FeSO_4 = 5.4 \times 10^{-4} \times$ Mol wt. of $FeSO_4.7H_2O$

$= 5.4 \times 10^{-4} \times 278 = 0.150$ g

Total weight of mixture = 5.5 g

Amount of ferric sulphate = 5.5 – 0.150 g = 5.35 g

$$\text{Hence Moles of ferric sulphate} = \frac{\text{Mass}}{\text{M. wt.}} = \frac{5.35}{562}$$

$$= \mathbf{9.5 \times 10^{-3}\ gram\text{-}mole}$$

(b) Using the relation, Mol. wt. = 2 × vapour density, we get

Mol. wt. = 2 × 38.3 = 76.6

$$\text{No. of moles} = \frac{\text{Mass}}{\text{Mol. wt.}} = \frac{100}{76.6} = 1.30 \qquad ....(i)$$

Let weight of NO_2 in mixture = x g

Then weight of N_2O_4 in mixture = $100 - x$

$$\text{No. of moles of } NO_2 = \frac{\text{Mass}}{\text{Mol. wt.}} = \frac{x}{46} \qquad ....(ii)$$

$$\text{No. of moles of } N_2O_4 = \frac{\text{Mass}}{\text{Mol. wt.}} = \frac{100-x}{92} \qquad ...(iii)$$

According to problem

$$1.30 = \frac{x}{46} + \frac{100-x}{92}$$

On solving the equation we find, $x = 20.1$

∴ weight of $NO_2 = 20.1$ g

$$\text{Moles of } NO_2 = \frac{\text{Mass}}{\text{M. wt.}} = \frac{20.1}{46} = \mathbf{0.437\ moles.}$$

6. Volume of oxygen taken = 30 ml,

Volume of unused oxygen = 15 ml

Volume of O_2 used = Volume of O_2 added – Volume of O_2 left $= 30 - 15 = 15$ ml

Volume of CO_2 produced

= Volume of gaseous mixture after explosion – Volume of unused oxygen

or Volume of CO_2 produced $= 25 - 15 = 10$ ml

Volume of hydrocarbon = 5 ml

General equation for combustion of a hydrocarbon is as follows -

$$\underset{\substack{\text{(Hydrocarbon)}\\ 5\text{ ml}}}{C_xH_y} + \underset{5\left(x+\frac{y}{4}\right)\text{ml}}{\left(x+\frac{y}{4}\right)O_2} \longrightarrow \underset{5x}{xCO_2} + \frac{y}{2}H_2O$$

∴ Volume of CO_2 produced = 5x, Since Volume of CO_2 = 10 ml

∴ $5x = 10 \Rightarrow x = 2$, Volume of O_2 used = 15 ml

$$\therefore 5\left(x+\frac{y}{4}\right) = 15 \Rightarrow x + \frac{y}{4} = 3$$

$$\Rightarrow 2 + \frac{y}{4} = 3 \quad (\because x = 2) \qquad \Rightarrow 8 + y = 12 \therefore y = 4$$

Hence Molecular formula of hydrocarbon is $\mathbf{C_2H_4}$.

7. **TIPS/Formulae :**

(i) Equate given mass of AgCl against mass obtained from NaCl and KCl

(ii) $2NaCl \equiv Na_2O$ & $2KCl \equiv K_2O$

Let amount of NaCl in mixture = x gm

∴ amount of KCl in mixture = $(0.118 - x)$ gm

$$\underset{58.5\text{ g}}{NaCl} + AgNO_3 \longrightarrow \underset{143.5\text{ g}}{AgCl} + NaNO_3$$

∵ 58.5 g NaCl gives AgCl = 143.5g

$$\therefore x\text{ g NaCl gives AgCl} = \frac{143.5}{58.5} \times x\text{ g}$$

Again

$$\underset{74.5\text{ g}}{KCl} + AgNO_3 \longrightarrow \underset{143.5\text{ g}}{AgCl} + KNO_3$$

∵ 74.5 g KCl gives AgCl = 143.5g

$$\therefore (0.118 - x)\text{ g KCl gives AgCl} = \left(\frac{143.5}{74.5} \times 0.118 - x\right)\text{g}$$

Total weight of AgCl = 0.2451g

$$\therefore \left(\frac{143.5}{58.5} \times x\right) + \left[\frac{143.5}{74.5} \times (0.118 - x)\right] = 0.2451$$

∴ $x = 0.0338$g

∴ Amount of NaCl in mixture = 0.0338g

∴ Amount of KCl in mixture = $0.118 - 0.0338 = 0.0842$g

$$\text{Since} \quad \underset{\substack{2\times 58.5\\ =117.0}}{2NaCl} \equiv \underset{62}{Na_2O}$$

∵ 117g NaCl is equivalent to = 62.0g Na_2O

$$\therefore \quad 0.0338\text{g NaCl is equivalent to} = \frac{62.0}{117} \times 0.0338 \text{ g } Na_2O = 0.0179\text{g}$$

$$\%\text{ of } Na_2O \text{ in 0.5g of feldspar} = \frac{0.0179}{0.500} \times 100 = 3.58\%$$

$$\underset{2\times 74.5 = 149}{2KCl} \equiv \underset{94}{K_2O}$$

∵ 149g of KCl is equivalent to = 94g K_2O

$$\therefore \quad 0.0842\text{g of KCl is equivalent to} = \frac{94}{149} \times 0.0842 = 0.0531\text{g } K_2O$$

$$\therefore \quad \%\text{ of } K_2O \text{ in 0.5g of feldspar} = \frac{0.0531}{0.5} \times 100 = 10.62\%$$

% of Na_2O in feldspar = 3.58%

% of K_2O in feldspar = 10.62%

8. According to problem, three atoms of M combine with 2 atoms of N

∴ Formula of compound is M_3N_2 (Where M is the metal)

$$\text{Equivalent wt of N} = \frac{14}{3} \ (\because \text{valency of N in compound is 3})$$

∵ 28 g N combines with = 72g metal

$$\therefore \quad 14/3 \text{ N combines with} = \frac{72}{28} \times \frac{14}{3} = 12$$

∴ Eq. wt. of metal = 12

At wt of metal = Eq. wt × valency = 12 × 2 = **24**

[Valency of metal = 2]

9. Following reactions take place-

$$3MnSO_4.4H_2O \xrightarrow{\text{heat}} \underset{\text{(residue)}}{Mn_3O_4} + 4H_2O\uparrow + 3SO_2\uparrow + O_2\uparrow$$

$$Mn_3O_4 + 2FeSO_4 + 4H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 3MnSO_4 + 4H_2O$$

Milliequivalents of $FeSO_4$ in 30 ml of 0.1N $FeSO_4$ $= 30 \times 0.1 = 3$ m. eq.

According to problem step (iv)

25 ml of $KMnO_4$ reacts with = 3 m eq of $FeSO_4$

Thus in step (iii) of the problem,

50 ml of $KMnO_4$ reacts with $= \frac{3}{25} \times 50$ m.eq. of $FeSO_4$

$= 6$ meq of $FeSO_4$

Milli eq. of 100 ml of 0.1N $FeSO_4 = 100 \times 0.1 = 10$ m eq.

$FeSO_4$ which reacted with $Mn_3O_4 = (10–6) = 4$ m eq.

Milli eq of $FeSO_4$ = Milli eq. of Mn_3O_4

($\because$ Milli eq of oxidising agent and reducing agent are equal)

$\because$ $Mn_3O_4 \equiv 3MnSO_4.4H_2O$

$\therefore$ 1 Meq of Mn_3O_4 = 3 Meq of $MnSO_4 . 4H_2O$

$\therefore$ 4 Meq of Mn_3O_4 = 12 Meq of $MnSO_4 . 4H_2O$

Eq. wt of $MnSO_4.4H_2O = \frac{\text{Mol wt.}}{2} = \frac{223}{2} = 111.5$

Wt of $MnSO_4.4H_2O$ in sample $= 12 \times 111.5$

$= 1338$ mg $=$ **1.338g.**

10. (a) $CaCl_2 \equiv CaCO_3 \equiv MgCl_2$

M.wt. 111 100 95

From this it is evident, that

111 mg $CaCl_2$ will give $CaCO_3$ = 100mg

$\therefore$ 1 mg $CaCl_2$ will give $CaCO_3 = \frac{100}{111}$ mg $= 0.90$ mg

95 mg $MgCl_2$ gives $CaCO_3$ = 100 mg

$\therefore$ 1 mg $MgCl_2$ gives $CaCO_3 = \frac{100}{95}$ mg $= 1.05$ mg

$\therefore$ Total $CaCO_3$ formed by 1 mg $CaCl_2$ and 1 mg $MgCl_2$ $= 0.90 + 1.05 = 1.95$ mg

$\therefore$ Amount of $CaCO_3$ present per litre of water = 1.95mg

$\therefore$ wt of 1 ml of water = 1g = 10^3 mg

$\therefore$ wt of 1000 ml of water $= 10^3 \times 10^3 = 10^6$mg

$\therefore$ Total hardness of water in terms of parts of $CaCO_3$ per 10^6 parts of water by weight = **1.95 parts.**

(b) Eq wt of $Ca^{++} = \frac{\text{Mol.wt}}{\text{Charge}} = \frac{40}{2} = 20$

$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$

1 milliequivalent of Ca^{2+} = 20 mg

1 milliequivalent of Na_2CO_3 is required to soften 1 litre of hard water.

(c) $2Mg + O_2 \longrightarrow 2MgO$

$2 \times 24 = 48g$ 32g $2(24 + 16) = 80g$

$\because$ 32g of O_2 reacts with = 48g Mg

$\therefore$ 0.5g of O_2 reacts with $= \frac{48}{32} \times 0.5 = 0.75g$

Weight of unreacted Mg $= 1.00 - 0.75 = 0.25g$

Thus Mg is left in excess.

Weight of MgO formed $= \frac{80}{48} \times 0.75 = 1.25g$

$MgO + H_2SO_4 \longrightarrow MgSO_4 + H_2O$

(40g)

According to reaction

$\because$ 40g MgO is dissolved it gives 1000 ml of 1 N. H_2SO_4

$\therefore$ 40 g MgO is dissolved it gives 2000 ml 0.5 N H_2SO_4

$\therefore$ 1.25 MgO is dissolved it gives

$= \frac{2000 \times 1.25}{40}$ ml of 0.5 N H_2SO_4

= 62.5ml of 0.5N H_2SO_4

11. Given $P = 1$ atm $V = 1$L, $T = 127°C = 127 + 273 = 400$ K

$PV = nRT$ (Ideal gas equation)

or $n = \frac{PV}{RT} = \frac{1 \times 1}{0.082 \times 400} = 0.0304$

Mol. wt $= \frac{\text{Mass}}{\text{Moles}} = \frac{2.8}{0.0304} = 92.10$

Element	wt. of element	Relative no. of atoms	Ratio of of atoms	Whole no. of atoms
C	10.5	10.5/12 = 0.875	0.875/0.875 = 1	1 × 7 = 7
H	1.0	1.0/1 = 1	1/0.875 = 1.14	1.14 × 7 = 8

$\therefore$ Emperical formula = C_7H_8

Emperical formula, wt $= 12 \times 7 + 1 \times 8 = 92$

$n = \frac{\text{Molecular wt}}{\text{Empirical formula wt}} = \frac{92.10}{92} = 1$

Molecular formula = $n \times$ empirical formula

$= 1(C_7H_8) =$ **C_7H_8**

12. (i) No. of C atoms in 14g of $^{14}C = 6.02 \times 10^{23}$

$\therefore$ No. of C atom in 7 mg (7/1000g) of ^{14}C

$= \frac{6.02 \times 10^{23} \times 7}{14 \times 1000} = 3.01 \times 10^{20}$

No. of neutrons in 1 carbon atom = 7

$\therefore$ Total no. of neutrons in 7 mg of $^{14}C = 3.01 \times 10^{20} \times 7$

$= 21.07 \times 10^{20}$

Wt of 1 neutron = wt of 1 hydrogen atom

$= \frac{1}{6.02 \times 10^{23}}$ g

$\therefore$ Wt of $3.01 \times 10^{20} \times 7$ neutrons

$= \frac{3.0 \times 10^{20} \times 7}{6.02 \times 10^{23}} =$ **3.5×10^{-3}g**

13. Weight of AgCl formed = 2.567 g

Amount of AgCl formed due to MCl = 1.341 g

($\because$ NaCl does not decompose on heating to 300°C)

$\therefore$ Weight of AgCl formed due to NaCl $= 2.567 - 1.341 = 1.226$g

$NaCl \equiv AgCl \equiv MCl$

58.5 143.5

$$\begin{Bmatrix} NaCl + AgNO_3 \rightarrow AgCl + NaNO_3 \\ MCl + AgNO_3 \rightarrow AgCl + MNO_3 \end{Bmatrix}$$

$\because$ 143.5g of AgCl is obtained from NaCl = 58.5g

$\therefore$ 1.226 g of AgCl is obtained from NaCl

$$= \frac{58.5}{143.5} \times 1.226 = 0.4997\,g$$

$\therefore$ Wt of MCl in 1 g of mixture = 1.000 – 0.4997 = 0.5003g

$\because$ 1.341 g of AgCl is obtained from MCl = 0.5003g

$\therefore$ 143.5g of AgCl is obtained from MCl

$$= \frac{0.5003}{1.341} \times 143.5 = 53.53\,g$$

$\therefore$ Molecular weight of MCl = **53.53**

14. The complete oxidation under acidic conditions can be represented as follows:

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$$

Since 34 g of H_2O_2 = 2000 ml of 1N . H_2O_2

$$\left(\because \text{Eq. wt or } H_2O_2 = \frac{34}{2}\right)$$

$\therefore$ 34 g of H_2O_2 = 2000 ml of 1N $KMnO_4$ [$\because N_1V_1 = N_2V_2$]

$$\text{or } \frac{X}{100}\,g \text{ of } H_2O_2 = \frac{2000 \times X}{100 \times 34}\,ml \text{ of } 1N\,KMnO_4$$

$$\text{Therefore the unknown normality} = \frac{2000 \times X}{34 \times 100 \times X}$$

$$= \frac{10}{17} \text{ or } \mathbf{0.588\,N}$$

15. Balance the reactions by ion electron method.

(i) $Cu_2O + 2H^+ \rightarrow 2Cu^{2+} + H_2O + 2e^-] \times 3$ ......(i)

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O] \times 2$ .....(ii)

$$3Cu_2O + 14H^+ + 2\,NO_3^- \rightarrow 6Cu^{2+} + 2NO + 7H_2O$$

(ii) $K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O$
$\rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(iii) $C_2H_5OH + 4I_2 + 8OH^-$
$\rightarrow CHI_3 + HCO_3^- + 5I^- + 6H_2O$

16. **Given** $2NH_2OH + 4Fe^{3+} \rightarrow N_2O + H_2O + 4Fe^{2+} + 4H^+$ .....(i)

and $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ ..(ii)

$\therefore 10NH_2OH + 4MnO_4^- + 12H^+ \rightarrow 5N_2O + 21H_2O + 4Mn^{2+}$

[On multiplying (i) by 5 and (ii) by 4 and then adding the resulting equations]

Molecular weight of NH_2OH = 33

Thus 4000 ml of 1M MnO_4^- would react with NH_2OH = 330g

$\therefore$ 12 ml of 0.02 M $KMnO_4$ would react with NH_2OH

$$= \frac{330 \times 12 \times 0.02}{400}\,g$$

$\therefore$ Amount of NH_2OH present in 1000 ml of diluted solution

$$= \frac{330 \times 12 \times 0.02 \times 1000}{4000 \times 50}\,g$$

Since 10 ml of sample of hydroxylamine is diluted to one litre

$\therefore$ Amount of hydroxyl amine in one litre of original solution

$$= \frac{330 \times 0.02 \times 12 \times 1000}{4000 \times 50} \times \frac{1000}{10}\,g = \mathbf{39.6\ g}$$

17. **TIPS/Formulae :**

(i) Mole fraction = $\dfrac{\text{Moles of substance}}{\text{Total moles}}$

(ii) 1 mole of $Na_2S_2O_3$ gives 2 moles of Na^+ and 1 mole of $S_2O_3^{2-}$

Molecular wt. of sodium thiosulphate solution ($Na_2S_2O_3$) = 23 × 2 + 32 × 2 + 16 × 3 = 158

(i) The percentage by weight of $Na_2S_2O_3$

$$= \frac{\text{wt of } Na_2S_2O_3}{\text{wt of solution}} \times 100 = \frac{3 \times 158 \times 100}{1000 \times 1.25} = \mathbf{37.92}$$

[Wt. of $Na_2S_2O_3$ = Molarity × Mol wt]

(ii) Mass of 1 litre solution = 1.25 × 1000 g = 1250 g [$\because$ density = 1.25g/l]

Mole fraction of $Na_2S_2O_3$

$$= \frac{\text{Number of moles of } Na_2S_2O_3}{\text{Total number of moles}}$$

$$\text{Moles of water} = \frac{1250 - 158 \times 3}{18} = 43.1$$

$$\text{Mole fraction of } Na_2S_2O_3 = \frac{3}{3 + 43.1} = 0.065$$

(iii) 1 mole of sodium thiosulphate ($Na_2S_2O_3$) yields 2 moles of Na^+ and 1 mole of $S_2O_3^{2-}$.

$$\text{Molality of } Na_2S_2O_3 = \frac{3 \times 1000}{776} = 3.87$$

Molality of Na^+ = 3.87 × 2 = **7.74m**

Molality of $S_2O_3^{2-}$ = **3.87m**

18. Weight of MCO_3 and BaO = 4.08 g (given)

Weight of residue = 3.64 g (given)

$\therefore$ Weight of CO_2 evolved on heating = (4.08 – 3.64) g
= 0.44 g

$$= \frac{0.44}{44} = 0.01 \text{ mole}$$

Number of moles of $MCO_3 \equiv$ 0.01 mole

$$\left[\because MCO_3 \xrightarrow{heat} MO + CO_2\right]$$

Volume of 1N HCl in which residue is dissolved = 100 ml

Volume of 1N HCl used for dissolution = (100 – 2.5 × 16) ml
= 60 ml

$$= \frac{60}{1000} = 0.06 \text{ equivalents}$$

The chemical equation for dissolution can be written as

$$\underbrace{BaO + MO}_{\text{Residue}} + 4HCl \longrightarrow BaCl_2 + MCl_2 + 2H_2O$$

[Number of moles of BaO and MO = 1 + 1 = 2]

$$\text{Number of moles of BaO + Number of moles of MO} = \frac{0.06}{2}$$

$$= 0.03$$

Number of moles of BaO = (0.03 – 0.01) = 0.02 moles
Molecular weight of BaO = 138 + 16 = 154
$\therefore$ Weight of BaO = (0.02 × 154) g = 3.08 g
Weight of MCO_3 = (4.08 – 3.08) = 1.0 g
Since weight of 0.01 mole of MCO_3 = 1.0 g

$$\therefore \text{Mol. wt. of } MCO_3 = \frac{1}{0.01} = 100$$

Hence atomic weight of unknown M = (100 – 60) = **40**
The atomic weight of metal is **40** so the metal M is **Ca**.

19. TIPS/Formulae :

Balance the atoms as well as charges by ion electron/ oxidation number method.

While balancing the equations, both the charges and atoms must balance.

(i) $4Zn + NO_3^- + 10H^+ \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

(ii) $Cr_2O_7^{2-} + 3C_2H_4O + 8H^+$

$$\longrightarrow 3C_2H_4O_2 + 2Cr^{3+} + 4H_2O$$

(iii) $2HNO_3 + 6HCl \longrightarrow 2NO + 3Cl_2 + 4H_2O$

(iv) $2Ce^{3+} + S_2O_8^{2-} \longrightarrow 2SO_4^{2-} + 2Ce^{4+}$

(v) $Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$

(vi) $2Mn^{2+} + 5PbO_2 + 4H^+ \rightarrow 2MnO_4^- + 2H_2O + 5Pb^{2+}$

(vii) $4S + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

(viii) $ClO_3^- + 6I^- + 6H_2SO_4 \rightarrow Cl^- + 6HSO_4^- + 3I_2 + 3H_2O$

(ix) $6Ag^+ + AsH_3 + 3H_2O \rightarrow 6Ag + H_3AsO_3 + 6H^+$

20. TIPS/Formulae :

Equivalents of A oxidised = Equivalents of A reduced. Since in acidic medium, A^{n+} is oxidised to AO_3^-, the change in oxidation state from

$$(+5) \text{ to } (+n) = 5 - n \qquad [\because \text{O.S. of A in } AO_3^- = +5]$$

$\therefore$ Total number of electrons that have been given out during oxidation of 2.68×10^{-3} moles of A^{n+}

$$= 2.68 \times 10^{-3} \times (5 - n)$$

Thus the number of electrons added to reduce 1.61×10^{-3} moles of MnO_4^- to Mn^{2+}, *i.e.*

$(+7)$ to $(+2) = 1.61 \times 10^{-3} \times 5$
[Number of electrons involved = + 7 – (+2) = 5]

$$\therefore \quad 1.61 \times 10^{-3} \times 5 = 2.68 \times 10^{-3} \times (5 - n)$$

$$5 - n = \frac{1.61 \times 5}{2.68} \text{ or } \quad n = 5 - \frac{8.05}{2.68} \approx \mathbf{2}$$

21. TIPS/Formulae :

(i) Find normality of acid mixture and $Na_2CO_3 . 10H_2O$. Equate them to find volume of H_2SO_4.

(ii) Meq. of $H_2SO_4 = V \times N = \dfrac{V \times N}{1000}$ eq.

(iii) Equivalent of SO_4^{2-} = equivalents of H_2SO_4 × Eq. wt. of SO_4^{--}

$N \times V$(ml.) = meq.

Acid mixture contains 5 ml of 8N, HNO_3, 4.8 ml of 5N, HCl and say, 'V' ml of 17 M ≡ 34 N, H_2SO_4.

[$1MH_2SO_4 = 2N.H_2SO_4$]

$$N \text{ of the acid mixture} = \frac{\text{meq. (total) of acid}}{\text{ml. of solution}}$$

$$= \frac{5 \times 8 + 4.8 \times 5 + V \times 34}{2000} \quad [\text{Total volume} = 2\text{ L} = 2000 \text{ ml}]$$

$$\text{or, } N_{\text{mixture}} = \frac{64 + 34V}{2000}$$

$$\because \text{Eq. of wt. of } Na_2CO_3.10H_2O = \frac{\text{Mol. wt.}}{2}$$

$$= \frac{106 + 180}{2} = 143$$

$$N \text{ of } Na_2CO_3 = \frac{\text{Meq. of } Na_2CO_3}{\text{Volume of solution (ml)}}$$

$$= \frac{\frac{1}{143}}{\frac{100}{1000}} = \frac{1}{143} \times \frac{1000}{100} = 0.069\text{N}$$

$N_1V_1 = N_2V_2$

$$\text{or } 30 \times \underset{\text{(acid)}}{N_{\text{mixture}}} = \underset{\text{(sod. carbonate)}}{42.9 \times 0.069}$$

$$\therefore N_{\text{mixture}} = \frac{42.9 \times 0.069}{30} = 0.0986N$$

$$\text{Hence } \frac{64 + 34V}{2000} = 0.0986$$

$64 + 34V = 0.0986 \times 2000$, $64 + 34V = 197.2$

$$34V = 197.2 - 64.0 = 133.2 \qquad \therefore \text{ or } V = \frac{133.2}{34} = 3.9 \text{ ml.}$$

Hence meq. of $H_2SO_4 = V \times N$ of H_2SO_4

$$= 3.9 \times 34 = 132.6 \text{ meq.}$$

$$= 0.1326 \text{ eq. of } H_2SO_4$$

$$= 0.1326 \text{ eq. of } SO_4^{2-}$$

$$= 0.1326 \times 48 \text{ g of } SO_4^{2-}$$

$$\left(\because \text{Eq. wt. of } SO_4^{2-} = \frac{32+64}{2} = 48\right)$$

= **6.3648 g** of SO_4^{2-} are in 3.9 ml of 17M H_2SO_4

22. $HI < I_2 < ICl < HIO_4$; O.N. of I in $I_2 = 0$, $HI = -1$, $ICl = +1$, $HIO_4 = +7$.

23. (i) From the given half-cell reaction,

Here Eq. wt. of $NaBrO_3 = \frac{\text{Mol. wt.}}{6} = \frac{151}{6} = 25.17$

[$\because$ number of electron involved = 6]

Now we know that

Meq. = Normality × Vol. in ml. = $85.5 \times 0.672 = 57.456$

Also $\text{Meq.} = \frac{W_{NaBrO_3}}{\text{Eq. wt.}_{NaBrO_3}} \times 1000$

$= \frac{W_{NaBrO_3}}{25.17} \times 1000$

$\frac{W_{NaBrO_3}}{25.17} \times 1000 = 57.456 \text{ g}$

$\therefore W_{NaBrO_3} = \mathbf{1.446\ g}$

Molarity of $NaBrO_3 = \frac{\text{Normality}}{\text{Valence factor}}$

$= \frac{0.672}{6} = \mathbf{0.112\ M}$

(ii) From the given half-cell reaction,

Eq. wt. of $NaBrO_3 = \frac{\text{Mol. wt.}}{5} = \frac{151}{5} = 30.2$

[Number of electron involved per $BrO_3^- = \frac{10}{2} = 5$]

Thus, the amount of $NaBrO_3$ required for preparing 1000 ml. of 1 N $NaBrO_3 = 30.2$ g

$\therefore$ The amount of $NaBrO_3$ required for preparing 85.5 ml of 0.672 N $NaBrO_3$.

$= \frac{30.2 \times 0.672 \times 85.5}{1000} = \mathbf{1.7532\ g}$

Hence, Molarity $= \frac{0.672}{5} = \mathbf{0.1344\ M}$

24. (i) Weight of sugar syrup = 214.2 g

Weight of sugar in the syrup = 34.2 g

$\therefore$ Weight of water in the syrup = 214.2 – 34.2 = 180.0 g

Mol. wt. of sugar, $C_{12}H_{22}O_{11} = 342$

$\therefore$ Molal concentration $= \frac{34.2 \times 1000}{342 \times 180} = \mathbf{0.56}$

(ii) Mol. wt. of water, H_2O = 18

$\therefore$ Mole fraction of sugar $= \frac{34.2/342}{180/18 + 34.2/342}$

$= \frac{0.1}{10+0.1} = \frac{0.1}{10.1} = \mathbf{0.0099}$

25. **TIPS/Formulae :**

No. of equivalents of $KMnO_4$

= No. of equivatents of hydrazine sulphate.

$$\underset{2}{N_2H_4} \longrightarrow \underset{0}{N_2}$$

Change in oxidation state for each $N_2H_4 = 2 \times 2 = 4$

Equivalent weight of $N_2H_6SO_4 = \frac{130}{4} = 32.5$

Normality of $KMnO_4 = 5 \times 450$ ($\because$ valence factor = 5)

Number of equivalents of $KMnO_4 = 20 \times \frac{5}{50 \times 1000} = \frac{1}{500}$

and if weight of hydrazin sulphate be x gm then equivalents of hydrazine sulphate $= \frac{x}{32.5}$

$\therefore \frac{1}{500} = \frac{x}{32.5}$ or $x = \frac{32.5}{500} = 0.065$ g

Hence wt. of $N_2H_6SO_4$ in 10 ml solution = 0.065 g

$\therefore$ Wt. of $N_2H_6SO_4$ in 1000 ml solution = **6.5 g**

26. **TIPS/Formulae :**

No. of equivalents of $KMnO_4$ in neutral medium

= No. of equivalents of reducing agent.

Assuming that $KMnO_4$ shows the following changes during its oxidising nature.

Acidic medium $Mn^{7+} + n_1e^- \rightarrow Mn^{a+}$ $\quad \therefore n_1 = 7 - a$

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

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

Let V ml. of reducing agent be used for $KMnO_4$ in different medium.

$\therefore$ Meq. of reducing agent

= Meq. of $KMnO_4$ in acid medium

Meq. of $KMnO_4$ in neutral medium

= Meq. of $KMnO_4$ in alkaline medium

$= 1 \times n_1 \times 20 = 1 \times n_2 \times 33.4 = 1 \times n_3 \times 100$

$= n_1 = 1.667\, n_2 = 5\, n_3$

Since n_1, n_2 and n_3 are integers and n_1 is not greater than 7

$\therefore \quad n_3 = 1$

Hence $n_1 = 5$ and $n_2 = 3$

$\therefore$ Different oxidation states of Mn in

Acidic medium $Mn^{7+} + 5e^- \rightarrow Mn^{a+}$ or $a = \mathbf{+2}$

Neutral medium $Mn^{7+} + 3e^- \rightarrow Mn^{b+}$ or $b = \mathbf{+4}$

Alkaline medium $Mn^{7+} + 1e^- \rightarrow Mn^{c+}$ or $c = \mathbf{+6}$

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

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

$1 \times 5 \times 20 = 1 \times 6 \times V$ $\quad [\because Cr^{+6} + 6e^- \rightarrow 2Cr^{+3}]$

$V = \mathbf{16.66\ mL}$ $\therefore$ 1M = 6 × 1N

27. **TIPS/Formulae :**

No. of equivalents of $KMnO_4$

= No. of equivatents of reducing agents.

Case I. Reaction of NaOH with $H_2C_2O_4$ and $NaHC_2O_4$.

(*i*) $H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$

(*ii*) $NaHC_2O_4 + NaOH \rightarrow Na_2C_2O_4 + H_2O$

Number of milliequivalents of NaOH $= N \times V = 3.0 \times 0.1 = 0.3$

$\therefore$ Combined normality of the mixture titrated with NaOH

$$= \frac{0.3}{10} = 0.03$$

Case II. Reaction of $C_2O_4^-$ ion and $KMnO_4$

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

$KMnO_4$ will react in same manner with both $NaHC_2O_4$ and $H_2C_2O_4$ as it can be seen from the above reaction.

Number of milliequivalents of $KMnO_4 = 4.0 \times 0.1 = 0.4$

$\therefore$ Combined normality of the mixture titrated with $KMnO_4$

$$= \frac{0.4}{10} = 0.04$$

The difference $(0.04\ N - 0.03\ N = 0.01\ N)$ is due to $NaHC_2O_4$

The total normality of $NaHC_2O_4$ will be $= 0.01 + 0.01 = 0.02\ N$

From equation (*ii*) in case I.

Eq. wt. of $NaHC_2O_4 = 112$

Amount of $NaHC_2O_4$ in one litre of solution formed

$= 0.01 \times 112 =$ **1.12 g** and amount of $H_2C_2O_4$

$= 2.02 -$ Wt. of $NaHC_2O_4 = 2.02 - 1.12 =$ **0.90 g**

28. **TIPS/Formulae :**

Let the amount of $NaNO_3$ in the mixture $= x$ g

$\therefore$ The amount of $Pb(NO_3)_2$ in the mixture $= (5 - x)$ g

Heating effect of sodium nitrate and lead nitrate

$$\underset{2(23+14+48)=170\text{ g}}{2NaNO_3} \xrightarrow{\Delta} 2NaNO_2 + \underset{2\times16=32\text{ g}}{O_2}$$

$$\underset{2(207+28+96)=662\text{ g}}{2Pb(NO_3)_2} \xrightarrow{\Delta}$$

$$2PbO_2 + \underbrace{\underset{4(14+32)=184\text{ g}}{4NO_2} + \underset{2\times16=32\text{ g}}{O_2}}_{216\text{ g}}$$

Now since, 170 g of $NaNO_3$ gives = 32 g of O_2

$$\therefore x \text{ g of } NaNO_3 \text{ gives} = \frac{32}{170} \times x \text{ g of } O_2$$

Similarly, 662 g of $Pb(NO_3)_2$ gives = 216 g of gases $(NO_2 + O_2)$

$$(5 - x) \text{ g of } Pb(NO_3)_2 \text{ gives} = \frac{216}{662} \times (5 - x) \text{ g of gases } (NO_2 + O_2)$$

Actual loss, on heating, is 28% of 5 g of mixture

$$= \frac{5 \times 28}{100} = 1.4 \text{ g}$$

$$\therefore \frac{32x}{170} + \frac{216}{662} \times (5 - x) = 1.4$$

$$32x \times 662 + 216(5 - x) \times 170 = 1.4 \times 170 \times 662$$

$$21184x + 183600 - 36720x = 157556$$

$$-15536x = -26044, x = 1.676 \text{ g}$$

Wt. of $NaNO_3 =$ **1.676 g**

and Wt. of $Pb(NO_3)_2 = 5 - 1.676$ g $=$ **3.324 g**

29. **TIPS/Formulae :**

$$\text{Molality} = \frac{\text{Mass of solute / M. wt. of solute}}{\text{Mass of solvent in kg}}$$

Mass of H_2SO_4 in 100 ml of 93% H_2SO_4 solution = 93 g

$\therefore$ Mass of H_2SO_4 in 1000 ml of the H_2SO_4 solution = 930 g

Mass of 1000 ml H_2SO_4 solution $= 1000 \times 1.84 = 1840$ g

Mass of water in 1000 ml of solution $= 1840 - 930$ g

$= 910$ g $= 0.910$ kg

$$\text{Moles of } H_2SO_4 = \frac{\text{Wt. of } H_2SO_4}{\text{Mol. wt. of } H_2SO_4} = \frac{930}{98}$$

$\therefore$ Moles of H_2SO_4 in 1 kg of water

$$= \frac{930}{98} \times \frac{1}{0.910} = 10.43 \text{ mol}$$

$\therefore$ Molality of solution = **10.43m**

30. In the given problem, a solution containing Cu^{2+} and $C_2O_4^{2-}$ is titrated first with $KMnO_4$ and then with $Na_2S_2O_3$ in presence of KI. In titration with $KMnO_4$, it is the $C_2O_4^{2-}$ ions that react with the MnO_4^- ions. The concerned balanced equation may be written as given below.

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

Thus according to the above reaction

$$2 \text{ mmol } MnO_4^- \equiv 5 \text{ mmol } C_2O_4^{2-}$$

However,

No. of mmol of MnO_4^- used in titration = Vol. in ml $\times$ M

$$= 22.6 \times 0.02 = 0.452 \text{ mmol } MnO_4^-$$

$$\text{Since } 2 \text{ mmol } MnO_4^- \equiv 5 \text{ mmol } C_2O_4^{2-}$$

$$0.452 \text{ mmol } MnO_4^- \equiv \frac{5}{2} \times 0.452 = 1.130 \text{ mmol } C_2O_4^{2-}$$

Titration with $Na_2S_2O_3$ in the presence of KI.

Here Cu^{2+} react and the reactions involved during titration are

$$2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2, 2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$$

$$\text{Thus } 2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-}$$

No. of m mol of $S_2O_3^{2-}$ used in titration

$$= 0.05 \times 11.3 = 0.565 \text{ mmol } S_2O_3^{2-}$$

Now since 2 mmol $S_2O_3^{2-} \equiv$ 2 mmol Cu^{2+} [From above equation]

$$0.565 \text{ mmol } S_2O_3^{2-} = \frac{2}{2} \times 0.565 \text{ mmol } Cu^{2+}$$

$$= 0.565 \text{ mmol } Cu^{2+}$$

$$\therefore \text{ Molar ratio of } Cu^{2+} \text{ to } C_2O_4^{2-} = \frac{0.565 \text{ mmol}}{1.130 \text{ mmol}} = \mathbf{1:2}$$

Balanced equations in two cases

Case I. $Mn^{+7} + 5e^- \rightarrow Mn^{+2}$

$C_2^{+3} \rightarrow 2C^{+4} + 2e^-$

Case II. $2Cu^{+2} + 2e^- \rightarrow Cu_2^+$

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

and $I_2 + 2e^- \rightarrow 2I^-$

$2S_2^{+2} \rightarrow S_4^{+3/2} + 2e^-$

31. Mass of Fe_2O_3 in the sample $= \frac{55.2}{100} \times 1 = 0.552$ g

Number of moles of $Fe_2O_3 = \frac{0.552}{159.8} = 3.454 \times 10^{-3}$

Number of moles of Fe^{3+} ions $= 2 \times 3.454 \times 10^{-3}$

$= 6.9 \times 10^{-3}$ mol $= 6.90$ mmol

Since its only 1 electron is exchanged in the conversion of Fe^{3+} to Fe^{2+}, the molecular mass is the same as equivalent mass.

$\therefore$ Amount of Fe^{2+} ion in 100 ml. of sol. = 6.90 meq

Volume of oxidant used for 100 ml of Fe^{2+} sol.

$= 17 \times 4 = 68$ ml.

Amount of oxidant used $= 68 \times 0.0167$ mmol

$= 1.1356$ mmol

Let the number of electrons taken by the oxidant = n

$\therefore$ No. of meq. of oxidant used $= 1.1356 \times n$

Thus $1.1356 \times n = 6.90 \Rightarrow n = \frac{6.90}{1.1356} = \mathbf{6}$

32. 1.5 g of sample require = 150 ml. of $\frac{M}{10}$ HCl

$\therefore$ 2 g of sample require $= \frac{150 \times 2}{1.5}$ ml. of $\frac{M}{10}$ HCl

$= 200$ ml. of $\frac{M}{10}$ HCl

On heating, the sample, only $NaHCO_3$ undergoes decomposition as given below.

$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2\uparrow$
2 moles 1 mole 1 mole
2 equ.

Neutralisation of the sample with HCl takes place as given below.

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$
1 eq. 1 eq.

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
1 mole 2 mole
2 eq. 2 eq.

Hence, 2 g sample ≡ 200 ml. of M/10 HCl

= 200 ml. of N/10 HCl = 20 meq = 0.020 eq

Number of moles of CO_2 formed, i.e.

$$n = \frac{PV}{RT} = \frac{750}{760} \times \frac{123.9}{1000} \times \frac{1}{0.082 \times 298} = 0.005$$

Moles of $NaHCO_3$ in the sample (2 g) $= 2 \times 0.005 = 0.01$

Equivalent of $NaHCO_3 = 0.01$

Wt. of $NaHCO_3 = 0.01 \times 84 = 0.84$ g

$$\% \text{ of } NaHCO_3 = \frac{0.84 \times 100}{2} = \mathbf{42\%}$$

Equivalent of $Na_2CO_3 = 0.02 - 0.01 = 0.01$

Wt. of $Na_2CO_3 = 0.01 \times 53 = 0.53$ g

$$\therefore \% \text{ of } Na_2CO_3 = \frac{0.53 \times 100}{2} = \mathbf{26.5\%}$$

$\therefore$ % of Na_2SO_4 in the mixture $= 100 - (42 + 26.5) = \mathbf{31.5\%}$

33. Reaction involved titration is

$$\underset{1 \text{ mole}}{KIO_3} + \underset{2 \text{ moles}}{2KI} + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$$

20 ml. of stock KI solution ≡ 30 ml. of $\frac{M}{10}$ KIO_3 solution

$$\text{Molarity of KI solution} = \frac{30 \times 1 \times 2}{20 \times 10} = \frac{3}{10}$$

$$\text{Millimoles in 50 ml. of KI solution} = 50 \times \frac{3}{10} = 15$$

Millimoles of KI left unreacted with $AgNO_3$ solution

$$= 2 \times 50 \times \frac{1}{10} = 10$$

$\therefore$ Millimoles of KI reacted with $AgNO_3 = 15 - 10 = 5$

Millimoles of $AgNO_3$ present in $AgNO_3$ solution = 5

Molecular weight of $AgNO_3 = 170$

$\therefore$ Wt. of $AgNO_3$ in the solution $= 5 \times 10^{-3} \times 170 = 0.850$ g

$$\% AgNO_3 \text{ in the sample} = \frac{0.850}{1} \times 100 = \mathbf{85\%}$$

34. Calculation of number of moles in 45 ml. of 0.025 M $Pb(NO_3)_2$

$$\text{Moles of } Pb(NO_3)_2 = 0.25 \times \frac{45}{1000} = 0.01125$$

$\therefore$ Initial moles of $Pb^{2+} = 0.01125$

Moles of $NO_3^- = 0.01125 \times 2 = 0.02250$

[1 mole $Pb(NO_3)_2 \equiv$ 2 moles of NO_3]

Calculation of number of moles in 25 ml. of 0.1 M chromic sulphate

Moles of chromic sulphate $(Cr_2(SO_4)_3$

$$= 0.1 \times \frac{25}{1000} = 0.0025 \text{ moles}$$

Moles of $SO_4^{2-} = 0.0025 \times 3 = 0.0075$ [1 Mole of chromic sulphate $\equiv$ 3 moles of SO_4^{2-}]

Moles of $PbSO_4$ formed = **0.0075** [SO_4^{2-} is totally consumed]

Moles of Pb^{2+} left $= 0.01125 - 0.0075 = 0.00375$

Moles of NO_3^- left = 0.02250 [NO_3^- remain unreacted]

Moles of chromium ions $= 0.0025 \times 2 = 0.005$

Total volume of the solution = 45 + 25 = 70 ml.

$\therefore$ Molar concentration of the species left

(*i*) $Pb^{2+} = \frac{0.00375}{70} \times 1000 = \mathbf{0.05357\ M}$

(*ii*) $NO_3^- = \frac{0.0225}{70} \times 1000 = \mathbf{0.3214\ M}$

(*iii*) $Cr^{3+} = \frac{0.005}{70} \times 1000 = \mathbf{0.0714\ M}$

35. In pure iron oxide (FeO), iron and oxygen are present in the ratio 1 : 1.

However, here number of Fe^{2+} present = 0.93

or No. of Fe^{2+} ions missing = 0.07

Since each Fe^{2+} ion has 2 positive charge, the total number of charge due to missing (0.07) Fe^{2+} ions $= 0.07 \times 2 = 0.14$

To maintain electrical neutrality, 0.14 positive charge is compensated by the presence of Fe^{3+} ions. Now since, replacement of one Fe^{2+} ion by one Fe^{3+} ion increases one positive charge, 0.14 positive charge must be compensated by the presence of 0.14 Fe^{3+} ions.

In short, 0.93 Fe^{2+} ions have 0.14 Fe^{3+} ions

100 Fe^{2+} ions have $= \frac{0.14}{0.93} \times 100 = \mathbf{15.05\%}$

36. The formula of Glauber's salt is $Na_2SO_4.10H_2O$

Molecular mass of $Na_2SO_4.10H_2O$

$= [2 \times 23 + 32.1 + 4 \times 16] + 10(1.01 \times 2 + 16) = 322.3 \text{ g mol}^{-1}$

Weight of the Glauber's salt taken = 80.575 gm

Out of 80.575 g of salt, weight of anhydrous Na_2SO_4

$$= \frac{142.1}{322.3} \times 80.575 = 35.525 \text{ g}$$

Number of moles of Na_2SO_4 per dm^3 of the solution

$$= \frac{35.525}{142.1} = 0.25$$

Molarity of the solution = **0.25 M**

Density of solution = 1077.2 kgm^{-3}

$$= \frac{1077.2 \times 10^3}{10^6} \text{ gm cm}^{-3} = 1.0772 \text{ g cm}^{-3}$$

Total weight of sol $= V \times d = 1\ dm^3 \times d$

$= 1000 \text{ cm}^3 \times 1.0772 \text{ gcm}^{-3} = 1077.2 \text{ g}$

Weight of water $= 1077.2 - 35.525 = 1041.67$ g

Molality of sol. $= \frac{0.25}{1041.67 \text{ g}} \times 1000 \text{ g} = 0.2399 = \mathbf{0.24\ m}$

Number of moles of water in the solution $= \frac{1041.67}{18} = 57.87$

Mole fraction of Na_2SO_4

$$= \frac{\text{No. of moles of } Na_2SO_4}{\text{Total number of moles}} = \frac{0.25}{0.25 + 57.87}$$

$$= 0.0043 = \mathbf{4.3 \times 10^{-3}}$$

37. TIPS/Formulae :

Find the milliequivalents and equate them as per data given in question.

For $Fe_3O_4 \rightarrow 3FeO$

$2e + Fe_3^{(8/3)+} \rightarrow 3Fe^{2+}$

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

For, $Fe_2O_3 \rightarrow 2FeO$; $2e + Fe_2^{3+} \rightarrow 2Fe^{2+}$ ...(1)

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* and *b* respectively.

$\therefore$ Meq. of Fe_3O_4 + Meq. Fe_2O_3 = Meq. of I_2 liberated

= Meq. of hypo used

$$a + b = \frac{11 \times 0.5 \times 100}{20} = 27.5$$

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

Note that in the change

$Fe^{2+} \rightarrow Fe^{3+} + e^-$; valence factor of Fe^{2+} is 1.

Thus,

Meq. of Fe^{2+} (from Fe_3O_4) + Meq. of Fe^{2+} (from Fe_2O_3)

= Meq. of $KMnO_4$ used .... (2)

If valence factor for Fe^{2+} is 2/3 from Eq. (1),

then Meq. of Fe^{2+} (from Fe_3O_4) = *a*

If valence factor for Fe^{2+} is 1

then Meq. of Fe^{2+} (from Fe_3O_4) = 3*a*/2 ... (3)

Similarly, from Eq. (2), Meq. of Fe^{2+} from (Fe_2O_3) = *b*.

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

or $3a + 2b = 64$ ....(4)

From Eqs. (3) and (4)

Meq. of $Fe_3O_4 = a = 9$ & Meq. of $Fe_2O_3 = b = 18.5$

$$\therefore W_{Fe_3O_4} = \frac{9 \times 232}{2 \times 1000} = 1.044 \text{ g}$$

$$\text{and } W_{Fe_2O_3} = \frac{18.5 \times 160}{2 \times 1000} = 1.48 \text{ g}$$

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

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

38. TIPS/Formulae :

Write the reactions taking place, balance them and equate moles of I_2 and $Na_2S_2O_3$.

$KIO_3 + 5KI \rightarrow 3K_2O + 3I_2$ i.e., $2I^{5+} + 10e^- \rightarrow I_2^0$

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

Now liberated I_2 reacts with $Na_2S_2O_3$
$I_2 + 2e^- \rightarrow 2I^-$
$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$
∴ millimole ratio of $I_2 : S_2O_3 = 1 : 2$
Thus, *m* mole of I_2 liberated

$$= m \text{ mole of } Na_2S_4O_6 \text{ used} \times \frac{1}{2} = 45 \times M \times \frac{1}{2}$$

[*M* is molarity of thiosulphate]

Also m mole of $KIO_3 = \frac{0.1}{214} \times 1000$
Now m mole ratio of $KIO_3 : I_2 = 1 : 3$

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

$$\therefore\ M = \frac{0.1 \times 1000 \times 3 \times 2}{214 \times 45} = \mathbf{0.062}$$

39. **TIPS/Formulae :**
Use molarity equation to find volume of H_2SO_4 solution.

$$\underset{\substack{63.5+12+48.98 \\ =123.5\,g}}{CuCO_3} + \underset{98g}{H_2SO_4} \rightarrow CuSO_4 + H_2O + CO_2\uparrow$$

∴ For 123.5 gms of Cu(II) carbonate 98 g of H_2SO_4 are required.
For 0.5 gms of Cu(II) carbonate weight of H_2SO_4 reqd.

$$= \frac{98 \times 0.5}{123.5} g = 0.39676\ g\ H_2SO_4$$

Weight of required $H_2SO_4 = 0.39676$ g
Weight of solute in grams

$$= \frac{\text{Mol.wt.} \times \text{Molarity} \times \text{Volume in mL}}{1000}$$

$$0.39676 = \frac{98 \times 0.5 \times V}{1000} \quad \text{or} \quad V = \frac{0.39676 \times 1000}{90 \times 0.5} \text{ml}$$

Volume of H_2SO_4 solution = **8.097 ml**

40. **TIPS/Formulae :**
(i) Volume of virus = $\pi r^2 \ell$ (Volume of cylinder)

(ii) Mass of single virus = $\frac{\text{Volume}}{\text{Sp. volume}}$

(iii) Molecular mass of virus
= Mass of single virus × 6.02×10^{23}

Volume of virus = $\pi r^2 l$

$$= \frac{22}{7} \times \frac{150}{2} \times \frac{150}{2} \times 10^{-16} \times 5000 \times 10^{-8}$$

$$= 0.884 \times 10^{-16}\ cm^3$$

$$\text{Weight of one virus} = \frac{0.884 \times 10^{-16}}{0.75} g$$

$$= 1.178 \times 10^{-16} g$$

∴ Mol. wt. of virus = $1.178 \times 10^{-16} \times 6.02 \times 10^{23}$
= $\mathbf{7.09 \times 10^7}$

41. **TIPS/Formulae :**
Write the balanced chemical reaction for change and apply mole concept.
The given reactions are

$$MnO_2 \downarrow + Na_2C_2O_4 + 2H_2SO_4 \longrightarrow MnSO_4 + CO_2 + Na_2SO_4 + 2H_2O$$

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

$$\therefore\ mM \text{ of } MnO_2 = \frac{4}{2} = 2 \quad \left[\begin{array}{l} Mn^{4+} + 2e \rightarrow Mn^{2+} \\ \therefore \text{Valance factor of } MnO_2 = 2 \end{array}\right]$$

$$\text{Now } 2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 \downarrow + K_2SO_4 + 2H_2O$$

Since eq. wt. of MnO_2 is derived from $KMnO_4$ and $MnSO_4$ both, thus it is better to proceed by mole concept
mM of $KMnO_4$ ≡ mM of $MnO_2 \times (2/5) = 4/5$

$$\text{Also } 5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$$

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

∴ $M_{H_2O_2} \times 20 = 2$ or $M_{H_2O_2} = \mathbf{0.1}$

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

$$2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + 2H_2SO_4 + K_2SO_4$$

$$MnO_2 + Na_2C_2O_4 + 2H_2SO_4 \longrightarrow MnSO_4 + 2CO_2 + Na_2SO_4 + 2H_2O$$

42. 1 litre water = 1 kg i.e. 1000 g water (∵ d = 1000 kg/m³)

$$\equiv \frac{1000}{18} = 55.55 \text{ moles of water}$$

So, molarity of water = **55.55M**

H. Assertion & Reason Type Questions

1. (b) **TIPS/Formulae :**
Write reaction for titration between Na_2CO_3 and HCl.
Method :

$$\underset{\substack{\text{(yellow colour} \\ \text{with HPh i.e.} \\ \text{phenolphthalein)}}}{Na_2CO_3{}_{(aq)}} + HCl_{(aq)} \longrightarrow \underset{\substack{\text{(no colour} \\ \text{with HPh i.e} \\ \text{phenolphthalein)}}}{NaHCO_3} + NaCl_{(aq)}$$

(Half neutralisation)

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl + H_2O + CO_2$$

(Complete neutralisation)

$$\underset{\substack{\text{(yellow colour} \\ \text{with methyl} \\ \text{orange)}}}{NaHCO_3} + HCl \longrightarrow \underset{\substack{\text{(red colour} \\ \text{with methyl} \\ \text{orange)}}}{NaCl} + H_2O + CO_2$$

From these reaction it is clear that

(i) 2 moles of HCl are required for complete neutralization of Na_2CO_3.

(ii) Titre value using phenolphthalein corresponds only to neutralisation of Na_2CO_3 to $NaHCO_3$, i.e. half of value required by Na_2CO_3 solution.

(iii) Titre value using methyl orange corresponds to complete neutralisation of Na_2CO_3

∴ Both S and E are correct but S is not correct explanation of E.

I. Integer Value Correct Type

1. The least significant figure in titre values is 3.

$$\text{Average titre value} = \frac{25.2+25.25+25}{3} = \frac{75.4}{3} = 25.1$$

The number of significant figures in average titre value will also be **3**.

2. $d = \frac{\text{mass}}{V} \Rightarrow$ 10.5 g/cc means in 1 cc

$\Rightarrow$ 10.5 g of Ag is present.

$$\text{Number of atoms of Ag in 1 cc} \Rightarrow \frac{10.5}{108} \times N_A$$

$$\text{In 1 cm, number of atoms of Ag} = \sqrt[3]{\frac{10.5}{108}N_A}$$

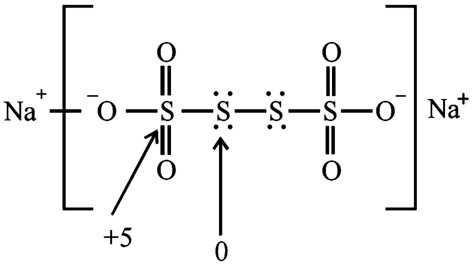
$$\text{In 1 cm}^2\text{, number of atoms of Ag} = \left(\frac{10.5}{108}N_A\right)^{2/3}$$

In 10^{-12} m^2 or 10^{-8} cm^2, number of atoms of Ag

$$= \left(\frac{10.5}{108}N_A\right)^{2/3} \times 10^{-8} = \left(\frac{10.5 \times 6.022 \times 10^{23}}{108}\right)^{2/3} \times 10^{-8} = 1.5 \times 10^7$$

Hence $x = 7$

3. **5**



Difference in oxidation number = 5 – 0 = 5

4. **4** $R = N_A \times k$

$= 6.023 \times 10^{23} \times 1.380 \times 10^{-23}$

$= 8.312$ which has 4 significant figures

Section-B JEE Main/ AIEEE

1. **(c)**

	Percentage	R.N.A	Simplest ratio
C	9	$\frac{9}{12} = \frac{3}{4}$	3
H	1	$\frac{1}{1} = 1$	4
N	3.5	$\frac{3.5}{14} = \frac{1}{4}$	1

Empirical formula $= C_3H_4N$

$(C_3H_4N)_n = 108, (12 \times 3 + 4 \times 1 + 14)_n = 108$

$(54)_n = 108 \Rightarrow n = \frac{108}{54} = 2$

∴ molecular formula $= C_6H_8N_2$

2. **(c)** Among all the given options molarity is correct because the term molarity involve volume which increases on increasing temperature.

3. **(a)** Fe (no. of moles) $= \frac{558.5}{55.85} = 10$ moles

C (no. of moles) in 60 g of C = 60/12 = 5 moles.

4. **(a)** $2BCl_3 + 3H_2 \rightarrow 2B + 6HCl$

or $BCl_3 + \frac{3}{2}H_2 \rightarrow B + 3HCl$

Now, since 10.8 gm boron requires hydrogen

$= \frac{3}{2} \times 22.4$ L at N.T.P

hence 21.6 gm boron requires hydrogen

$\frac{3}{2} \times \frac{22.4}{10.8} \times 21.6 = 67.2$ L at N. T. P.

5. **(d)** $25 \times N = 0.1 \times 35; N = 0.14$

$Ba(OH)_2$ is diacid base

hence $N = M \times 2$ or $M = \frac{N}{2} \Rightarrow M = 0.07$ M

6. **(b)** Moles of urea present in 100 ml of sol. $= \frac{6.02 \times 10^{20}}{6.02 \times 10^{23}}$

$$\therefore M = \frac{6.02 \times 10^{20} \times 1000}{6.02 \times 10^{23} \times 100} = 0.01\text{M}$$

[∵ M = Moles of solute present in 1L of solution]

7. **(a)** $N_1V_1 = N_2V_2$

(Note : H_3PO_3 is dibasic ∴ $M = 2N$)

$20\times 0.2 = 0.1\times V$ (Thus. $0.1\,M = 0.2\,N$)

∴ $V = 40$ ml

8. **(a)** H_2SO_4 is dibasic.

$0.1\,M\ H_2SO_4 = 0.2N\ H_2SO_4$ $[\because M = 2\times N]$

M_{eq} of H_2SO_4 taken = $= 100\times 0.2 = 20$

M_{eq} of H_2SO_4 neutralised by NaOH $= 20\times 0.5 = 10$

M_{eq} of H_2SO_4 neutralised by NH_3 $= 20 - 10 = 10$

$$\%\text{ of } N_2 = \frac{1.4\times M_{eq}\text{ of acid neutrialised by }NH_3}{\text{wt. of organic compound}}$$

$$= \frac{1.4\times 10}{0.3} = 46.6$$

$$\%\text{ of nitrogen in urea } = \frac{14\times 2\times 100}{60} = 46.6$$

[Mol. wt of urea = 60]

Similarly % of Nitrogen in Benzamide

$$= \frac{14\times 100}{121} = 11.5\%\quad [C_6H_5CONH_2 = 121]$$

$$\text{Acetamide} = \frac{14\times 1\times 100}{59} = 23.4\%\ [CH_3CONH_2 = 59]$$

$$\text{Thiourea} = \frac{14\times 2\times 100}{76} = 36.8\%\quad [NH_2CSNH_2 = 76]$$

Hence the compound must be urea.

9. **(b)** **TIPS/Formulae :**

From the molarity equation.

$M_1V_1 + M_2V_2 = MV$

Let M be the molarity of final mixture,

$$M = \frac{M_1V_1 + M_2V_2}{V}\quad \text{where } V = V_1 + V_2$$

$$M = \frac{480\times 1.5 + 520\times 1.2}{480 + 520} = 1.344\ M$$

10. **(d)** Relative atomic mass

$$= \frac{\text{Mass of one atom of the element}}{1/12^{th}\text{ part of the mass of one atom of Carbon} - 12}$$

$$\text{or } \frac{\text{Mass of one atom of the element}}{\text{mass of one atom of the C} - 12}\times 12$$

Now if we use $^1/_6$ in place of $^1/_{12}$ the formula becomes

$$\text{Relative atomic mass} = \frac{\text{Mass of one atom of element}}{\text{Mass of one atom of carbon}}\times 6$$

∴ Relative atomic mass decrease twice

11. **(d)** 1 Mole of $Mg_3(PO_4)_2$ contains 8 mole of oxygen atoms

∴ 8 mole of oxygen atoms ≡ 1 mole of $Mg_3(PO_4)_2$ mole of $Mg_3(PO_4)_2$

$$0.25\text{ mole of oxygen atom} \equiv \frac{1}{8}\times 0.25\text{ mole of }Mg_3(PO_4)_2$$

$= 3.125\times 10^{-2}$ mole of $Mg_3(PO_4)_2$

12. **(a)** **TIPS/Formulae :**

$$\text{Apply the formula } d = M\left(\frac{1}{m} + \frac{M_2}{1000}\right)$$

$$\therefore\ 1.02 = 2.05\left(\frac{1}{m} + \frac{60}{1000}\right)$$

On solving we get, $m = 2.288$ mol/kg

13. **(d)** Since molarity of solution is 3.60 M. It means 3.6 moles of H_2SO_4 is present in its 1 litre solution.

Mass of 3.6 moles of H_2SO_4

= Moles × Molecular mass = 3.6 × 98 g = 352.8 g

∴ 1000 ml solution has 352.8 g of H_2SO_4

Given that 29 g of H_2SO_4 is present in = 100 g of solution

∴ 352.8 g of H_2SO_4 is present in

$$= \frac{100}{29}\times 352.8\text{ g of solution } = 1216\text{ g of solution}$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{1216}{1000} = 1.216\text{ g/ml} = 1.22\text{ g/ml}$$

14. **(a)** $2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3H_2(g)$

∵ 6 moles of HCl produces = 3 moles of H_2

= 3 × 22.4 L of H_2 at S.T.P

$$\therefore\ 1\text{ mole of HCl produces} = \frac{3\times 22.4}{6}\text{ L of }H_2\text{ at S.T.P}$$

= 11.2 L of H_2 at STP

15. **(c)** On balancing the given equations we get

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

So, x = 2, y = 5 & z = 16

16. **(d)** ∵ 18 g, H_2O contains = 2 gm H

$$\therefore\ 0.72\text{ gm }H_2O\text{ contains} = \frac{2}{18}\times 0.72\text{ gm} = 0.08\text{ gm H}$$

∵ 44 gm CO_2 contains = 12 gm C

$$\therefore\ 3.08\text{ gm }CO_2\text{ contains} = \frac{12}{44}\times 3.08 = 0.84\text{ gm C}$$

$$\therefore C : H = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08 = 7 : 8$$

∴ Empirical formula = C_7H_8

17. **(b)** For a one mole of the oxide

Moles of M = 0.98, Moles of O^{2-} = 1

Let moles of $M^{3+} = x$

Moles of $M^{2+} = 0.98 - x$

on balancing charge

$(0.98 - x)\times 2 + 3x - 2 = 0 \Rightarrow x = 0.04$

$$\%\text{ of } M^{3+}\ \frac{0.04}{0.98}\times 100 = 4.08\%$$