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.** 0.588 N **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 :** $\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$

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

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

4. **TIPS/Formulae :**

1 Mole = 6.023×10^{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 $3 + 4 + 3x - 14 = 0$

$\Rightarrow$ $3x + 7 - 14 = 0$ or $x = +\frac{7}{3}$

C. MCQs with ONE Correct Answer

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

At. wt. of Al = 27

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

$$\therefore 27\text{ g of Al reacts with oxygen} = \frac{3 \times 32}{4 \times 27} \times 27\text{ g} = 24\text{ g}$$

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

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

$\therefore$ 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 = 6.02×10^{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 $N_2O_5 = \frac{1}{2} \times 6.02 \times 10^{23}$ 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 = 28g, Mol. wt. of O_2 = 32g

28 g of N_2 has = 6.02×10^{23} molecules of nitrogen

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

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

32 g of O_2 has = 6.02×10^{23} molecules of oxygen

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

Thus, ratio of molecules of oxygen : nitrogen

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

6. **(a)**

$$\begin{tikzcd} \underset{2.76}{Ag_2CO_3} \arrow[r, "\Delta"] & Ag_2O + CO_2 \arrow[d, "\Delta"] \\ & \underset{\text{(residue)}}{2Ag + \frac{1}{2}O_2} \end{tikzcd}$$

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

$$\therefore 2.76\text{ g of }Ag_2CO_3\text{ on heating gives} = \frac{216}{276} \times 2.76 = 2.16\text{g of Ag}$$

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

$$\therefore 0.2\text{ moles of }Na_3PO_4\text{ will yield } Ba_3(PO_4)_2 = \frac{1}{2} \times 0.2 = \mathbf{0.1\ mol.}$$

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.

$N_2H_4 \rightarrow Y + 10e^-$, 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
$x+5\times 0+0=+2. \quad \therefore\ x=+2$

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

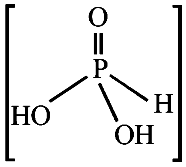
Reduction reaction:

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

Net reaction:

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

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 $= 0.3 \times 2 = 0.6$

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)

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

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

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

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

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

$\therefore$ 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

$\therefore$ 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 & $[Co(NH_3)_5Br]\,SO_4$ 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

$\therefore$ 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

$\therefore$ 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 $AgNO_3 \rightarrow Y$

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

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

$\therefore$ No. of moles of $Y = 0.01$

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

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

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

$\therefore$ 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

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

$$\text{(ii)}\quad \underset{24\ g}{Mg} + 2HCl \longrightarrow MgCl_2 + \underset{22400\ ml\ at\ NTP}{H_2}$$

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.
$$\underset{\substack{3\,(54.9 + 32) \\ = 260.7\ g}}{3\,MnO_2} \longrightarrow \underset{\substack{(3 \times 54.9 + 64) \\ = 228.7\ g}}{Mn_3O_4} + O_2$$

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

$$\underset{3 \times 54.9 = 164.7\ g}{3\,Mn} = \underset{3 \times 54.9 + 64 = 228.7g}{Mn_3O_4}$$

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 $FeSO_4 . 7H_2O$

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

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

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

Let weight of NO_2 in mixture = x g

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

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

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

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 = 0.0842g

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

∵ 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)

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

∵ 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 × 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)

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

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

$\therefore \quad$ 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) $2Mg + O_2 \longrightarrow 2MgO$

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

$\because$ 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 $V = 1L$, $T = 127°C = 127 + 273 = 400$ 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

$= 1(C_7H_8) = \mathbf{C_7H_8}$

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

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

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

$$\left\{\begin{matrix} NaCl + AgNO_3 \rightarrow AgCl + NaNO_3 \\ MCl + AgNO_3 \rightarrow AgCl + MNO_3 \end{matrix}\right\}$$

$\because$ 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:

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

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 $KMnO_4$ [$\because N_1V_1 = N_2V_2$]

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

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

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

15. Balance the reactions by ion electron method.

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

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

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

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

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

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

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

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

[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 = $\frac{\text{Moles of substance}}{\text{Total moles}}$

(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

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

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 $H_2SO_4 = V \times N = \frac{V \times N}{1000}$ 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.
[$1M H_2SO_4 = 2N. H_2SO_4$]

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

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

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

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

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

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

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

$N_1V_1 = N_2V_2$
or $30 \times N_{\text{mixture}} = 42.9 \times 0.069$
(acid) (sod. carbonate)

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

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

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

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

Hence meq. of H_2SO_4 = $V \times N$ of H_2SO_4
= 3.9 × 34 = 132.6 meq.
= 0.1326 eq. of H_2SO_4
= 0.1326 eq. of SO_4^{2-}
= 0.1326 × 48 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 $\text{Eq. wt. of } NaBrO_3 = \frac{\text{Mol. wt.}}{6} = \frac{151}{6} = 25.17$

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

Now we know that

Meq. = Normality × Vol. in ml. = 85.5 × 0.672 = 57.456

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

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

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

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

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

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

(ii) From the given half-cell reaction,

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

[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 $NaBrO_3$.

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

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

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, $C_{12}H_{22}O_{11} = 342$

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

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

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

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

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 $N_2H_4 = 2 \times 2 = 4$

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

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

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

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

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

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

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

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

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

$\therefore$ $n_3 = 1$

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 $K_2Cr_2O_7$

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

$V =$ **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 $= N \times V = 3.0 \times 0.1 = 0.3$

∴ 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 $KMnO_4 = 4.0 \times 0.1 = 0.4$

∴ 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

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

Heating effect of sodium nitrate and lead nitrate

$$\underset{2(23+14+48)=170\text{ g}}{2NaNO_3} \xrightarrow{\Delta} 2NaNO_2 + \underset{2\times 16=32\text{ g}}{O_2}$$

$$\underset{2(207+28+96)=662\text{ g}}{2Pb(NO_3)_2} \xrightarrow{\Delta} 2PbO_2 + \underbrace{\underset{4(14+32)=184\text{ g}}{4NO_2} + \underset{2\times 16=32\text{ g}}{O_2}}_{216\text{ g}}$$

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

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

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

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

$21184x + 183600 - 36720x = 157556$

$-15536x = -26044, x = 1.676$ 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

∴ 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

$= 910\text{ g} = 0.910$ kg

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

∴ Moles of H_2SO_4 in 1 kg of water

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

∴ 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 × M

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

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

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

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.

∴ 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

∴ 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

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

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

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

$$\underset{\substack{\text{2 moles} \\ \text{2 equ.}}}{2NaHCO_3} \rightarrow \underset{\text{1 mole}}{Na_2CO_3} + H_2O + \underset{\text{1 mole}}{CO_2 \uparrow}$$

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

$$\underset{\text{1 eq.}}{NaHCO_3} + \underset{\text{1 eq.}}{HCl} \rightarrow NaCl + H_2O + CO_2$$

$$\underset{\substack{\text{1 mole} \\ \text{2 eq.}}}{Na_2CO_3} + \underset{\substack{\text{2 mole} \\ \text{2 eq.}}}{2HCl} \rightarrow 2NaCl + H_2O + CO_2$$

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

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

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

33. Reaction involved titration is

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

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

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

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

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

Molecular weight of $AgNO_3 = 170$

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

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

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

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

∴ 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-} $=0.0025\times3=0.0075$ [1 Mole of chromic sulphate ≡ 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 $=0.0025\times2=0.005$

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

∴ Molar concentration of the species left

(*i*) $Pb^{2+}=\frac{0.00375}{70}\times1000=\mathbf{0.05357\ M}$

(*ii*) $NO_3^-=\frac{0.0225}{70}\times1000=\mathbf{0.3214\ M}$

(*iii*) $Cr^{3+}=\frac{0.005}{70}\times1000=\mathbf{0.0714\ M}$

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 $=0.07\times2=0.14$

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 $=\frac{0.14}{0.93}\times100=\mathbf{15.05\%}$

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

Molecular mass of $Na_2SO_4.10H_2O$

$=[2\times23+32.1+4\times16]+10(1.01\times2+16)=322.3\text{ g mol}^{-1}$

Weight of the Glauber's salt taken = 80.575 gm

Out of 80.575 g of salt, weight of anhydrous Na_2SO_4

$$=\frac{142.1}{322.3}\times80.575=35.525\text{ g}$$

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}

$$=\frac{1077.2\times10^3}{10^6}\text{ gm cm}^{-3}=1.0772\text{ g cm}^{-3}$$

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

$=1000\text{ cm}^3\times1.0772\text{ gcm}^{-3}=1077.2\text{ g}$

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

Molality of sol. $=\frac{0.25}{1041.67\text{ g}}\times1000\text{ g}=0.2399=\mathbf{0.24\ m}$

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

Mole fraction of Na_2SO_4

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

$=0.0043=\mathbf{4.3\times10^{-3}}$

37. TIPS/Formulae :

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

For $Fe_3O_4\rightarrow3FeO$

$2e+Fe_3^{(8/3)+}\rightarrow3Fe^{2+}$

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

For, $Fe_2O_3\rightarrow2FeO$; $2e+Fe_2^{3+}\rightarrow2Fe^{2+}$ ...(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.

∴ Meq. of Fe_3O_4 + Meq. Fe_2O_3 = Meq. of I_2 liberated
= Meq. of hypo used

$$a+b=\frac{11\times0.5\times100}{20}=27.5$$

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) = $3a/2$ ... (3)

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

∴ $3a/2+b=0.25\times5\times12.8\times100/50=32$

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

From Eqs. (3) and (4)

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

$$\therefore\ W_{Fe_3O_4}=\frac{9\times232}{2\times1000}=1.044\text{ g}$$

$$\text{and }W_{Fe_2O_3}=\frac{18.5\times160}{2\times1000}=1.48\text{ g}$$

$$\therefore\ \%\text{ of }Fe_3O_4=\frac{1.044\times100}{3}=\mathbf{34.8}$$

$$\text{and }\%\text{ of }Fe_2O_3=\frac{1.48\times100}{3}=\mathbf{49.33}$$

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., $2\,I^{5+} + 10e^- \rightarrow I_2^0$

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

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

$= m$ mole of $Na_2S_4O_6$ 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 $KIO_3 : I_2 = 1 : 3$

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

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

$0.39676 = \frac{98 \times 0.5 \times V}{1000}$ or $V = \frac{0.39676 \times 1000}{90 \times 0.5}$ 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 = $\pi r^2 l$

$= \frac{22}{7} \times \frac{150}{2} \times \frac{150}{2} \times 10^{-16} \times 5000 \times 10^{-8}$
$= 0.884 \times 10^{-16}\,cm^3$

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

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

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 $KMnO_4 \equiv$ mM of $MnO_2 \times (2/5) = 4/5$
Also $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

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

$\therefore\ M_{H_2O_2} \times 20 = 2$ 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 (∵ $d = 1000\,kg/m^3$)

$\equiv \frac{1000}{18} = 55.55$ 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. $d = \frac{\text{mass}}{\text{V}} \Rightarrow$ 10.5 g/cc means in 1 cc

$\Rightarrow$ 10.5 g of Ag is present.

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

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

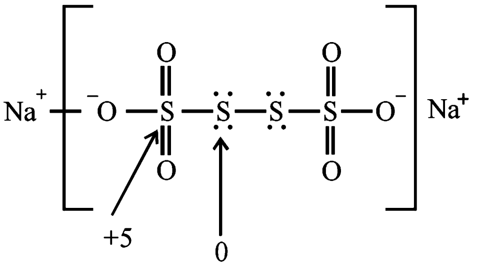
$$\text{In 1 cm}^2\text{, number of atoms of Ag} = \left(\frac{10.5}{108}N_A\right)^{2/3}$$

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

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

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

hence 21.6 gm boron requires hydrogen

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

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. $= \frac{6.02 \times 10^{20}}{6.02 \times 10^{23}}$

$$\therefore M = \frac{6.02 \times 10^{20} \times 1000}{6.02 \times 10^{23} \times 100} = 0.01M$$

[∵ M = Moles of solute present in 1L of solution]

7. **(a)** $N_1V_1 = N_2V_2$

(Note : H_3PO_3 is dibasic $\therefore$ M = 2N)

$20 \times 0.2 = 0.1 \times V$ (Thus. 0.1 M = 0.2 N)

$\therefore V = 40$ 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

$$= \frac{14 \times 100}{121} = 11.5\% \quad [C_6H_5CONH_2 = 121]$$

$$\text{Acetamide} = \frac{14 \times 1 \times 100}{59} = 23.4\% \quad [CH_3CONH_2 = 59]$$

$$\text{Thiourea} = \frac{14 \times 2 \times 100}{76} = 36.8\% \quad [NH_2CSNH_2 = 76]$$

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,

$$M = \frac{M_1V_1 + M_2V_2}{V} \quad \text{where } V = V_1 + V_2$$

$$M = \frac{480 \times 1.5 + 520 \times 1.2}{480 + 520} = 1.344\text{ M}$$

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

$$\text{Relative atomic mass} = \frac{\text{Mass of one atom of element}}{\text{Mass of one atom of carbon}} \times 6$$

$\therefore$ Relative atomic mass decrease twice

11. **(d)** 1 Mole of $Mg_3(PO_4)_2$ contains 8 mole of oxygen atoms

$\therefore$ 8 mole of oxygen atoms $\equiv$ 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

$\therefore$ 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

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

$\because$ 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)** $\because$ 18 g, H_2O contains = 2 gm H

$$\therefore 0.72\text{ gm } H_2O\text{ contains} = \frac{2}{18} \times 0.72\text{ gm} = 0.08\text{ gm H}$$

$\because$ 44 gm CO_2 contains = 12 gm C

$$\therefore 3.08\text{ gm } CO_2\text{ contains} = \frac{12}{44} \times 3.08 = 0.84\text{ gm C}$$

$$\therefore C : H = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08 = 7 : 8$$

$\therefore$ 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

$(0.98 - x) \times 2 + 3x - 2 = 0 \Rightarrow x = 0.04$

$$\%\text{ of } M^{3+}\ \frac{0.04}{0.98} \times 100 = 4.08\%$$