EQUIVALENT CONCEPT & TITRATIONS

CONTENTS

JEE(ADVANCED) SYLLABUS

Concept of oxidation and reduction, redox reactions, oxidation number, balancing redox reactions and normality, Law of Equivalence, titration, Application of redox titration, hardness of water, parts per million (PPM), Bleaching powder, Hydrogen peroxide (H_2O_2), Oleum.

JEE(MAIN) SYLLABUS

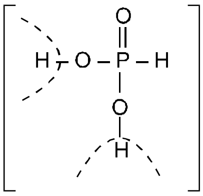
Electronic concepts of oxidation and reduction, redox reactions, oxidation number, rules for assigning oxidation number, balancing of redox reactions, concept of equivalents, titration, hardness of water.

EQUIVALENT CONCEPT & TITRATION

Calculation of Valency factor / n-factor :

- **For Elements :** Valency factor = valency of the element.
- **For Acids :** Valency factor = number of replaceable H^+ ions per acid molecule.

Solved Examples

Example-1	HCl ,	H_2SO_4	H_3PO_4	H_3PO_3 
Solution. Valency factor→	1	2	3	2
Eq. wt. (E) →	M/1	M/2	M/3	M/2

{see there are only two replaceable H^+ions}

(assume 100% dissicoiation)

❍ Replaceable hydrogen atoms are those hydrogen atoms which are attached with the atoms of group VI and group VII i.e. O,S,Se,Te, & F, Cl ,Br ,I.

- **For Bases :**

  Valency factor = number of replacable OH^- ions per base molecule.

Solved Examples

Example-2		NaOH,	KOH
Solution.	v .f. →	1	1
	Eq. wt. →	M/1	M/1

❍ Bases may be defined as the substances in which OH group is/are directly attached with group I elements (Li,Na, K,Rb,Cs), group II elements (Be, Mg,Ca,Ba) or group III elements (Al, Ga,In,Tl), transition metals, non-metallic cations like PH_4^+, NH_4^+ etc.

- **Acid-base reaction :**

  In case of acid base reaction, the valence factor is the actual number of H^+ or OH^- replaced in the reaction. The acid or base may contain more number of replaceble H^+ or OH^- than actually replaced in reaction.

❍ **v. f.** for base is the number of H^+ ion from the acid replaced by each molecule of the base

Solved Examples

Example-3 $\underset{\text{Base}}{2NaOH} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$

Solution. Valency factor of base = 1

Here, two molecule of NaOH replaced $2H^+$ ion from the H_2SO_4. Therefore, each molecule of NaOH replaced only one H^+ ion of acid, so v.f. = 1.

❍ **v. f.** for acid is the number of OH^- replaced from the base by each molecule of acid.

Solved Examples

Example-4 $NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$

Base Acid

Solution. Valency factor of acid = 1

Here, one of molecule of H_2SO_4 replaced one OH^- from NaOH. Therefore, valency factor for H_2SO_4 is one

$$\therefore \quad \text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol.wt}}{1}$$

- **Salts :**

(a) In non-reacting condition

○ **Valency factor =** Total number of positive charge or negative charge present in the compound.

Solved Examples

Example-5		Na_2CO_3,	$Fe_2(SO_4)_3$,	$FeSO_4.7H_2O$
Solution.	V.f.	2	2×3 = 6	2
	Eq.wt.	M/2	M/6	M/2

Note : In case of hydrated salt, positive/negative charge of water molecule is not counted.

(b) In reacting condition

Solved Examples

Example-6 $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

Base Acid

Solution. It is an acid base reaction, therefore valency factor for Na_2CO_3 is one while in non-reacting condition, it will be two.

(c) Equivalent weight of oxidising / reducing agents in a redox reaction

In case of redox change , **v.f. =** Total number of electrons lost or gained per molecule .

Solved Examples

Example-7 $KMnO_4 + H_2O_2 \longrightarrow Mn^{2+} + O_2$

Solution. Mn in $KMnO_4$ is going from +7 to +2 , so change in oxidation number per molecule of $KMnO_4$ is 5. So the valency factor of $KMnO_4$ is 5.

CONCEPT OF EQUIVALENTS

Equivalent mass of element : Number of parts by mass of an element which reacts or displaces from a compound 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine, is known as the equivalent weight of that element.

e.g. $2Mg + O_2 \longrightarrow 2MgO$

48 g 32 g

12 g 8 g

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

$\therefore$ 8 g of $O_2 = \frac{48 \times 8}{32} = 12$ g

$\therefore$ Equivalent weight of Mg = 12

Similarly, $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

65.5 g 32.75

$\therefore$ Equivalent weight of Zn = $\frac{65.5}{2} = 32.75$ g

$$Al + \frac{3}{2}Cl_2 \longrightarrow AlCl_3$$

27 g $\frac{3}{2} \times 71$ g

$\because$ 111.5 g chlorine reacts with 27 g of Al.

$\therefore$ 35.5 chlorine reacts with $\frac{27 \times 35.5}{111.5} = 9.0$ g of Al

$\therefore$ Equivalent weight of aluminium = $\frac{27}{3} = 9.0$

As we can see from the above examples that equivalent weight is the ratio of atomic weight and a factor (say n-factor or valency factor) which in the above three cases is their respective valencies.

Equivalent weight (E) :

In general, $$\text{Eq. wt. (E)} = \frac{\text{Atomic weight or Molecular weight}}{\text{valency factor(v.f)}} = \frac{\text{Mol. wt.}}{\text{n}-\text{factor}} = \frac{M}{x}$$

Equivalents :

- For an oxidant or reductant, number of equivalents are same as number of moles of electrons gained or lost.
- For acid number of equivalents are same as number of moles of H^+ released.
- For base number of equivalents are same as number of moles of OH^- released or number of moles of H^+ gained.
- In general

  Number of Equivalents = Moles × n-factor.

  Number of Equivalents = $\frac{\text{mass of species}}{\text{eq. wt. of that species}}$

  For a solution, Number of equivalents = N_1V_1, where N is the normality and V is the volume in litres
- Equivalent mass is a pure number which, when expressed in gram, is called gram equivalent mass.
- The equivalent mass of a substance may have different values under different conditions.
- There is no hard and fast rule that equivalent weight will be always less than the molecular mass.

Normality :

Normality of a solution is defined as the number of equivalents of solute present in one litre (1000 mL) solution.

Let V mL of a solution is prepared by dissolving W g of solute of equivalent weight E in water.

- Number of equivalents of solute = $\frac{W}{E}$

  VmL of solution contain $\frac{W}{E}$ equivalents of solute

$\therefore$ 1000 mL solution will contain $\frac{W \times 1000}{E \times V}$ equivalents of solute.

- **Normality (N) =** $\frac{W \times 1000}{E \times V}$
- **Relations between Normality and Molarity :**
  Normality (N) = Molarity x Valency factor
  or N × V (in mL) = M × V (in mL) × n
  or **milliequivalents = millimoles × n**

Solved Examples

Example-8 Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

Solution. **Normality (N) =** $\frac{W \times 1000}{E \times V}$

Here W = 15.8 g , V = 50 mL E = $\frac{\text{molar mass of } KMnO_4}{\text{Valency factor}}$ = 158/5 = 31.6

So, normality = 10 N

Example-9 Calculate the normality of a solution containing 50 mL of 5 M solution of $K_2Cr_2O_7$ in acidic medium.

Solution. Normality (N) = Molarity × valency factor = 5 x 6 = 30 N

Law of Equivalence :

The law states that one equivalent of an element combine with one equivalent of the other. In a chemical reaction, equivalents and milli equivalents of reactants react in equal amount to give same number of equivalents or milli equivalents of products separately.

Accordingly

(i) $aA + bB \rightarrow mM + nN$; meq of A = meq of B = meq of M = m.eq. of N

(ii) In a compound M_xN_y ; meq of M_xN_y = meq of M = meq of N

Solved Examples

Example-10 Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium.

The reaction is $KMnO_4 + Cu_2S \longrightarrow Mn^{2+} + Cu^{2+} + SO_2$

Solution. From law of equivalence,

equivalents of Cu_2S = equivalents of $KMnO_4$

moles of Cu_2S × v.f. = moles of $kMnO_4$ × v.f.

1 × 8 = moles of $KMnO_4$ × 5 $\Rightarrow$ moles of $KMnO_4$ **= 8/5**

($\therefore$ v.f. of Cu_2S = 2 (2 – 1) + 1 (4 – (–2))) = 8 and v.f. of $KMnO_4$ = 1 (7 –2) = 5)

Example-11 The number of moles of oxalate ions oxidized by one mole of MnO_4^- ion in acidic medium are :

(A) $\frac{5}{2}$ (B) $\frac{2}{5}$ (C) $\frac{3}{5}$ (D) $\frac{5}{3}$

Solution. Equivalents of $C_2O_4^{2-}$ = equivalents of MnO_4^-

x(mole) × 2 = 1 × 5

($\therefore$ v.f. of $C_2O_4^{2-}$ = 2 (4 – 3) = 2 and v.f. of MnO_4^- = 1 (7 – 2) = 5).

x = $\frac{5}{2}$ mole of $C_2O_4^{2-}$ ions.

Drawbacks of Equivalent concept :

- Since equivalent weight of a substance (for example oxidising or reducing agent) may be variable hence it is better to use mole concept.

  e.g. $5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 2H_2O$ $\therefore$ Eq.wt of $MnO_4^- = \dfrac{\text{Mol. wt. of } MnO_4^-}{5}$

  e.g. $3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$ $\therefore$ Eq.wt of $MnO_4^- = \dfrac{\text{Mol. wt. of } MnO_4^-}{3}$

  Thus, the number of equivalents of MnO_4^- will be different in the above two cases but number of moles will be same.

- **Normality of any solution depends on reaction while molarity does not.**
  For example :
  Consider 0.1mol $KMnO_4$ dissolved in water to make 1L solution. Molarity of this solution is 0.1 M. However, its normality is NOT fixed. It will depend upon the reaction in which $KMnO_4$ participates. e.g. if $KMnO_4$ forms Mn^{2+}, normality = 0.1 x 5 = 0.5 N. This *same* sample of $KMnO_4$, if employed in a reaction giving MnO_2 as product (Mn in +4 state), will have normality 0.1 × 3 = 0.3 N.

- **The concept of equivalents is handy, but it should be used with care.** One must never equate equivalents in a sequence which involves same element in more than two oxidation states. Consider an example, KIO_3 reacts with KI to liberate iodine and liberated Iodine is titrated with standard hypo solution. The reactions are :

  (i) $IO_3^- + I^- \longrightarrow I_2$ (ii) $I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$
  meq of hypo = meq of I_2 = meq of IO_3^- = meq of I^-
  $\therefore$ meq of hypo = meq of IO_3^-.

  This is wrong. Note that I_2 formed by equation (i) has v.f. = 5/3 & in equation (ii) has v.f. = 2.
  $\because$ v.f. of I_2 in both the equation are different, therefore we cannot equate milli equivalents in sequence. In this type of case, students are advised to use mole concept.

Solved Examples

Example-12 How many millilitres of 0.02 M $KMnO_4$ solution would be required to exactly titrate 25 mL of 0.2 M $Fe(NO_3)_2$ solution in acidic medium ?

Solution. **Method -1 : Mole concept method**

Starting with 25 mL of 0.2 M Fe^{2+}, we can write :
Millimoles of Fe^{2+} = 25 x 0.2 ....(1)
and in volume V (in milliliters) of the $KMnO_4$,
Millimoles of MnO_4^- = V (0.02) ....(2)
The balanced reaction is :

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

This requires that at the equivalent point,

$$\frac{\text{m.moles of } MnO_4^-}{1} = \frac{\text{m.moles of } Fe^{2+}}{5}$$

$$\therefore \quad \frac{V(0.02)}{1} = \frac{(25)(0.2)}{5} \quad \text{(from (1) \& (2))}$$

$\therefore$ V = 50 mL.

Method -2 : Equivalent Method :

At the equivalence point,
milliequivalents of MnO_4^- = milliequivalents of Fe^{2+}
$M_1 \times vf_1 \times V_1 = M_2 \times vf_2 \times V_2$
$0.02 \times 5 \times V_1 = 0.2 \times 1 \times 25$ ($\because MnO_4^- \longrightarrow Mn^{2+}$; v.f. = 5, $Fe^{2+} \longrightarrow Fe^{3+}$; v.f. = 1)
$\therefore$ V_1 = 50 mL.

Titrations :

Titration is a procedure for determining the concentration of a solution by allowing its carefully measured volume to react with a standard solution of another substance, whose concentration is known.

Standard solution - It is a solution whose concentration is known and is taken in burette. It is also called **Titrant.**

There are two type of titrants :

- **Primary titrants/standard :** These reagents can be accurately weighed and their solutions are not to be standardised before use.
  Ex : Oxalic acid, $K_2Cr_2O_7$, $AgNO_3$, $CuSO_4$, ferrous ammonium sulphate, hypo etc.
- **Secondary titrants/standard :** These reagents cannot be accurately weighed and their solutions are to be standardised before use.
  Ex : NaOH, KOH, HCl, H_2SO_4, I_2, $KMnO_4$ etc.

Titrate : Solution consisting of substance to be estimated, its generally taken in a beaker .

Equivalence point : It is the point when number of equivalents of titrant added becomes equal to number of equivalents of titrate.

At equivalence point :

$$n_1V_1M_1 = n_2V_2M_2$$

Indicator : An auxiliary substance added for physical detection of completion of titration at equivalence point. It generally show colour change on completion of titration.

Type of Titrations :

- Acid-base titrations (to be studided in Ionic equilibrium)
- **Redox Titrations**

Some Common Redox Titrations

Table of Redox Titrations : (Excluding Iodometric / Iodimetric titrations)

	Estimation of	By titrating with	Reactions	Relation*between OA and RA
1.	Fe^{2+}	MnO_4^{-}	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5Fe^{2+} \equiv MnO_4^{-}$ Eq. wt. of Fe^{2+} = M/1
2.	Fe^{2+}	$Cr_2O_7^{2-}$	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$ Eq.wt. of $Cr_2O_7^{2-}$ = M/6
3.	$C_2O_4^{2-}$	MnO_4^{-}	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5C_2O_4^{2-} \equiv 2MnO_4^{-}$ Eq. wt. of $C_2O_4^{2-}$ = M/2
4.	H_2O_2	MnO_4^{-}	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5H_2O_2 \equiv 2MnO_4^{-}$ Eq.wt. of H_2O_2 = M/2
5.	As_2O_3	MnO_4^-	$As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. of As_2O_3 = M/4
6.	AsO_3^{3-}	BrO_3^-	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$ $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$	Eq. wt. of AsO_3^{3-} = M/2 Eq.wt. of BrO_3^- = M/6

Permanganate Titrations :

- $KMnO_4$ is generally used as an oxidising agent in acidic medium generally provided by dilute H_2SO_4 .
- $KMnO_4$ works as self indicator persistent pink color is the indication of end point.
- Mainly used for estimation of Fe^{2+} , oxalic acid ,oxalates, H_2O_2 etc.

Solved Examples

Example-13 Write the balanced reaction of titration of $KMnO_4$ Vs oxalic acid in presence of H_2SO_4.

Solution. Reaction : $2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

Redox Changes : $C_2^{3+} \longrightarrow 2C^{4+} + 2e$ $\left(E_{H_2C_2O_4} = \frac{M}{2}\right)$

$5e + Mn^{7+} \longrightarrow Mn^{2+}$ $\left(E_{KMnO_4} = \frac{M}{5}\right)$

Indicator : $KMnO_4$ acts as self indicator.

Example-14 Write the balanced reaction of titration of $KMnO_4$ vs ferrous ammonium sulphate in presence of H_2SO_4.

Solution. Reaction : $2KMnO_4 + 10[FeSO_4(NH_4)_2SO_4.6H_2O] + 8H_2SO_4 \longrightarrow$
$5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + K_2SO_4 + 2MnSO_4 + 68H_2O$

Redox Changes : $Fe^{2+} \longrightarrow Fe^{3+} + e$ $\left(E_{FeSO_4} = \frac{M}{1}\right)$

$Mn^{7+} + 5e \longrightarrow Mn^{2+}$ $\left(E_{KMnO_4} = \frac{M}{5}\right)$

Indicator : $KMnO_4$ acts as self indicator

Iodometric/Iodimetric Titrations :

Compound containing iodine are widely used in titrations.

(i) Iodide ions can be oxidised to I_2 by suitable oxidising agent.

$$2I^- \text{ (aq)} \longrightarrow I_2 \text{ (s)} + 2e^-$$

(ii) Iodine (V) ions, IO_3^- , will oxidise I^- to I_2.

$$IO_3^- \text{ (aq)} + 5I^- \text{ (aq)} + 6H^+ \text{ (aq)} \longrightarrow 3I_2 \text{ (s)} + 3H_2O\ (\ell)$$

(iii) Thiosulphate ions, $S_2O_3^{2-}$, can reduce iodine to iodide ions.

$$\underset{\text{colourless}}{2S_2O_3^{2-} \text{ (aq)}} + \underset{\text{black}}{I_2 \text{ (s)}} \longrightarrow \underset{\text{colourless}}{S_4O_6^{2-}} + 2I^-$$

Iodometric Titrations (Titration Solution is of $Na_2S_2O_3 . 5H_2O$)

S.No.	Estimation of	Reaction	Relation between O.A. and R.A.
1.	I_2	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$ or $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	$I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq.wt. of $Na_2S_2O_3$ = M/1
2.	$CuSO_4$	$2CuSO_4 + 4KI \longrightarrow 2CuI + 2K_2SO_4 + I_2$ or $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$ white ppt	$2CuSO_4 \equiv I_2 \equiv 2I = 2Na_2S_2O_3$ Eq.wt.of $CuSO_4$ = M/1
3.	$CaOCl_2$	$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$ $Cl_2 + 2KI \longrightarrow 2KCl + I_2$ $Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq.wt. of $CaOCl_2$ = M/2
4.	MnO_2	$MnO_2 + 4HCl(conc.) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$ $Cl_2 + 2KI \longrightarrow 2KCl + I_2$ or $MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$ $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2Na_2S_2O_3$ Eq.wt. of MnO_2 = M/2
5.	IO_3^-	$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$ Eq.wt. of IO_3^- = M/6
6.	H_2O_2	$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$	$H_2O_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq.wt. of H_2O_2 = M/2
7.	Cl_2	$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	$Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq.wt. of Cl_2 = M/2
8.	O_3	$O_3 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$O_3 \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$ Eq.wt. of O_3 = M/6
9.	ClO^-	$ClO^- + 2I^- + 2H^+ \longrightarrow H_2O + Cl^- + I_2$	$ClO^- \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq.wt. of OCl^- = M/2
10.	$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$	$Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I$ Eq.wt. of $Cr_2O_7^{2-}$ = M/6
11.	MnO_4^-	$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$	$2MnO_4^- \equiv 5I_2 \equiv 10I$ Eq.wt. of MnO_4^- = M/5
12.	BrO_3^-	$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$	$BrO_3^- \equiv 3I_2 \equiv 6I$ Eq.wt. of BrO_3^- = M/6
13.	As(V)	$H_2AsO_4 + 2I^- + 3H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$	$H_3AsO_4 \equiv I_2 \equiv 2I$ Eq.wt. of H_3AsO_4 = M/2
14.	HNO_2	$2HNO_2 + 2I^- \longrightarrow I_2 + 2NO + H_2O$	$2HNO_2 \equiv I_2 \equiv 2I$ Eq.wt. of HNO_2 = M/1
15.	HClO	$HClO + 2I^- + H^+ \longrightarrow Cl^- + I_2 + H_2O$	$HClO \equiv I_2 \equiv 2Na_2S_2O_3$ Eq.wt. of HClO = M/2

Iodimetric Titrations

S.No.	Estimation of	Reaction	Relation between O.A. and R.A.
1.	H_2S (in acidic medium)	$H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$	$H_2S \equiv I_2 \equiv 2I$ Eq.wt. of H_2S = M/2
2.	SO_3^{2-} (in acidic medium)	$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2H^+$	$SO_3^{2-} \equiv I_2 \equiv 2I$ Eq.wt. of SO_3^{2-} = M/2
3.	Sn^{2+} (in acidic medium)	$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$	$Sn^{2+} \equiv I_2 \equiv 2I$ Eq.wt. of Sn^{2+} = M/2
4.	As(III) (at pH 8)	$H_2AsO_3^- + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 3H^+$	$H_2AsO_3^- \equiv I_2 \equiv 2I$ Eq.wt. of $H_2AsO_3^-$ = M/2
5.	N_2H_4	$N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$	$N_2H_4 = 2I_2 \equiv 4I$ Eq.wt. of N_2H_4 = M/4

Solved Examples

Example-15 The sulphur content of a steel sample is determined by converting it to H_2S gas, absorbing the H_2S in 10 mL of 0.005 M I_2 and then back titrating the excess I_2 with 0.002 M $Na_2S_2O_3$. If 10 mL $Na_2S_2O_3$ is required for the titration, how many milligrams of sulphur are contained in the sample?

Reactions : $H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$; $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

Solution. Used millimoles of I_2 = (m.moles of I_2 taken initially) – $\dfrac{\text{m.moles of hypo used}}{2}$

$$= 0.005 \times 10 - 0.002 \times \frac{10}{2}$$

$$= 0.04 = \text{millimoles of } H_2S$$

$\therefore$ weight of sulphur = $0.04 \times 10^{-3} \times 32 \times 10^3$ mg = 1.28 mg.

Calculation of Available Chlorine from a sample of Bleaching Powder :

The weight of available Cl_2 released from the given sample of bleaching powder on reaction with dilute acids or CO_2 is called available chlorine.

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$$

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

Method of determination :

$$\underset{\text{(Sample of bleaching powder)}}{CaOCl_2} + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$\underset{\text{v.f. = 2}}{I_2} + \underset{\text{v.f. = 1}}{2Na_2S_2O_3} \xrightarrow{\text{Starch as indicator}} Na_2S_4O_6 + 2NaI$$

End point is indicated by disappearance of blue colour.

Let M = Molarity of hypo ($Na_2S_2O_3$) solution

$\therefore$ millimoles of Cl_2 produced = m.moles of I_2 used by hypo

$$= \frac{M \times V}{2}$$ where V = vol of hypo solution used in ml.

mass of Cl_2 produced $= \dfrac{M \times V \times 10^{-3}}{2} \times 71$

$= 35.5 \times M \times V \times 10^{-3}$

$\therefore$ % of available chlorine $= \dfrac{35.5 \times M \times V \times 10^{-3}}{W} \times 100$

where W = amount of belaching powder taken in g.

or **% of available Cl_2 = $\dfrac{3.55 \times M \times V}{W}$**

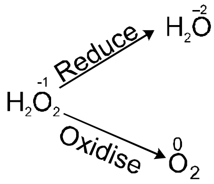
Solved Examples

Example-16 3.55 g sample of bleaching powder suspended in H_2O was treated with enough acetic acid and KI solution. Iodine thus liberated required 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine.

Solution. % of Cl_2 = $\dfrac{3.55 \times 0.2 \times 80}{3.55}$ = 16%

Hydrogen peroxide (H_2O_2)

H_2O_2 can behave both like oxidising and reducing agent in both the mediums (acidic and basic).



- **Oxidising agent : ($H_2O_2 \rightarrow H_2O$)**

  (a) Acidic medium : $2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O$
  v.f. = 2

  (b) Basic medium : $2e^- + H_2O_2 \longrightarrow 2OH^-$
  v.f = 2

- **Reducing agent : ($H_2O_2 \rightarrow O_2$)**

  (a) Acidic medium : $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$
  v.f = 2

  (b) Basic medium : $2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$
  v.f = 2

therefore, the valency factor of H_2O_2 is always 2.

Volume strength of H_2O_2 : Strength of H_2O_2 is represented as 10V , 20 V , 30 V etc.

20V H_2O_2 means **one litre** of this sample of H_2O_2 on decomposition gives **20L of O_2** gas at **STP.**

Decomposition of H_2O_2 is given as :

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$$

1 mole $\quad \dfrac{1}{2} \times 22.4$ L O_2 at STP

= 34g $\quad$ = 11.2 L O_2 at STP

- **Molarity of H_2O_2 (M) = $\dfrac{\text{Volume strength of } H_2O_2}{11.2}$**

  Strength (in g/L) : Denoted by S

  Strength = Molarity × Mol. wt = Molarity × 34

Hardness of water :

Hard water does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.

$2C_{17}H_{35}COONa(aq) + M^{2+}(aq) \rightarrow (C_{17}H_{35}COO)_2M \downarrow +2Na^{+}(aq)$; M is Ca/Mg

Hardness of water is of two types

(a) Temporary Hardness

(b) Permanent Hardness

Temporary Hardness :- This is due to presence of bicarbonate of calcium and magnesium. Rain water dissolves a small quantities of CO_2 from the atmospher forming a very dilute solution of carbonic acid.

This water attacks Ca and Mg carbonate in any rock

$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$

Temporary hardness in water is easily removed by boiling, as the bicarbonates decomposes readily and the insoluble carbonates are precipitated.

$$Ca(HCO_3)_2 \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{CaCO_3} + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{MgCO_3} + H_2O + CO_2$$

Temporarily hardness can also be removed by clark's process which involves the addition of slaked lime Ca(OH)

$$Ca(HCO_3)_2 + Ca(OH)_2 \xrightarrow{\text{Boil}} \underset{\text{(Insoluble)}}{2CaCO_3} + 2H_2O$$

Permanent Hardness :- Permanent hardness is due to presence of sulphates and chlorides of both calcium and magnesium. This type of hardness cannot be removed by boiling or by $Ca(OH)_2$;. Substance used to remove the hardness of water are known as water softener. This various water softeners are

(i) **Washing soda :-** It removes both the temporary and permanent hardness by converting soluble Ca and Mg compounds into insoluble Carbonates.

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

$C aSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$

$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow \underset{\text{(Insoluble)}}{CaCO_3} + \underset{\text{(Insoluble)}}{NaHCO_3}$

(ii) **Permutit:** Permutit is technical name given to certain hydrated silicates of aluminium and sodium.or sodium alumunium orthosilicate or sodium zeolite.

Example : $Na_2 Al_2 Si_2 O_8 xH_2O$.

$Na_2 Al_2 Si_2 O_8 xH_20 + Ca^{+2} \longrightarrow Ca Al_2 Si_2 O_8 xH_2O + 2Na^{\oplus}$

$Na_2 Al_2 Si_2 O_8 xH_2O + Mg^{+2} \longrightarrow Mg Al_2 Si_2 O_8 xH_2O + 2Na^{\oplus}$

These ions can be re-exchanged by treating it with brine (NaCl) solution.

$Ca Al_2 Si_2 O_8 xH_2O + 2NaCl \longrightarrow Na_2 Al_2 Si_2 O_8 xH_2O + CaCl_2$

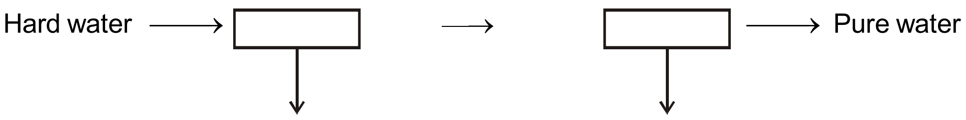
This method is useful for the removal of both temporary and permanent hardness of water.

(iii) CALGON: Tlie complex salt of metaphosphoric acid, sodium hexametaphosphate $(Na_4(PO_3)_6$ is called Calgon. It is represented as $Na_2[Na_4(PO_3)_6]$.

$$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + Na_2SO_4$$

$$2MgSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6] + Na_2SO_4$$

(iv) Ion exchange Resins:- Ion exchange resins are the most popular water softener thease days. This resins are synthetic substance. The cation exchanger consists of granular insoluble organic acid resins having giant molecules with $-SO_3H$ or -COOH groups while the anion exchanges contains giant organic molecules with basic groups derived from amine. Ion exchange resins removes all soluble mineral from water.



Cation exchanger	Cation exchanger
Remove cation like	Remove anion like
Na^+, Mg^{2+} or Ca^{2+}	SO_4^{2-}, Cl^- or NO_3^+
and furnish H^+	and furnish OH^-

$$H^+ + OH^- \longrightarrow H_2O$$

$$Ca^{2+} + RH_2 \longrightarrow R_2Ca + 2H^+$$

The water coming from cation exchanger is acidic due to H®. This water is then passed through another bed containing anion exchanger. This exchanger removes anion like Cl^-, SO_4^{2-}, NO_3 by exchanging with OH– ions.

Reaction at Cation exchanger :

$$Ca^{+2} + RH_2 \longrightarrow R_2Ca + 2H^{\oplus}$$

$$Mg^{+2} + RH_2 \longrightarrow R_2Mg + 2H^{\oplus}$$

Reaction at Anion exchanger :

$$R.(OH)_2 + Cl^- \longrightarrow RC1_2 + OH^-$$

$$R.(OH)_2 + SO_4^{2-} \longrightarrow RSO_4 + OH^-$$

NOTE : Degree of Hardness of water is measured in terms of ppm of $CaCO_3$ which is defined as number of parts of $CaCO_3$ by mass present in one million parts by mass of water whose equivalent is equal to the gram equivalent of various calcium & magnesium salts.

For **example** consider the sample of hard water which is found to contain 36 mg of $MgSO_4$ per kg of water.

gm equivalent of $CaCO_3$ = gm eq. of $MgSO_4$

$$\frac{W_{CaCO_3}}{100} \times 2 = \frac{36 \times 10^{-3}}{120} \times 2$$

$$W_{CaCO_3} = 3 \times 10^{-2} gm$$

degree of hardness = ppm of $CaCO_3$ = $\frac{3 \times 10^{-2}}{1000} \times 10^6 = 30$

Solved Examples

Example-17 0.00012% $MgSO_4$ and 0.000111% $CaCl_2$ is present in water. What is the measured hardness of water and millimoles of washing soda required to purify water 1000 L water ?

Solution. Basis of calculation = 100 g hard water

$$MgSO_4 = 0.00012g = \frac{0.00012}{120} \text{ mole}$$

$$CaCl_2 = 0.000111g = \frac{0.000111}{111} \text{mole}$$

$$\therefore \quad \text{equivalent moles of } CaCO_3 = \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \text{ mole}$$

$$\therefore \quad \text{mass of } CaCO_3 = \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \times 100 = 2 \times 10^{-4} \text{ g}$$

$$\text{Hardness (in terms of ppm of } CaCO_3) = \frac{2 \times 10^{-4}}{100} \times 10^6 = 2 \text{ ppm}$$

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$
$$NaSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$$

$$\therefore \quad \text{Required } Na_2CO_3 \text{ for 100g of water} = \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \text{mole}$$

$$= 2 \times 10^{-6} \text{ mole}$$

$$\therefore \quad \text{Required } Na_2CO_3 \text{ for 1000 litre water} = \frac{2 \times 10^{-6}}{100} \times 10^6 = \frac{2}{100} \text{ mole} \qquad (\because d = 1g/mL)$$

$$= \frac{20}{1000} \text{ mole} = 20 \text{ m mole}$$

Strength of Oleum :

Oleum is SO_3 dissolved in 100% H_2SO_4. Sometimes, oleum is reported as more than 100% by weight, say y% (where y > 100). This means that (y – 100) grams of water, when added to 100 g of given oleum sample, will combine with all the free SO_3 in the oleum to give 100% sulphuric acid.

Hence, weight % of free SO_3 in oleum = 80(y –100)/18

Solved Examples

Example-18 What volume of water is required (in mL) to prepare 1 L of 1 M solution of H_2SO_4 (density = 1.5g/mL) by using 109% oleum and water only (Take density of pure water = 1 g/mL).

Solution. 1 mole H_2SO_4 in 1L solution = 98 g H_2SO_4 in 1500 g solution = 98 g H_2SO_4 in 1402 g water.

Also, in 109% oleum, 9 g H_2O is required to form 109 g pure H_2SO_4 & so, to prepare 98 g H_2SO_4, water needed is 9/109 × 98 = 8.09 g.

Total water needed = 1402 + 8.09 = 1410.09 g = **1410.09 mL**

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

1. Find the valency factor for following acids

(i) CH_3COOH	(ii) NaH_2PO_4	(iii) H_3BO_3
Ans. (i) 1	(ii) 2	(iii) 1

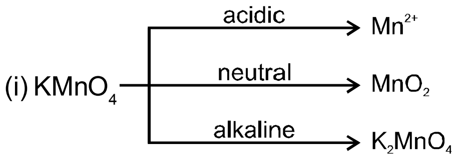
2. Find the valency factor for following bases :

(i) $Ca(OH)_2$	(ii) CsOH	(iii) $Al(OH)_3$
Ans. (i) 2	(ii) 1	(iii) 3

3. Find the valence factor for following salts :

(i) $K_2SO_4.Al_2(SO_4)_3.24H_2O$	(ii) $CaCO_3$
Ans. (i) 8	(ii) 2

4. Find the valency factor for following redox reactions :



(ii) $K_2Cr_2O_7 \xrightarrow{\text{acidic}} Cr^{3+}$

(iii) $C_2O_4^{2-} \longrightarrow CO_2$ (iv) $Fe^{2+} \longrightarrow Fe^{3+}$

Ans. (i) 5, 3, 1; (ii) 6 ; (iii) 2 ; (iv) 1

5. Calculate the normality of a solution obtained by mixing 50 mL of 5 M solution of $K_2Cr_2O_7$ and 50 mL of 2 M $K_2Cr_2O_7$ in acidic medium.

Sol. v.f. of $K_2Cr_2O_7 = 6$

so $$N_f = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} = \frac{5 \times 6 \times 50 + 2 \times 6 \times 50}{50 + 50} = 21\text{ N}$$

6. Calculate the normality of a solution containing 13.4 g of Sodium oxalate in 100 mL Sol.

Sol. $$\text{Normality} = \frac{\text{wt. in g/eq. wt}}{\text{vol of solution in litre}}$$

Here, eq. wt. of $Na_2C_2O_4 = 134/2 = 67$

so $$N = \frac{13.4/67}{100/1000} = 2N$$

7. The number of moles of ferrous oxalate oxidised by one mole of $KMnO_4$ in acidic medium is :

(A) 5/2 (B) 2/5 (C) 3/5 (D) 5/3

Sol. Eq. of FeC_2O_4 = Eq. of $KMnO_4$

moles of $FeC_2O_4 \times 3$ = moles of $KMnO_4 \times 5$

so, moles of $FeC_2O_4 = 5/3$ **Ans. (D)**

8. How many moles of $KMnO_4$ are needed to oxidise a mixture of 1 mole of each $FeSO_4$ & FeC_2O_4 in acidic medium ?

(A) 4/5 (B) 5/4 (C) 3/4 (D) 5/3

Sol. Eq. of $KMnO_4$ = Eq. of $FeSO_4$ + Eq. of FeC_2O_4

moles of $KMnO_4 \times 5$ = moles of $FeSO_4 \times 1$ + moles of $FeC_2O_4 \times 3$

$\therefore$ moles of $KMnO_4 = 4/5$ **Ans. (A)**

9. A sample of hydrazine sulphate [$N_2H_6SO_4$] was dissolved in 100 mL water. 10 mL of this solution was treated with excess of $FeCl_3$ Sol. Ferrous ions formed were estimated and it required 20 mL of M/50 $KMnO_4$ solution in acidic medium.

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

$$MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$$

(a) Write the balanced redox reactions.

(b) Estimate the amount of hydrazine sulphate in one litre of Sol.

Sol. (a) Given $4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$

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

(b) In 10 mL solution, eq. of $N_2H_6SO_4$ = Eq. of Fe^{2+} = Eq. of $KMnO_4$

$$= 20 \times \frac{1}{50} \times 5 \times 10^{-3} = 2 \times 10^{-3}$$

v.f. of $N_2H_6SO_4 = 4$

so, weight of $N_2H_6SO_4$ in 1 L solution $= \frac{2 \times 10^{-3} \times 1000}{4 \times 10} \times 130 = 6.5$ g.

10. Write the balanced redox reaction and calculate the equivalent weight of oxidising agent and reducing agent for titration of $K_2Cr_2O_7$ Vs Ferrous ammonium sulphate.

Ans. The reaction : $6[FeSO_4(NH_4)_2SO_4.6H_2O] + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow$

$3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 6(NH_4)_2SO_4 + 43H_2O$

Redox changes : $\left(E_{FeSO_4} = \frac{M}{1}\right)$; $\left(E_{K_2Cr_2O_7} = \frac{M}{6}\right)$

11. One litre of acidified $KMnO_4$ solution containing 15.8 g $KMnO_4$ is decolorized by passing sufficient SO_2. If SO_2 is produced by FeS_2, what is the amount of FeS_2 required to give desired SO_2 ?

Ans. 15 g.

Sol. v.f. of $KMnO_4$ = 5 & v.f. of SO_2 = 2

Now, Eq. of $KMnO_4$ = Eq. of SO_2

$$\frac{15.8}{158/5} = \text{moles of } SO_2 \times 2$$

so, moles of SO_2 = 1/4

Now, applying POAC on S, we get :

2 × mole of FeS_2 = 1 × moles of SO_2

so, moles of $FeS_2 = \frac{1}{4} \times \frac{1}{2} = \frac{1}{8}$

so, weight of $FeS_2 = \frac{1}{8} \times 120 = 15$ g.

12. An aqueous solution containing 0.1 g KIO_3 (formula weight = 214) and an excess of KI was acidified with HCl. The liberated I_2 consumed 45 mL of thiosulphate. The molarity of sodium thiosulphate solution is :

The reaction involved is : $IO_3^- + I^- + H^+ \longrightarrow I_2 + H_2O$

(A) 0.0623 M (B) 0.0313 M (C) 0.126 M (D) 0.252 M

Sol. $IO_3^- + 5I^- + H^+ \longrightarrow 3I_2 + H_2O$

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

Now, Moles of $KIO_3 = \frac{0.1}{214}$

So, Moles of $I_2 = 3 \times \frac{0.1}{214}$

Now, Moles of $Na_2S_2O_3 = 2 \times 3 \times \frac{0.1}{214}$

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

Now, Molarity of hypo solution $= 2 \times 3 \times \frac{0.1}{214} \times \frac{1000}{45} = 0.0623$ M **Ans. (A)**

13. Calculate the percentage of available chlorine in a sample of 3.55 g of bleaching powder which was dissolved in 100 mL of water. 25 mL of this solution, on treatment with KI and dilute acid, required 20 mL of 0.125 N sodium thiosulphate Sol.

Ans. 10 %

Sol. $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

$Cl_2 + 2KI \longrightarrow 2KCl + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_2O_6 + 2NaI$

In 25 mL solution, moles of $Na_2S_2O_3 = \frac{20}{1000} \times \frac{0.125}{1} = 25 \times 10^{-4}$

So, moles of $I_2 = \frac{1}{2} \times$ moles of $Na_2S_2O_3$

$= \frac{1}{2} \times 25 \times 10^{-4} = 12.5 \times 10^{-4}$

So, in 100 mL solution, moles of $Cl_2 = 4 \times 12.5 \times 10^{-4} = 50 \times 10^{-4}$

So, weight of $Cl_2 = 50 \times 10^{-4} \times 71$ g

% of available $Cl_2 = \frac{50 \times 10^{-4} \times 71}{3.55} \times 100 = 10\%$

14. 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 $KMnO_4$ solution is just decolorized 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 equations involved in the reactions and calculate the molarity of H_2O_2.

Sol. Let molarity of H_2O_2 solution is M_1

20 ml, M_1 molar H_2O_2 react with 20 ml $KMnO_4$ in H_2SO_4 solution

$$H_2O_2 + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + H_2O + O_2$$

no. of gram equivalent of H_2O_2 = no. of gram equivalent of $KMnO_4$

$$(M \times n_f \times V)_{H_2O_2} = (M \times n_f \times V)_{KMnO_4}$$

$$M_1 \times 2 \times 20 = M_{KMnO_4} \times 5 \times 20 \quad ....(i)$$

20 ml $KMnO_4$ decolourise by 10 ml $MnSO_4$ in neutral medium.

$$KMnO_4 + MnSO_4 + H_2O \rightarrow MnO_2 + H_2SO_4 + KHSO_4$$

no. of gram equivalent of $KMnO_4$ = no. of gram equivalent of MnO_2

$M_{KMnO_4} \times 3 \times 20ml$ = no. of gram equivalent of MnO_2

$$M_{KMnO_4} \times 3 \times 20 \times 10^{-3} = n_{MnO_2} \times 6/5 \quad ......(ii)$$

and obtained MnO_2 dissolved in 10 ml, 0.2 M $Na_2C_2O_4$

$$MnO_2 + Na_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + CO_2 + Na_2SO_4 + H_2O$$

no. of gram equivalent of MnO_2 = no. of gram equivalent of $Na_2C_2O_4$

$$n_{MnO_2} \times 2 = 0.2 \times 2 \times 10 \times 10^{-3}$$

$$n_{MnO_2} = 2 \times 10^{-3} \text{ moles} \quad ....(iii)$$

From equaiton (ii)

$$M_{KMnO_4} \times 3 \times 20 \times 10^{-3} = 2 \times 10^{-3} \times \frac{6}{5}$$

$$M_{KMnO_4} = \frac{2}{50}$$

From equation (1)

$$M_1 \times 2 \times 20 = \frac{2}{50} \times 5 \times 20$$

$M_1 = 0.1M$

15. A mixture of FeO and Fe_2O_3 is reacted with acidified $KMnO_4$ solution having a concentration of 2/5 M, 100 mL of which was used. The solution was then titrated with Zn dust which converted Fe^{3+} of the solution to Fe^{2+}. The Fe^{2+} required 1000 mL of 2/15 M $K_2Cr_2O_7$ solution. Find the % by mol of FeO and Fe_2O_3.

Sol. Let no. of moles of FeO is x millimoles & Fe_2O_3 is y millimoles in mixture.

$FeO + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

no. of milligram equivalent of FeO = no. of milli gram equivalent of $KMnO_4$.

$$x \times 1 = \frac{2}{5} \times 5 \times 100$$

x = 200 m moles.

Zn - dust convert all Fe^{3+} to Fe^{2+}

So no. of millimoles of Fe^{2+} in solution is = (x + 2y).

$Fe^{2+} + K_2Cr_2O_7 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe^{3+} + K_2SO_4 + H_2O$

no. of milli gram equivalent of Fe^{2+} = no. of milligram equivalent of $K_2Cr_2O_7$

$$(x + 2y) \times 1 = \frac{2}{15} \times 6 \times 1000$$

$$(200 + 2y) = \frac{2}{15} \times 1000$$

y = 300 millimoles.

$$\% \text{ FeO (by moles)} = \frac{x}{x+y} \times 100 = \frac{200}{500} \times 100 = 40\%$$

% Fe_2O_3 (by moles) = 60%

16. 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the normality of dichromatic solution.

Sol. Let Normality of $K_2Cr_2O_7$ solution is N

$Fe^{2+} + K_2Cr_2O_7 + H^+ \rightarrow Fe^{3+} + Cr^{3+} + H_2O$

no. of gram eq. of Fe^{2+} = no. of gram eq. of $K_2Cr_2O_7$

$$n_{Fe^{2+}} \times 1 = N \times x \times 10^{-3}$$

$$\frac{W_{Fe^{2+}}}{56} \times 1 = N \times x \times 10^{-3}$$

$$\frac{\frac{x}{100} \times 0.84}{56} \times 1 = N \times x \times 10^{-3}$$

N = 0.15

Exercise-1

✍ Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Calculation of n-factor, Equivalent weight , Normality for Acid, Base, Oxidant and Reductant

A-1. Calculate 'n' factor of following acids -

(i) HCl (ii) H_3PO_2 (iii) H_3PO_3 (iv) H_3PO_4
(v) HCOOH (vi) HNO_2 (vii) $H_4P_2O_7$ (viii) CO_2
(ix) SO_3 (x) N_2O_5

A-2. Calculate 'n' factor of following bases -

(i) $Mn(OH)_2$ (ii) $Al(OH)_3$ (iii) NH_4OH (iv) $Zn(OH)_2$
(v) $Sr(OH)_2$ (vi) NH_3 (vii) Na_2O (viii) MgO
(ix) K_2O (x) Al_2O_3

A-3. Find the n-factor of underlined species in the following unbalanced non redox reaction.

(1) $NaOH + \underline{H_3PO_4} \longrightarrow Na_2HPO_4 + H_2O$
(2) $NaOH + \underline{H_2SO_4} \longrightarrow NaHSO_4 + H_2O$
(3) $\underline{Ca(OH)_2} + HCl \longrightarrow Ca(OH)Cl + H_2O$
(4) $\underline{Na_2CO_3} + HCl \longrightarrow NaHCO_3 + NaCl$
(5) $\underline{Na_2CO_3} + HCl \longrightarrow NaCl + H_2O + CO_2$

A-4. Find out the equivalent weight of the underlined species in the following reaction :

(i) $\underline{ClO_3^-} + Fe^{2+} + H^+ \longrightarrow Cl^- + Fe^{3+} + H_2O$
(ii) $CuO + \underline{NH_3} \longrightarrow Cu + N_2 + H_2O$

A-5.✍ 1.12 litre dry chlorine gas at STP was passed over a heated metal when 5.56 g of chloride of the metal was formed. What is the equivalent weight of the metal?

A-6.✍ A mixture of CuS (molecular weight = M_1) and Cu_2S (molecular weight = M_2) is oxidised by $KMnO_4$ (molecular weight = M_3) in acidic medium, where the product obtained are Cu^{2+}, Mn^{2+} and SO_2. Find the equivalent weight of CuS, Cu_2S and $KMnO_4$ respectively.

A-7. Determine the equivalent weight of the following oxidising and reducing agents :

(a) $KMnO_4$ (reacting in acidic medium $MnO_4^- \longrightarrow Mn^{2+}$)
(b) $KMnO_4$ (reacting in neutral medium $MnO_4^- \longrightarrow MnO_2$)

Section (B) : Equivalent Concept for Acid Base Titration and Precipitation Reactions

B-1. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is :

B-2. Calculate volume of 1N H_2SO_4 required to react with 20 ml 1 M $Al(OH)_3$ solution

B-3. H_3PO_4 is a tri basic acid and one of its salt is NaH_2PO_4. What volume in ml of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4 ?

B-4. A dilute solution of H_2SO_4 is made by adding 5 mL of 3N H_2SO_4 to 245 mL of water. Find the normality and molarity of the diluted solution.

B-5.✍ What volume at NTP of gaseous ammonia will be required to be passed into 30 cm^3 of 1 N H_2SO_4 solution to bring down the acid strength of the latter to 0.2 N ?

B-6. 0.98 g of the metal sulphate was dissolved in water and excess of barium chloride was added. The precipitated barium sulphate weighted 0.95 g. Calculate the equivalent weight of the metal.

Section (C) : Equivalent Concept for Redox reactions, $KMnO_4$ / $K_2Cr_2O_7$ v/s Reducing Agents & their Redox Titration

C-1. How many moles of $K_2Cr_2O_7$ required to oxidise 3 moles of KHC_2O_4

C-2. How many moles of I_2 gas liberate when excess KI solution react with 25 ml , 2M $K_2Cr_2O_7$ solution.

C-3. Calculate number of moles of I_2 required to oxidised, 100 ml of 2M $Na_2S_2O_3$ into $Na_2S_4O_6$.

C-4. It requires 40 mL of 1 M Ce^{4+} to titrate 20 mL of 1M Sn^{2+} to Sn^{4+}. What is the oxidation state of the Cerium in the product ?

C-5. 25 mL of a solution of Fe^{2+} ions was titrated with a solution of the oxidizing agent $Cr_2O_7^{2-}$. 50 mL of 0.01 M $K_2Cr_2O_7$ solution was required. What is the molarity of the Fe^{2+} solution ?

C-6.✍ How many mL of 0.3M $K_2Cr_2O_7$ (acidic) is required for complete oxidation of 5 mL of 0.2 M SnC_2O_4 solution.

Section (D) : Iodometric/Iodimetric Titration, Back titration, Calculation of Available Chlorine from a sample of Bleaching Powder

D-1. 50 gm of a sample of $Ca(OH)_2$ is dissolved in 50 ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.3N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of $Ca(OH)_2$

D-2. 10 g $CaCO_3$ were dissolved in 250 ml of 1 M HCl. What volume of 2 M KOH would be required to neutralise excess HCl.

D-3. 5 g of pyrolusite (impure MnO_2) were heated with conc. HCl and Cl_2 evolved was pssed through excess of KI solution. The iodine liberated required 40 mL of N/10 hypo solution. Find the % of MnO_2 in the pyrolusite.

D-4. One gram of Na_3AsO_4 is boiled with excess of solid KI in presence of strong HCl. The iodine evolved is absorbed in KI solution and titrated against 0.2 N hypo solution. Assuming the reaction to be

$$AsO_4^{3-} + 2H^+ + 2I^- \longrightarrow AsO_3^{3-} + H_2O + I_2$$

calculate the volume of hypo consumed. [Atomic weight of As = 75]

D-5.✍ A 100 mL sample of water was treated to convert any iron present to Fe^{2+}. Addition of 25 mL of 0.002 M $K_2Cr_2O_7$ resulted in the reaction :

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

The excess $K_2Cr_2O_7$ was back-titrated with 7.5 mL of 0.01 M Fe^{2+} solution. Calculate the parts per million (ppm) of iron in the water sample.

Section (E) : Volume strength of H_2O_2 , Hardness of water

E-1. 20 ml of H_2O_2 after acidification with dil H_2SO_4 required 30 ml of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. Detemine the volume strength of H_2O_2 solution.

E-2. A 5.0 cm^3 solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. **[JEE' 1995]**

E-3. One litre of a sample of hard water contains 10 mg of $CaCl_2$ & 9.5 mg of $MgCl_2$. What is degree of hardness in terms of ppm of $CaCO_3$

E-4. By which reason temporary and permanent hardness occur ?

E-5. Define two method by which we can soften the water sample.

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Calculation of n-factor, Equivalent weight , Normality for Acid, Base, Oxidant and Reductant

A-1. Equivalent wt. of H_3PO_4 in each of the reaction will be respectively -
$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$
$H_3PO_4 + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O$
$H_3PO_4 + 3OH^- \rightarrow PO_4^{3-} + 3H_2O$
(A) 98 , 49 , 32.67 (B) 49 , 98 , 32 , 67 (C) 98 , 32.67 , 49 (D) 32.67 , 49 , 98

A-2. MnO_4^- is good oxidising agent in different medium changing to -
$MnO_4^- \longrightarrow Mn^{2+}$
$\longrightarrow MnO_4^{2-}$
$\longrightarrow MnO_2$
$\longrightarrow Mn_2O_3$
Changes in oxidation number respectively are -
(A) 1, 3, 4, 5 (B) 5, 4, 3, 2 (C) 5, 1, 3, 4 (D) 2, 6, 4, 3

A-3.✍ When N_2 is converted into NH_3, the equivalent weight of nitrogen will be :
(A) 1.67 (B) 2.67 (C) 3.67 (D) 4.67

A-4. In the ionic equation $2K^+BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O + 2K^+$, the equivalent weight of $KBrO_3$ will be:
(A) M/5 (B) M/2 (C) M/6 (D) M/4
(where M = molecular weight of $KBrO_3$)

A-5.✍ An ion is reduced to the element when it absorbs 6×10^{20} electrons. The number of equivalents of the ion is:
(A) 0.1 (B) 0.01 (C) 0.001 (D) 0.0001

A-6.✍ x g of the metal gave y g of its oxide. Hence equivalent weight of the metal

(A) $\frac{y-x}{x} \times 8$ (B) $\frac{x}{(y-x)} \times 8$ (C) $\frac{x}{y} \times 8$ (D) $\frac{x+y}{x} \times 8$

A-7. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. Equivalent weidht of the metal is :
(A) 33.25 (B) 3.325 (C) 12 (D) 20

Section (B) : Equivalent Concept for Acid Base Titration and Precipitation Reactions

B-1. If one mole of H_2SO_4 reacts with one mole of NaOH, equivalent weight of H_2SO_4 will be :
(A) 98 (B) 49 (C) 96 (D) 48

B-2. Calculate volume of 1N H_3PO_4 required to react with 20 ml 2N $Ca(OH)_2$ solution
(A) 40 ml (B) 20 ml (C) 60 ml (D) 10 ml

B-3. How many millilitres of 0.1N H_2SO_4 solution will be required for complete reaction with a solution containing 0.125 g of pure Na_2CO_3:
(A) 23.6 mL (B) 25.6 mL (C) 26.3 mL (D) 32.6 mL

B-4.✍ One litre of a solution contains 18.9 g of HNO_3 and one litre of another solution contains 3.2 g of NaOH. In what volume ratio must these solution be mixed to obtain a neutral solution?
(A) 3 : 8 (B) 8 : 3 (C) 15 : 4 (D) 4 : 15

Section (C) : Equivalent Concept for Redox reactions, $KMnO_4$ / $K_2Cr_2O_7$ v/s Reducing Agents & their Redox Titration

C-1. If equal volumes of 0.1 M $KMnO_4$ and 0.1 M $K_2Cr_2O_7$ solutions are allowed to oxidise Fe^{2+} to Fe^{3+} in acidic medium, then Fe^{2+} oxidised will be :

(A) more by $KMnO_4$ (B) more by $K_2Cr_2O_7$
(C) equal in both cases (D) cannot be determined.

C-2.✍ Which of the following solutions will exactly oxidize 25 mL of an acid solution of 0.1 M iron (II) oxalate:

(A) 25 mL of 0.1 M $KMnO_4$ (B) 25 mL of 0.2 M $KMnO_4$
(C) 25 mL of 0.6 M $KMnO_4$ (D) 15 mL of 0.1 M $KMnO_4$

C-3.✍ An element A in a compound ABD has oxidation number –n. It is oxidised by $Cr_2O_7^{2-}$ in acid medium. In the experiment, 1.68×10^{-3} moles of $K_2Cr_2O_7$ were used for 3.36×10^{-3} moles of ABD. The new oxidation number of A after oxidation is :

(A) 3 (B) 3 – n (C) n – 3 (D) +n

C-4. The number of moles of oxalate ions oxidized by one mole of MnO_4^- ion in acidic medium is :

(A) 5/2 (B) 2/5 (C) 3/5 (D) 5/3

Section (D) : Iodometric/Iodimetric Titration, Back titration, Calculation of Available Chlorine from a sample of Bleaching Powder

D-1. What can be the maximum percentage of available chlorine possible in a given bleaching powder sample (Take formula of bleaching powder as $CaOCl_2$) ?

(A) 52.9% (B) 55.9 % (C) 58% (D) 60%

D-2.✍ A 0.2 g sample containing copper (II) was analysed iodometrically, where copper(II) is reduced to copper (I) by iodide ions. $2Cu^{2+} + 4I^- \longrightarrow 2\,CuI + I_2$

If 20 mL of 0.1 M $Na_2S_2O_3$ solution is required for titration of the liberated iodine, then the percentage of copper in the sample will be :

(A) 31.75 % (B) 63.5 % (C) 53 % (D) 37 %

D-3. x mmol of XeF_4 quantitatively oxidized KI to I_2 and liberated Xe, alongwith formation of KF. This iodine required 20 ml of decinormal hypo solution for exact titration. The value of x is

(A) 0.5 (B) 1.0 (C) 2.0 (D) 5.0

Section (E) : Volume strength of H_2O_2, Hardness of water

E-1. A substance which participates readily in both acid-base and oxidation-reduction reactions is :

(A) Na_2CO_3 (B) KOH (C) $KMnO_4$ (D) $H_2C_2O_4$

E-2._ A fresh H_2O_2 solution is labeled as 11.2 V. Calculate its concentration in wt/vol percent.

(A) 3.4 (B) 6.8 (C) 1.7 (D) 13.6

E-3.✍ The amount of lime, $Ca(OH)_2$ required to remove the hardness in 60 L of pond water containing 1.62 mg of calcium bicarbonate per 100 ml of water, will be :

(A) 4.44 g (B) 0.222 g (C) 2.22 g (D) 0.444 g

E-4. What will the concentration of $[Ca^{+2}]$ in a sample of 1 litre hard water if after treatment with washing soda 10 g insoluable $CaCO_3$ is precipitated.

(A) 0.2 M (B) 0.1 M (C) 0.3 M (D) 0.4 M

PART - III : MATCH THE COLUMN

1.

Column I	Column II
(A) 4.1 g H_2SO_3	(p) 200 mL of 0.5 N base is used for complete neutralization
(B) 4.9 g H_3PO_4	(q) 200 millimoles of oxygen atoms
(C) 4.5 g oxalic acid ($H_2C_2O_4$)	(r) Central atom is in its highest oxidation number
(D) 5.3 g Na_2CO_3	(s) May react with an oxidising agent

Exercise-2

✍ **Marked Questions may have for Revision Questions.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1.✍ The equivalent weight of a metal is double that of oxygen. How many times is the weight of its oxide greater than weight of the metal?

(A) 1.5 (B) 2 (C) 0.5 (D) 3

2.✍ 1.60 g of a metal A and 0.96 g of a metal B when treated with excess of dilute acid, separately, produced the same amount of hydrogen. Calculate the equivalent weight of A if the equivalent weight of B is 12.

(A) 10 (B) 20 (C) 30 (D) 40

3. Oxalic acid, $H_2C_2O_4$, reacts with paramagnet ion according to the balanced equation $5H_2C_2O_4\,(aq) + 2MnO_4^-\,(aq) \rightleftharpoons 2\,Mn^{2+}\,(aq) + 10\,CO_2\,(g) + 8\,H_2O\,(l)$. The volume in mL of 0.0162 M $KMnO_4$ solution required to react with 25.0 mL of 0.022 M $H_2C_2O_4$ solution is :

(A) 13.6 (B) 18.5 (C) 33.8 (D) 84.4

4.✍ x mmol of $KMnO_4$ react completely with y mmol of $MnSO_4$ in presence of fluoride ions to give MnF_4 quantitatively. Then :

(A) $x = y$ (B) $4x = y$ (C) $x > y$ (D) $x < y$

5.✍ 1 mol each of H_3PO_2, H_3PO_3 and H_3PO_4 will neutralise respectively x mol of NaOH, y mol of $Ca(OH)_2$ and z mol of $Al(OH)_3$ (assuming all as strong electrolytes). x, y, z are in the ratio of :

(A) 3 : 1.5 : 1 (B) 1 : 2 : 3 (C) 3 : 2 : 1 (D) 1 : 1 : 1

6. The amount of wet NaOH containing 15% water required to prepare 70 litres of 0.5 N solution is :

(A) 1.65 kg (B) 1.4 kg (C) 16.5 kg (D) 140 kg

7.✍ $28\,NO_3^- + 3As_2S_3 + 4H_2O \longrightarrow 6AsO_4^{3-} + 28NO + 9SO_4^{2-} + 8H^+$.

What will be the equivalent mass of As_2S_3 in above reaction : (Molecular mass of As_2S_3 = M)

(A) $\frac{M}{2}$ (B) $\frac{M}{4}$ (C) $\frac{M}{24}$ (D) $\frac{M}{28}$

8. If 25 mL of a H_2SO_4 solution reacts completely with 1.06 g of pure Na_2CO_3, what is the normality of this acid solution :

(A) 1 N (B) 0.5 N (C) 1.8 N (D) 0.8 N

9. 125 mL of 63% (w/v) $H_2C_2O_4 \cdot 2H_2O$ solution is made to react with 125 mL of a 40%(w/v) NaOH solution. The resulting solution is: (ignoring hydrolysis of ions)

(A) neutral (B) acidic (C) strongly acidic (D) alkaline

10.✍ 25 mL of a 0.1 M solution of a stable cation of transition metal Z reacts exactly with 25 mL of 0.04 M acidified $KMnO_4$ solution. Which of the following is most likely to represent the change in oxidation state of Z correctly :

(A) $Z^+ \rightarrow Z^{2+}$ (B) $Z^{2+} \rightarrow Z^{3+}$ (C) $Z^{3+} \rightarrow Z^{4+}$ (D) $Z^{2+} \rightarrow Z^{4+}$

11. How many litres of Cl_2 at STP will be liberated by the oxidation of NaCl with 10 g $KMnO_4$ in acidic medium: (Atomic weight : Mn = 55 and K = 39)

(A) 3.54 (B) 7.08 (C) 1.77 (D) None of these

12.✍ 10 g sample of bleaching powder was dissolved into water to make the solution one litre. To this solution 35 mL of 1.0 M Mohr salt solution was added containing enough H_2SO_4. After the reaction was complete, the excess Mohr salt required 30 mL of 0.1 M $KMnO_4$ for oxidation. The % of available Cl_2 approximately is (mol wt = 71)

(A) 7.1 % (B) 14.2 % (C) 3.05 % (D) 28.4 %

13. If 10 g of V_2O_5 is dissolved in acid and is reduced to V^{2+} by zinc metal, how many mole of I_2 could be reduced by the resulting solution, if it is further oxidised to VO^{2+} ions :
[Assume no change in state of Zn^{2+}ions] (Atomic masses : V = 51, O = 16, I = 127)

(A) 0.11 (B) 0.22 (C) 0.055 (D) 0.44

14. During the disproportionation of Iodine to iodide and iodate ions, the ratio of iodate and iodide ions formed in alkaline medium is :

(A) 1 : 5 (B) 5 : 1 (C) 3 : 1 (D) 1 : 3

15.✍ If 1 mL of a $KMnO_4$ solution react with 0.140 g Fe^{2+} and if 1 mL of $KHC_2O_4 . H_2C_2O_4$ solution react with 0.1mL of previous $KMnO_4$ solution, how many millilitres of 0.20 M NaOH will react with 1 mL of previous $KHC_2O_4 . H_2C_2O_4$ solution in which all the protons (H^+) are ionisable ?

(A)15/16 mL (B) 13/16 (C) 11/14 (D) None of these

16. 100 ml sample of hard water containing only Ca^{2+} hardness is passed through a column of cation exchange resin (H^+ – resin). The water coming out the column require 20 ml of 0.02M NaOH for its titration. What is hardness of water as ppm of Ca^{2+}

(A) 80 (B) 60 (C) 90 (D) 100

17. An aqueous solution containing 0.10 g KIO_3 (formula wt. 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.

(A) 0.3 (B) 0.0626 (C) 0.8 (D) 0.9

18. A mixture of $NaHC_2O_4$ and $KHC_2O_4 . H_2C_2O_4$ required equal volumes of 0.2 N $KMnO_4$ and 0.12 N NaOH separately. What is the molar ratio of $NaHC_2O_4$ and $KHC_2O_4 . H_2C_2O_4$ in the mixture ?

(A) 6 : 1 (B) 1 : 2 (C) 1 : 3 (D) 3 : 1

PART - II : NUMERICAL TYPE QUESTIONS

1. How many equivalents of Mg would have to react in order to liberate 4 N_A electrons? ($Mg - 2e^- \longrightarrow Mg^{2+}$)

2. A certain weight of pure $CaCO_3$ is made to react completely with 20 mL of a HCl solution to give 224 mL of CO_2 gas at STP. The normality of the HCl solution is:

3._✍ The volume of 3 M $Ba(OH)_2$ solution required to neutralize completly 120 mL of 1.5M H_3PO_4 solution is:

4. In an experiment, 50 mL of 0.1 M solution of a salt reacted with 25 mL of 0.1 M solution of sodium sulphite. The half equation for the oxidation of sulphite ion is :

$$SO_3^{2-}(aq) + H_2O \longrightarrow SO_4^{2-}(aq) + 2H^+ + 2e^-$$

If the oxidation number of metal in the salt was 3, what would be the new oxidation number of metal :

5.✍ When tetracarbonylnickel(0) is heated, it dissociates into its components. If 5 moles of this compound is heated and the resulting gaseous component is absorbed by sufficient amount of I_2O_5, liberating I_2. What volume of 4M Hypo solution will be required to react with this I_2 : $Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO$

6. 1 mole of OH^- ions is obtained from 85 g of hydroxide of a metal. What is the equivalent weight of the metal?

7.✍ An oxide of a metal contains 40% oxygen, by weight. What is the equivalent weight of the metal?

8. In the following reaction, $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$, if the atomic weight of iron is 56, then its equivalent weight will be :

9. What volume of 0.05 M $Ca(OH)_2$ solution is needed for complete conversion of 10 mL of 0.1 M H_3PO_4 into $Ca(H_2PO_4)_2$?

10.✍ Potassium acid oxalate $K_2C_2O_4 . 3H_2C_2O_4 . 4H_2O$ can be oxidized by MnO_4^- in acid medium. Calculate the volume of (in mL) 1 M $KMnO_4$ reacting in acid solution with 5.08 gram of the acid oxalate.

11. In the following reaction, SO_2 acts as a reducing agent :

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

Find the equivalent weight of SO_2.

12. 80 gm of a sample of Anhydrous $CuSO_4$ was dissolved in water and made to 250 mL. 25 mL of this solution after taking usual precaution was treated with a little excess of KI solution. A white ppt. of Cu_2I_2 and iodine was evolved. The iodine so evolved required 40 mL of 1 M hypo solution. What is the approximate purity of $CuSO_4$ solution. [Mol. wt. of $CuSO_4$ = 160]

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. In the titration of $K_2Cr_2O_7$ and ferrous sulphate, following data is obtained :
V_1 mL of $K_2Cr_2O_7$ solution of molarity M_1 requires V_2 mL of $FeSO_4$ solution of molarity M_2.
Which of the following relations is/are true for the above titration :
(A) $6\ M_1V_1 = M_2V_2$ (B) $M_1V_1 = 6\ M_2V_2$ (C) $N_1V_1 = N_2V_2$ (D) $M_1V_1 = M_2V_2$

2.✍ Choose the correct statement(s) :
(A) 1 mole of MnO_4^- ion can oxidise 5 moles of Fe^{2+} ion in acidic medium.
(B) 1 mole of $Cr_2O_7^{2-}$ ion can oxidise 6 moles of Fe^{2+} ion in acidic medium.
(C) 1 mole of Cu_2S can be oxidised by 1.6 moles of MnO_4^- ion in acidic medium.
(D) 1 mole of Cu_2S can be oxidised by 1.33 moles of $Cr_2O_7^{2-}$ ion in acidic medium.

3. Which of the following samples of reducing agents is /are chemically equivalent to 25 mL of 0.2 N $KMnO_4$ to be reduced to Mn^{2+} and water :
(A) 25 mL of 0.2 M $FeSO_4$ to be oxidized to Fe^{3+}
(B) 50 mL of 0.1 M H_3AsO_3 to be oxidized to H_3AsO_4
(C) 25 mL of 0.1 M H_2O_2 to be oxidized to H^+ and O_2
(D) 25 mL of 0.1 M $SnCl_2$ to be oxidized to Sn^{4+}

4.✍ To a 25 ml H_2O_2 solution excess acidified solution of KI was added. The iodine liberated 20 ml of 0.3 N sodium thiosulphate solution. Use these data to choose the correct statements from the following :
(A) The weight of H_2O_2 present in 25 ml solution is 0.102 g
(B) The molarity of H_2O_2 solution is 0.12 M
(C) The weight of H_2O_2 present in 1 L of the solution is 0.816 g
(D) The volume strength of H_2O_2 is 1.344 L

5. There are two sample of HCl having molarity 1N and 0.25 N. Find volume of these sample taken in order to prepare 0.75 N HCl solution. (Assume no water is used) :

(A) 20 mL, 10 mL (B) 100 mL, 50 mL (C) 40 mL, 20 mL (D) 50 mL, 25 mL

6. If mass of KHC_2O_4 (potassium acid oxalate) required to reduce 100 mL of 0.02 M $KMnO_4$ in acidic medium is x g and to neutralise 100 mL of 0.05 M $Ca(OH)_2$ is y g, then which of the following options may be correct :

(A) If x is 1 g then y is 2 g (B) If x is 5.5g then y is 11 g

(C) If x is 2 g then y is 1 g (D) If x is 11 g then y is 5.5 g

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Equivalent Mass :

The equivalent mass of a substance is defined as the number of parts by mass of it which combine with or displace 1.0078 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine. The equivalent mass of a substance expressed in grams is called **gram equivalent mass.**

The equivalent mass of a substance is not constant. It depends upon the reaction in which the substance is participating. A compound may have different equivalent mass in different chemical reactions and under different experimental conditions.

(A) Equivalent mass of an acid : It is the mass of an acid in grams which contains 1.0078 g of replaceable H^+ ions or it is the mass of acid which contains one mole of replaceable H^+ ions. It may be calculated as :

Equivalent mass of acid = $\dfrac{\text{Molecular mass of acid}}{\text{Basicity of acid}}$

Basicity of acid = number of replaceable hydrogen atoms present in one molecule of acid

(B) Equivalent mass of a base : It is the mass of the base which contains one mole of replaceable OH^- ions in molecule.

Equivalent mass of base = $\dfrac{\text{Molecular mass of base}}{\text{Aciditiy of base}}$

Acidity of base = Number of replaceable OH^- ions present in one molecule of the base

Equivalent mass of an oxidising agent :

(a) Electron concept : Equivalent mass of oxidising agent = $\dfrac{\text{Molecular mass of oxidi sin g agent}}{\text{Number of electrons gained by one molecule}}$

(b) Oxidation number concept : Equivalent mass of oxidising agent = $\dfrac{\text{Molecular mass of oxidi sin g agent}}{\begin{array}{c}\text{Total change in oxidation number}\\ \text{per molecule of oxidi sin g agent}\end{array}}$

1. Equivalent mass of $Ba(MnO_4)_2$ in acidic medium is : (where M stands for molar mass)

(A) M/5 (B) M/6 (C) M/10 (D) M/2

2. Equivalent mass of $Fe_{0.9}$ O in reaction with acidic $K_2Cr_2O_7$ is : (M = Molar mass)

(A) 7 M/10 (B)10 M/7 (C) 7 M/9 (D) 9 M/7

3. Equivalent weight of oxalic acid salt in following reaction is : (Atomic masses : O = 16, C = 12, K = 39)

$H_2C_2O_4 + Ca(OH)_2 \longrightarrow CaC_2O_4 + H_2O$

(A) 90 (B) 45 (C) 64 (D) 128

Comprehension # 2

Some amount of “20V” H_2O_2 is mixed with excess of acidified solution of KI. The iodine so liberated required 200 mL of 0.1 N $Na_2S_2O_3$ for titration.

4. The volume of H_2O_2 solution is :
(A) 11.2 mL (B) 37.2 mL (C) 5.6 mL (D) 22.4 mL

5. The mass of $K_2Cr_2O_7$ needed to oxidise the above volume of H_2O_2 solution is :
(A) 3.6 g (B) 0.8 g (C) 4.2 g (D) 0.98 g

6. The volume of O_2 at STP that would be liberated by above H_2O_2 solution on disproportionation is :
(A) 56 mL (B) 112 mL (C) 168 mL (D) 224 mL

Exercise-3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

*** Marked Questions may have more than one correct option.**

1. In basic medium, I^- is oxidised by MnO_4^-. In this process, I^- changes to : **[JEE 2004, 3/144]**
(A) IO_3^- (B) I_2 (C) IO_4^- (D) IO^-

2. 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 : **[JEE 2007, 3/162]**
(A) 3 (B) 4 (C) 5 (D) 6

3. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is : **[JEE 2012, 3/136]**
(A) 0.48 M (B) 0.96 M (C) 0.24 M (D) 0.024 M

4.* For the reaction : $I^- + ClO_3^- + H_2SO_4 \longrightarrow Cl^- + HSO_4^- + I_2$
The correct statement(s) in the balanced equation is/are : **[JEE (Advanced) 2014, 3/120]**
(A) Stoichiometric coefficient of HSO_4^- is 6.
(B) Iodide is oxidized.
(C) Sulphur is reduced.
(D) H_2O is one of the products.

5. In neutral or faintly alkaline solution, 8 moles permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. the magnitude of X is **[JEE- 2016]**

6. To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using the reaction, **[JEE- 2018]**
$MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCl$ (equation not balanced).
Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 g) was added in portions till the colour of the permanganate ion disappeard. The quantity of $MnCl_2$ (in mg) present in the initial solution is _____.
(Atomic weights in g mol^{-1} : Mn = 55, Cl = 35.5)

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. When $KMnO_4$ acts as an oxidising agent and ultimately forms MnO_4^{2-} , MnO_2, Mn_2O_3 and Mn^{2+}, then the number of electrons transferred in each case is : **[AIEEE 2002, 3/225]**

(1) 4, 3, 1, 5 (2) 1, 5, 3, 7 (3) 1, 3, 4, 5 (4) 3, 5, 7, 1

2. What will happen if the solution of potassium chromate reacts with excess amount of nitric acid

(1) Cr reduces in the oxidation state +3 from CrO_4^{2-}. **[AIEEE 2003, 3/225]**
(2) Cr oxidises in the oxidation state +7 from CrO_4^{2-}.
(3) Cr^{+3} and $Cr_2O_7^{2-}$ will be formed.
(4) $Cr_2O_7^{2-}$ and H_2O will be formed.

3. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is : **[AIEEE 2005, 3/225]**

(1) + 4 (2) + 6 (3) + 2 (4) + 3

4. Amount of oxalic acid present in a solution can be determined by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl : **[AIEEE 2008, 3/105]**

(1) furnishes H^+ ions in addition to those from oxalic acid.
(2) reduces permanganate to Mn^{2+}.
(3) oxidises oxalic acid to carbon dioxide and water.
(4) gets oxidised by oxalic acid to chlorine.

5. 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is : **[AIEEE 2010, 4/144]**

(1) 59.0 (2) 47.4 (3) 23.7 (4) 29.5

6. Consider the following reaction : $xMnO_4^- + yC_2O_4^{2-} + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O$

The values of x, y and z in the reaction are, respectively : **[JEE(Main) 2013, 4/120]**

(1) 5, 2 and 16 (2) 2, 5 and 8 (3) 2, 5 and 16 (4) 5, 2 and 8

7. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is : **[JEE(Main) 2014, 4/120]**

(1) 6% (2) 10% (3) 3% (4) 5%

8. In the reaction of oxalate with permaganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is : **[JEE(Main)-(Jan.)-2019]**

(1) 10 (2) 2 (3) 1 (4) 5

9. The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing 10^{-3} M $CaSO_4$ is : (molar mass of $CaSO_4$ = 136 g mol^{-1}) **[JEE(Main)-(Jan.)-2019]**

(1) 100 ppm (2) 50 ppm (3) 10 ppm (4) 90 ppm

10. 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is : **[JEE(Main)-(Jan.)-2019]**

(1) 4 g (2) 2 g (3) 8 g (4) 1 g

11. In order to oxidise a mixture one mole of each of FeC_2O_4, $Fe_2(C_2O_4)_3$, $FeSO_4$ and $Fe_2(SO_4)_3$ in acidic medium, the number of moles of $KMnO_4$ required is - **[JEE(Main)-(April)-2019]**

(1) 3 (2) 2 (3) 1 (4) 1.5

12. 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of $CaCO_3$ is:
(molar mass of calcium bicarbonate is 162 g mol^{-1} and magnesium bicarbonate is 146 $gmol^{-1}$)

(1) 1,000 ppm (2) 10,000 ppm **[JEE(Main)-(April)-2019]**
(3) 100 ppm (4) 5,000 ppm

13. 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution? **[JEE(Main)-(Jan)-2019]**

(1) 25 mL (2) 50 mL (3) 12.5 mL (4) 75 mL

ANSWER KEY

EXERCISE # 1

PART - I

A-1. (i) 1 (ii) 1 (iii) 2 (iv) 3 (v) 1 (vi) 1 (vii) 4 (vii) 2
(ix) 2 (x) 2

A-2. (i) 2 (ii) 3 (iii) 1 (iv) 2 (v) 2 (vi) 1 (vii) 2 (viii) 2
(ix) 2 (x) 6

A-3. (1) 2 (2) 1 (3) 1 (4) 1 (5) 2

A-4. (i) $\frac{83.5}{6}$; (ii) $\frac{17}{3}$ **A-5.**✍ 20.1 **A-6.**✍ $\frac{M_1}{6}, \frac{M_2}{8}, \frac{M_3}{5}$

A-7. (a) 31.6 (b) 52.67 **B-1.** 40 **B-2.** 60 ml

B-3. 200 mL **B-4.** 0.06 N, 0.03 M **B-5.**✍ 537.6 mL

B-6. 72.61 **C-1.** 1 **C-2.** 0.15 moles **C-3.** 0.1 moles

C-4. + 3 **C-5.** 0.12 M. **C-6.**✍ 2.22 mL. **D-1.** 1.406%

D-2. V = 25 mL **D-3.** 3.48 % **D-4.** 48.1 mL **D-5.**✍ 126 ppm

E-1. 0.7 V **E-2.** 4.48 **E-3.** 19

E-4. Temporary hardness - due to bicarbonates of Ca & Mg
Permanent hardness - due to chlorides & sulphates of Ca & Mg.

E-5. There are some method by which we can soften the water sample.

(a) By boiling : $2HCO_3^- \longrightarrow H_2O + CO_2 + CO_3^{2-}$

or By Slaked lime : $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + 2H_2O$
$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$

(b) By Washing Soda : $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

(c) By ion exchange resins : $Na_2R + Ca^{2+} \longrightarrow CaR + 2Na^+$

(d) By adding chelating agents like $(PO_3^-)_3$ etc.

PART - II

A-1.	(A)	**A-2.**	(C)	**A-3.**✍	(D)	**A-4.**	(A)	**A-5.**✍	(C)
A-6.✍	(B)	**A-7.**	(A)	**B-1.**	(A)	**B-2.**	(A)	**B-3.**	(A)
B-4.✍	(D)	**C-1.**	(B)	**C-2.**✍	(D)	**C-3.**✍	(B)	**C-4.**	(A)
D-1.	(B)	**D-2.**✍	(B)	**D-3.**	(A)	**E-1.**	(D)	**E-2.**	(A)
E-3.✍	(D)	**E-4.**	(B)						

PART - III

1. (A – p,s) ; (B – q,r) ; (C – p,q,s) ; (D – r)

EXERCISE # 2

PART - I

1.✍	(A)	**2.**✍	(B)	**3.**	(A)	**4.**✍	(D)	**5.**✍	(D)
6.	(A)	**7.**✍	(D)	**8.**	(D)	**9.**	(A)	**10.**✍	(D)
11.	(A)	**12.**✍	(A)	**13.**	(A)	**14.**	(A)	**15.**✍	(A)
16.	(A)	**17.**	(B)	**18.**	(D)				

PART - II

1.	4	**2.**	1	**3.**_✍	90	**4.**	2	**5.**✍	2
6.	68	**7.**✍	12	**8.**	21	**9.**	10 mL	**10.**✍	16
11.	32	**12.**	80%						

PART - III

1.	(AC)	**2.**✍	(ABCD)	**3.**	(ACD)	**4.**✍	(ABD)
5.	(ABCD)	**6.**	(AB)				

PART - IV

1.	(C)	**2.**	(B)	**3.**	(C)	**4.**	(C)	**5.**	(D)
6.	(B)								

EXERCISE # 3

PART - I

1.	(A)	**2.**	(D)	**3.**	(C)	**4.**	(ABD)	**5.**	6
6.	126								

PART - II

1.	(3)	**2.**	(4)	**3.**	(4)	**4.**	(2)	**5.**	(3)
6.	(3)	**7.**	(2)	**8.**	(3)	**9.**	(1)	**10.**	(1)
11.	(2)	**12.**	(2)	**13.**	(1)				

✍ **Marked Questions may have for Revision Questions.**

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1. In the reaction : $Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow Na_2SO_4 + H_2SO_4 + 8HCl$, the equivalent weight of $Na_2S_2O_3$ will be : (M = molecular weight of $Na_2S_2O_3$)
(A) M/4 (B) M/8 (C) M/1 (D) M/2

2. In the reaction, $2CuSO_4 + 4KI \longrightarrow 2Cu_2I_2 + I_2 + 2K_2SO_4$
the equivalent weight of $CuSO_4$ will be :
(A) 79.75 (B) 159.5 (C) 329 (D) None of these

3. The number of moles of ferrous oxalate oxidised by one mole of $KMnO_4$ in acidic medium is :
(A) 5/2 (B) 2/5 (C) 3/5 (D) 5/3

4. How many moles of $KMnO_4$ are needed to oxidise a mixture of 1 mole of each $FeSO_4$ & FeC_2O_4 in acidic medium :
(A) 4/5 (B) 5/4 (C) 3/4 (D) 5/3

5. 22.7 mL of (N/10) Na_2CO_3 solution neutralises 10.2 mL of a dilute H_2SO_4 solution. The volume of water that must be added to 400 mL of this H_2SO_4 solution in order to make it exactly N/10.
(A) 490.2 mL (B) 890.2 mL (C) 90.2 mL (D) 290.2 mL

6. The mass of oxalic acid crystals ($H_2C_2O_4.2H_2O$) required to prepare 50 mL of a 0.2 N solution is :
(A) 4.5 g (B) 6.3 g (C) 0.63 g (D) 0.45 g

7. When HNO_3 is converted into NH_3, the equivalent weight of HNO_3 will be :
(A) M/2 (B) M/1 (C) M/6 (D) M/8
(M = molecular weight of HNO_3)

8. In the conversion $NH_2OH \longrightarrow N_2O$, the equivalent weight of NH_2OH will be :
(A) M/4 (B) M/2 (C) M/5 (D) M/1
(M = molecular weight of NH_2OH)

9. When hypo solution is added to $KMnO_4$ solution then
(A) $Na_2S_2O_3$ is converted to Na_2SO_4
(B) $Na_2S_2O_3$ is converted to $Na_2S_4O_6$
(C) $KMnO_4$ is converted to K_2MnO_4
(D) $KMnO_4$ is converted to $MnSO_4$

10. Which of the following equations is a balanced one :
(A) $5BiO_3^- + 22H^+ + Mn^{2+} \longrightarrow 5Bi^{3+} + 7H_2O + MnO_4^-$
(B) $5BiO_3^- + 14H^+ + 2Mn^{2+} \longrightarrow 5Bi^{3+} + 7H_2O + 2MnO_4^-$
(C) $2BiO_3^- + 4H^+ + Mn^{2+} \longrightarrow 2Bi^{3+} + 2H_2O + MnO_4^-$
(D) $6BiO_3^- + 12H^+ + 3Mn^{2+} \longrightarrow 6Bi^{3+} + 6H_2O + 3MnO_4^-$

11. 10 mL of sulphuric acid solution (specific gravity = 1.84) contains 98% by weight of pure acid. Calculate the volume of 2 N NaOH solution required to just neutralize the acid.
(A) 9.2 mL (B) 92 mL (C) 18.4 mL (D)184 mL

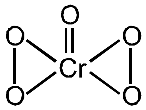
12. The equivalent mass of $MnSO_4$ is half its molecular mass when it is converted to :
(A) Mn_2O_3 (B) MnO_2 (C) MnO_4^- (D) MnO_4^{2-}

13. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is :
(A) 40 mL (B) 20 mL (C) 10 mL (D) 4 mL

14. In the reaction $H_2O_2^{18} + O_3 \rightarrow$ water + oxygen, radioactivity will be shown by which of the product :
(A) water (B) oxygen (C) both (A) & (B) (D) none of these

15. Which amongst the following has the highest normality ?
(A) 16.0 g of NaOH in 200 mL of water (B) 1 N oxalic acid
(C) 2 M sulphuric acid (D) 1.5 hydrochloric acid

16. CrO_5 has structure as shown



The oxidation number of chromium in the above compound is
(A) 4 (B) 5 (C) 6 (D) 0

17. The normality of orthophosphoric acid having purity of 70% by weight and specific gravity 1.54 is :
(A) 11 N (B) 22 N (C) 33 N (D) 44 N

18. The normality of mixture obtained by mixing 100 mL of 0.2 M H_2SO_4 and 200 mL of 0.2 M HCl is :
(A) 0.0267 (B) 0.2670 (C) 1.0267 (D) 1.1670

19. 100 milli moles of dichloroacetic acid ($CHCl_2COOH$) can neutralize how many moles of ammonia to form ammonium dichloroacetate :
(A) 0.0167 (B) 0.1 (C) 0.3 (D) 0.6

20. In alkaline medium, $KMnO_4$ reacts as follows (Atomic weights K = 39.09, Mn = 54.94, O = 16.00)
$$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + [O]$$
Hence, its equivalent weight is :
(A) 31.6 (B) 63.2 (C) 126.4 (D) 158

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

21. HNO_3 oxidises NH_4^+ ions to nitrogen and itself gets reduced to NO_2. The moles of HNO_3 required by 1 mole of $(NH_4)_2SO_4$ is :

22. Number of moles of CaO required to remove hardness from 1000 litre water having 324 ppm of calcium bicarbonate and 74.5 ppm of potassium chloride is :

23. A 5.0 cm^3 solution of H_2O_2 liberates 0.508 g of I_2 from an acidified KI solution. The strength of H_2O_2 solution in terms of volume strength at STP is :

24. 1 mole of how many of the following acids neutralize exactly one mol of NaOH, under required favourable conditions?

HCl, HNO_3, H_2SO_4, H_2SO_3, H_3PO_4, H_3PO_3, H_3PO_2, $H_4P_2O_5$, H_3BO_3

25. What volume of water should be added to 1600 ml of a 0.205 N solution so that the resulting solution will be 0.2 N ?

PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

  Full Marks : +3 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1. Volume V_1 mL of 0.1M $K_2Cr_2O_7$ is needed for complete oxidation of 0.678 g N_2H_4 in acidic medium. The volume of 0.3 M $KMnO_4$ needed for same oxidation in acidic medium will be:

(A) $\frac{2}{5}V_1$ (B) $\frac{5}{2}V_1$ (C) 113 V_1 (D) can not be determined

2. 10 mL of 1 N HCl is mixed with 20 mL of 1 M H_2SO_4 and 30 mL of 1 M NaOH. The resultant solution has :

(A) 20 meq of H^+ ions (B) 20 meq of OH^-
(C) 0 meq of H^+ or OH^- (D) 30 milli moles of H^+

3. 20 mL of H_2O_2 after acidification with dilute H_2SO_4 required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. The strength of H_2O_2 solution is : [Molar mass of H_2O_2 = 34]

(A) 2 g/L (B) 4 g/L (C) 8 g/L (D) 6 g/L

4. x gram of pure As_2S_3 is completely oxidised to respective highest oxidation states by 50 mL of 0.1 M hot acidified $KMnO_4$, then mass of As_2S_3 taken is : (Molar mass of As_2S_3 = 246)

(A) 22.4 g (B) 43.92 g (C) 64.23 g (D) None of these

SECTION-II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 If only (all) the correct option(s) is (are) chosen.
  Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.
  Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.
  Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.
  Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).
  Negative Marks : –1 In all other cases.
- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

---

5. Consider the redox reaction $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2\,I^-$:

(A) $S_2O_3^{2-}$ gets reduced to $S_4O_6^{2-}$ (B) $S_2O_3^{2-}$ gets oxidised to $S_4O_6^{2-}$

(C) I_2 gets reduced to I^- (D) I_2 gets oxidised to I^-

6. Which of the following relations is/are correct for solutions ?

(A) 3 N $Al_2(SO_4)_3$ = 0.5 M $Al_2(SO_4)_3$ (B) 3 M H_2SO_4 = 6 N H_2SO_4

(C) 1 M H_3PO_4 = 1/3 N H_3PO_4 (D) 1 M $Al_2(SO_4)_3$ = 6 N $Al_2(SO_4)_3$

7. Which of the following statements is/are correct :

(A) 0.2 moles of $KMnO_4$ will oxidise one mole of ferrous ions to ferric ions in acidic medium.

(B) 1.5 moles of $KMnO_4$ will oxidise 1 mole of ferrous oxalate to one mole of ferric ion and carbon dioxide in acidic medium in acidic medium.

(C) 0.6 moles of $KMnO_4$ will oxidise 1 mole of ferrous oxalate to one mole of ferric ion and carbon dioxide in acidic medium.

(D) 1 mole of $K_2Cr_2O_7$ will oxidise 2 moles of ferrous oxalate to ferric ions and carbon dioxide in acidic medium.

8. $H_2C_2O_4$ and $NaHC_2O_4$ behave as acids as well as reducing agents. Which are the correct statements?

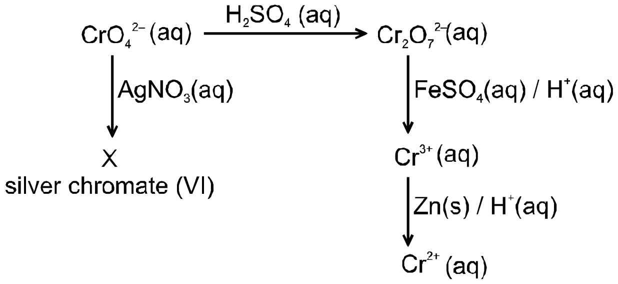
(A) equivalent weight of $H_2C_2O_4$ and $NaHC_2O_4$ are equal to their molecular weights when behaving as reducing agents.

(B) 100 ml of 1 (N) solution of each is neutralised by equal volume of 1 (M) $Ca(OH)_2$

(C) 100 ml of (N) solution $H_2C_2O_4$ is neutralised by equal volumes of 1(N) $Ca(OH)_2$

(D) 100 ml of (M) solution of each is oxidised by same volume of 1 (M) $KMnO_4$

9. Consider the reactions shown below :



Which of the following statements is True : [Atomic Mass of Zinc = 65.4]

(A) Silver chromate (VI) has the formula Ag_2CrO_4.

(B) The minimum mass of zinc required to reduce 0.1 mole of Cr^{3+} to Cr^{2+} is 6.54 g.

(C) The conversion of CrO_4^{2-} into $Cr_2O_7^{2-}$ is not a redox reaction.

(D) The equation $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$ correctly describes the reduction of $Cr_2O_7^{2-}$ by acidified $FeSO_4$.

10. Three different solutions of oxidising agents $KMnO_4$, $K_2Cr_2O_7$ and I_2 is titrated separately with 0.158 gm of $Na_2S_2O_3$. If molarity of each oxidising agent is 0.1 M and reactions are

$$MnO^-_4 + S_2O_3^{2-} \rightarrow MnO_2 + SO_4^{2-}$$

$$Cr_2O_7^{2-} + S_2O_3^{2-} \rightarrow Cr^{3+} + SO_4^{2-}$$

$$I_2 + Na_2S_2O_3 \xrightarrow{\text{Starch}} Na_2S_4O_6 + I^-$$

Then

(A) volume of $KMnO_4$ used is maximum

(B) volume of iodine used is minimum

(C) wt. of I_2 used in titration is maximum

(D) volume of $Cr_2O_7^{-2}$ used is maximum

11. Which of the following sample of reducing agents is/are chemically equivalent to 25ml of 0.2 N $KMnO_4$ in acidic medium -

(A) 50 mL of 0.1M $FeSO_4$ to be oxidized to Fe^{3+}

(B) 50 mL of 0.05 M $SnCl_2$ to be oxidized to Sn^{4+}

(C) 25 mL of 0.1M H_3AsO_3 to be oxidized to H_3AsO_4

(D) 25 mL of 0.1M H_2O_2 to be oxidized to H^+ and O_2

12. Choose correct statement-

(A) In the balanced redox reaction $xAs_2S_3 + yNO_3^- + 4H_2O \rightarrow aAsO_4^{3-} + bNO + cSO_4^{2-} + 8H^+$ molar ratio of x:y = 3:28

(B) When NH_4SCN oxidizes into SO_4^{2-}, CO_3^{2-} and NO_3^-, its equivalent weight will be M/24

(C) When Bi_2S_3 converted into Bi^{5+} and S, n-factor will be 7

(D) Equivalent weight of H_3PO_2 when it disproportionate into PH_3 and H_3PO_3 is 3M/4

SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +3 If ONLY the correct numerical value is entered as answer.

  Zero Marks : 0 In all other cases.

13. A 3 mole mixture of $FeSO_4$ and $Fe_2(SO_4)_3$ required 100 mL of 2M $KMnO_4$ solution in acidic medium. Find the mole of $FeSO_4$ in the mixture.

14. A 7.1 g sample of bleaching powder suspended in H_2O was treated with enough acetic acid and KI solution. Iodine thus liberated required 80 mL of 0.2 N hypo solution for titration. Calculate the % of available chlorine:

15. If the number of N-atoms in 1 molecule of Hyponitrous acid is x and the basicity of Boric acid is y, find the sum (x + y).

16. Find the valency factor (n) for NH_2OH in given reaction :

$$Fe^{3+} + NH_2OH \longrightarrow Fe^{2+} + N_2O + H^+ + H_2O$$

17. A solution of $Na_2S_2O_3$ is standardised iodometrically against 3.34 g of pure $KBrO_3$ (converted to Br^-), requiring 40 mL $Na_2S_2O_3$ solution. What is the molarity of $Na_2S_2O_3$ solution ? (molar mass of $KBrO_3$ = 167 g mol^{-1})

18. 2 moles of a mixture of O_2 and O_3 is reacted with excess of acidified solution of KI. The iodine liberated require 1L of 2M hypo solution for complete reaction. The weight % of O_3 in the initial sample is x. Find $\frac{x}{10}$.

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

1. If the equivalent weight of an element is 32, then the percentage of oxygen in its oxide is **[NSEC-2000]**

(A) 16 (B) 40 (C) 32 (D) 20

2. In alkaline medium, $KMnO_4$ reacts as follows (Atomic weights K = 39.09, Mn = 54.94, O = 16.00)

$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + [O]$ **[NSEC-2000]**

Hence, its equivalent weight is :

(A) 31.6 (B) 63.2 (C) 126.4 (D) 158

3. When 25 g of Na_2SO_4 is dissolved in 10^3 Kg of solution , its concentration will be : **[NSEC-2000]**

(A) 2.5 ppm (B) 25 ppm (C) 250 ppm (D) 100 ppm

4. Which amongst the following has the highest normality ? **[NSEC-2002]**

(A) 16.0 g of NaOH in 200 mL of water (B) 1 N oxalic acid

(C) 2 M sulphuric acid (D) 1.5 M hydrochloric acid

5. The volume of water which must be added to 0.4 dm^3 of 0.25 N oxallic acid in order to make it exactly decinormal is : **[NSEC-2002]**

(A) 0.2 dm^3 (B) 0.4 dm^3 (C) 0.6 dm^3 (D) 0.8 dm^3

6. The quantity of electricity requird to reduce 0.05 mol of MnO_4^- to Mn^{2+} in acidic medium would be **[NSEC-2003]**

(A) 0.01 F (B) 0.05 F (C) 0.15 F (D) 0.25 F

7. You are given a solution of an alkali. In order to estimate its concentration in terms of normality, you need to know **[NSEC-2003]**
(A) the volume of the solution, the volume of the alkali present in it and its formula weight
(B) the mass of the solution, the mass of the alkali present in its and its equivalent weight.
(C) the volume of the solution, the mass of the alkali present in it and its equivalent weight
(D) the mass of the solution, the volume of the alkali present in it and equivalent weight.

8. The normality of '20 volume' H_2O_2 solution is **[NSEC-2005]**
(A) 2.0 (B) 2.5 (C) 3.0 (D) 3.5

9. Hydrazine N_2H_4 acts as a reducing agent. To prepare 100 ml of 2 N hydrazine solution, the weight required will be : **[NSEC-2006]**
(A) 6.4 g (B) 1.6 g (C) 3.2 g (D) 0.8 g

10. For the reaction shown below, which statement is true ? **[NSEC-2007]**

$2Fe + 3CdCl_2 \rightleftharpoons 2FeCl_3 + 3Cd$
(A) Fe is the oxidizing agent (B) Cd undergoes oxidation
(C) Cd is the reducing agent (D) Fe undergoes oxidation

11. Oxalic acid ($H_2C_2O_4$) reacts with permanganate ion according to the balanced equation given below :
$5H_2C_2O_4(aq) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(\ell)$ **[NSEC-2008]**
How many mL of 0.0154 M $KMnO_4$ solution are required to react with 25.0 mL of 0.0208 M $H_2C_2O_4$solution.
(A) 13.5 mL (B) 18.5 mL (C) 33.8 mL (D) 84.4 mL

12. What volume of water should be added to 1600 ml of a 0.205 N solution so that the reasulting solution will be 0.2 N? **[NSEC-2008]**
(A) 40 mL (B) 50 mL (C) 100 mL (D) 20 mL

13. Oxalic acid, $H_2C_2O_4$, reacts with paramaganate ion according to the balanced equation

$5H_2C_2O_4(aq) + 2MnO_4^- + 6H^+(aq) \rightleftharpoons 2Mn^{2+}(aq) + 10CO_2(g) + 8\,H_2O(\ell)$
The volume in mL of 0.0162 M $KMnO_4$ solution required to react with 25.0 mL of 0.022 M $H_2C_2O_4$ solution is : **[NSEC-2011]**
(A*) 13.6 (B) 18.5 (C) 33.8 (D) 84.4

14. A 500 g toothpaste sample has 0.4 g fluoride concentration. The fluoride concentration in terms of ppm will be **[NSEC-2012]**
(A) 200 (B) 400 (C) 500 (D) 800

15. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate $[Fe(C_2O_4)]$ in acidic solution is : **[NSEC-2012]**
(A) 1 (B) 2/5 (C) 3/5 (D) 4/5

16. I. $5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$
II. $H_2O_2 + Ag_2O \rightarrow 2Ag + H_2O + + O_2$
The role of hydrogen peroxide in the above reaction is : **[NSEC-2014]**
(A) oxidising in I and reducing in II (B) reducing in I and oxidising in II
(C) reducing in I as well as in II (D) oxidising in I as well as in II

17. A bottle of H_3PO_4 solution contains 70% w/w acid. If the density of the solution is 1.54 g cm^{-3}, the volume of the H_3PO_4 solution required to prepare 1L of 1 N solution is **[NSEC-2015]**
(A) 90 mL (B) 45 mL (C) 30 mL (D) 23 mL

18. The unbalanced equation for the reaction of P_4S_3 with nitrate in aqueous acidic medium is given below.
$P_4S_3 + NO_3^- \rightarrow H_3PO_4 + SO_4^{2-} + NO$
The number of mol of water required per mol of P_4S_3 **[NSEC-2015]**
(A) 18 (B) 8/3 (C) 8 (D) 28

19. In the redox reaction $2MnO_4^- + 5C_2O_4^{2-} + 16\ H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8\ H_2O$, 20 mL of 0.1 M $KMnO_4$ react quantitatively with **[NSEC-2015]**
(A) 20 mL of 0.1 M oxalate (B) 40 mL of 0.1 M oxalate
(C) 50 mL of 0.25 M oxalate (D) 50 mL of 0.1 M oxalate

20. 1.250 g of metal carbonate (MCO_3) was treated with 500 mL of 0.1 M HCl solution. The unreacted HCl required 50.0 mL of 0.500 M NaOH solution for neutralization. Identify the metal M **[NSEC-2016]**
(A) Mg (B) Ca (C) Sr (D) Ba

21. Battery acid (H_2SO_4) has density 1.285 g cm^{-3} . 10.0 cm^3 of this acid is diluted to 1L. 25.0 cm^3 of this diluted solution requires 25.0 cm^3 of 0.1 N sodium hydroxide solution for neutralization. The percentage of sulphuric acid by mass in the battery acid is : **[NSEC-2016]**
(A) 98 (B) 38 (C) 19 (D) 49

22. A sample of water from a river was analyzed for the presence of metal ions and the observation were recorded as given below

Reagent added	Observation
dil. HCl	No change
aq. Na_2CO_3	White precipitate
aq. Na_2SO_4	No Change

The water sample is likely to contain **[NSEC-2018]**
(A) Ba^{2+} (B) Cu^{2+} (C) Li^+ (D) Mg^{2+}

23. An ion exchange resin, RH_2 can replace Ca^{2+} in hard water as $RH_2 + Ca^{2+} \longrightarrow RCa^{2+} + 2H^+$. When a 1.0 L hard water sample was passed through the resin, all H^+ ions were replaced by Ca^{2+} ions and the pH of eluted water was found to be 2.0. The hardness of water (as ppm of Ca^{2+}) in the sample of water treated is : **[NSEC-2018]**
(A) 50 (B) 100 (C) 125 (D) 200

PART - 4 : ADDITIONAL PROBLEMS

ONLY ONE OPTION CORRECT TYPE

1. During the titration of a mixture of Na_2CO_3 and $NaHCO_3$ against HCl :
(A) Phenolphthalein is used to detect the first end point
(B) Phenolphthalein is used to detect the second end point
(C) Methyl orange is used to detect the first end point
(D) Phenolphthalein is used to detect the first and second end point

2. In the reaction $CrO_5 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + H_2O + O_2$, one mole of CrO_5 will liberate how many moles of O_2 :
(A) 5/2 (B) 5/4 (C) 9/2 (D) 7/4

3. 0.14 g of a substance when burnt in oxygen yields 0.28 g of oxide. The substance is –
(A) nitrogen (B) carbon (C) sulphur (D) phosphorous

4. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate $[Fe(C_2O_4)]$ in acidic solution is :
(A) 1 (B) 2/5 (C) 3/5 (D) 4/5

5. $Hg_5(IO_6)_2$ oxidizes KI to I_2 in acid medium and the other product containing iodine is K_2HgI_4. If the I_2 liberated in the reaction requires 0.004 mole of $Na_2S_2O_3$, the number of moles of $Hg_5(IO_6)_2$ that have reacted is :
(A) 10^{-3} (B) 10^{-4} (C) 2.5×10^{-4} (D) 2.5×10^{-2}

6. 40 mL of 0.05 M solution of sodium sesquicarbonate ($Na_2CO_3.NaHCO_3.2H_2O$) is titrated against 0.05 M HCl. When phenoplhthalein is used as indicator, x mL HCl is used. In a separate titration of same using methyl orange as indicator, y ml of HCl is used. The value of (y – x) is :

(A) 80 mL (B) 30 mL (C) 120 mL (D) 180 mL

7. In the following reaction $2MnO_4^- + 5H_2O_2^{18} + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

The radioactive oxygen will appear in :

(A) H_2O (B) O_2

(C) both (D) above reaction does not take place

8. The reagent commonly used to determine hardness of water titrimetrically is :

(A) oxalic acid (B) disodium salt of EDTA

(C) sodium citrate (D) sodium thiosulphate

9. 0.7 g of $(NH_4)_2SO_4$ sample was boiled with 100 mL of 0.2 N NaOH solution till all the NH_3 gas is evolved. The resulting solution was diluted to 250 mL. 25 mL of this solution was neutralized using 10 mL of a 0.1 N H_2SO_4 solution. The percentage purity of the $(NH_4)_2SO_4$ sample is :

(A) 94.3 (B) 50.8 (C) 47.4 (D) 79.8

10. A mixture of 0.02 mole of $KBrO_3$ and 0.01 mole of KBr was treated with excess of KI and acidified. The volume of 0.1 M $Na_2S_2O_3$ solution required to consume the liberated iodine will be :

(A) 1000 mL (B) 1200 mL (C) 1500 mL (D) 800 mL

11. 10 mL of a H_2SO_4 solution is diluted to 100 mL. 25 mL of this diluted solution is mixed with 50 mL of 0.5 N NaOH solution. The resulting solution requires 0.265 g Na_2CO_3 for complete neutralization. The normality of original H_2SO_4 solution is :

(A) 12 N (B) 11 N (C) 3 N (D) 0.275 N

12. Dichloroacetic acid ($CHCl_2COOH$) is oxidised to CO_2, H_2O and Cl_2 by 600 meq of an oxidising agent. Same amount of acid can neutralize how many moles of ammonia to form ammonium dichloroacetate :

(A) 0.0167 (B) 0.1 (C) 0.3 (D) 0.6

13. 1.2 g of carbon is burnt completely in oxygen (limited supply) to produce CO and CO_2. This mixture of gases is treated with solid I_2O_5 (to know the amount of CO produced). The liberated iodine required 120 mL of 0.1 M hypo solution for complete titration. The % of carbon converted into CO is :

(A) 60% (B) 100% (C) 50% (D) 30%

14. A mixed solution of potassium hydroxide and sodium carbonate required 15 mL of an N/20 HCl solution when titrated with phenolphthalein as an indicator. But the same amount of the solution, when titrated with methyl orange as an indicator, required 25 mL of the same acid. The amount of KOH present in the solution is :

(A) 0.014 g (B) 0.14 g (C) 0.028 g (D) 1.4 g

15. Phenolphthalein is not a good indicator for titrating :

(A) NaOH against oxalic acid (B) NaOH against HCl

(C) Ferrous sulphate against $KMnO_4$ (D) NaOH against H_2SO_4

16. A 1 g sample of H_2O_2 solution containing x % H_2O_2 by mass requires x cm^3 of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution.

(A) 0.588 N (B) 0.294 N (C) 0.882 N (D) 0.735 N

17. A solution of H_2O_2 labelled as '20 V' was left open. Due to this some, H_2O_2 decomposed and volume strength of the solution decreased. To determine the new volume strength of the H_2O_2 solution, 10 mL of the solution was taken and it was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.0245 M $KMnO_4$ solution under acidic condition. Calculate the volume strength of the H_2O_2 solution.

(A) 15.00 V (B) 17.15 V (C) 20.00 V (D) 12.30 V

SUBJECTIVE QUESTIONS

18. A solution contains a mixture of Na_2CO_3 and NaOH. Using phenolphthalein as indicator, 25 mL of mixture required 19.5 mL of 0.995 N HCl for the end point. With methyl orange (MeOH), 25 mL of the solution required 25 mL of the same HCl for the end point. Calculate gram per litre of each substance in the mixture.

19. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$(20mL) 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.

SINGLE AND DOUBLE VALUE INTEGER TYPE

20. If a mixture of Na_2CO_3 and NaOH in equimolar quantities when reacts with 0.1 M HCl in presence of phenolphthalein indicator consumes 30 ml of the acid. What will be the volume (in mL) of 0.15 M H_2SO_4 used in the separate titration of same mixture in presence of methyl orange indicator.

COMPREHENSION

Paragraph For Questions 21 to 23

The overall equation for the reaction between sodium carbonate solution and dilute hydrochloric acid is

$$Na_2CO_3\,(aq.) + 2HCl\,(aq.) \longrightarrow NaCl\,(aq) + CO_2(g) + H_2O\,(\ell)$$

If you had the two solutions of the same concentration, you would have to use double volume of HCl to reach the equivalence point.

Indicators change their colours at the end point of the reaction and hence we are able to know the end points (equivalence points of reactions).

21. How many ml of 1N HCl are required for X milimoles of Na_2CO_3 with methyl orange indicator

(A) X ml (B) 2 X ml (C) 3 X ml (D) 4X ml

22. How many ml of 1N HCl are required for X milimoles of NaOH + Y milimoles of Na_2CO_3 + Z milimoles of $NaHCO_3$ with methyl orange indicator

(A) (2X + Y + Z) ml (B) (X + 2 Y + 2 Z) ml

(C) (X + 2 Y + 3 Z) ml (D) (X + 2 Y + Z) ml

23. 25 ml of Na_2CO_3 solution requires 100ml of 0.1M HCl to reach end point with phenolphthalein indicator. Molarity of HCO_3^- ions in the resulting solution is

(A) 0.008 M (B) 0.04M (C) 0.16M (D) 0.08M

MATCH THE COLUMN

24. Match each List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists.

List-I	**List-II**
(A) Sn^{+2} + MnO_4^- (acidic) 3.5 mole 1.2 mole	(p) Amount of oxidant available decides the number of electrons transfer
(B) $H_2C_2O_4$ + MnO_4^- (acidic) 8.4 mole 3.6 mole	(q) Amount of reductant available decides the number of electrons transfer
(C) $S_2O_3^{-2}$ + I_2 7.2 mole 3.6 mole	(r) Number of electrons involved per mole of oxidant > Number of electrons involved per mole of reductant
(D) Fe^{+2} + $Cr_2O_7^{-2}$ (acidic) 9.2 mole 1.6 mole	(s) Number of electrons involved per mole of oxidant < Number of electrons involved per mole of reductant.

RRP ANSWER KEY

PART- 1

SECTION–I

1.	(B)	**2.**	(B)	**3.**	(D)	**4.**	(A)	**5.**	(A)
6.	(C)	**7.**	(D)	**8.**	(B)	**9.**	(A)	**10.**	(B)
11.	(D)	**12.**	(B)	**13.**	(A)	**14.**	(B)	**15.**	(C)
16.	(C)	**17.**	(C)	**18.**	(B)	**19.**	(B)	**20.**	(D)

SECTION–II

21.	6	**22.**	2	**23.**	4.48 V	**24.**	4	**25.**	40 mL

PART 2

SECTION–I

1.	(A)	**2.**	(A)	**3.**	(A)	**4.**	(D)

SECTION–II

5.	(BC)	**6.**	(ABD)	**7.**	(ACD)	**8.**	(CD)	**9.**	(ACD)
10.	(AB)	**11.**	(ABCD)	**12.**	(ABD)				

SECTION–III

13.	1	**14.**	8	**15.**	3	**16.**	2	**17.**	3
18.	6								

PART - 3

1.	(D)	**2.**	(D)	**3.**	(B)	**4.**	(C)	**5.**	(C)
6.	(D)	**7.**	(C)	**8.**	(D)	**9.**	(B)	**10.**	(D)
11.	(A)	**12.**	(A)	**13.**	(A)	**14.**	(D)	**15.**	(C)
16.	(C)	**17.**	(C)	**18.**	(B)	**19.**	(D)	**20.**	(B)
21.	(B)	**22.**	(D)	**23.**	(D)				

PART - 4

1.	(A)	**2.**	(D)	**3.**	(C)	**4.**	(C)	**5.**	(C)
6.	(A)	**7.**	(B)	**8.**	(B)	**9.**	(A)	**10.**	(B)
11.	(A)	**12.**	(B)	**13.**	(D)	**14.**	(A)	**15.**	(C)
16.	(A)	**17.**	(B)	**18.**	Na_2CO_3 = 23.2 g/L, NaOH = 22.28 g/L.						
19.	0.1 M	**20.**	15	**21.**	(B)	**22.**	(D)	**23.**	(D)
24.	(A) – p, r ; (B) – q, r ; (C) – p, q, r ; (D) – q, r								

RRP SOLUTIONS

PART- 1

2. $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + I_2 + 2K_2SO_4$.

$Cu^{2+} + 1e^- \longrightarrow Cu^+$.

E_{Cu} = ?. V.F. = 1.

$$E_{CuSO_4} = \frac{159.5}{1} = 159.5$$

3. Equivalents of FeC_2O_4 = equivalents of $KMnO_4$

$x \text{ (mole)} \times 3 = 1 \times 5$

$$x = \frac{5}{3} \text{ mole}$$

4. Equivalent of $KMnO_4$ = equivalent of $FeSO_4$ + equivalent of FeC_2O_4

$x \times 5 = 1 \times 1 + 1 \times 3$

$$x = \frac{4}{5} \text{ mole}$$

5. meq of Na_2CO_3 = meq of H_2SO_4

$$\frac{1}{10} \times 22.7 = N \times 10.2$$

Normality = 0.2225 N

$$0.2225 \times 400 = \frac{1}{10} \times V_f$$

or $V_f = 890.2$ mL

∴ Volume of H_2O mixed = 890.2 – 400 = 490.2 mL

6. $H_2C_2O_4 . 2H_2O = 2 + 24 + 64 + 36 = 126$ and Equivalent wt. = $\left[\frac{126}{2}\right]$

$$0.2 = \frac{W \times 1000}{\left(\frac{126}{2}\right) \times 50} \qquad \therefore W = 0.63 \text{ g}$$

7. $H\overset{+5}{N}O_3 \longrightarrow \overset{-3}{N}H_3$ ∴ V.f. of HNO_3 = 8

Eq. wt. = M/8.

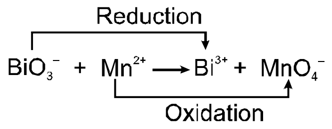
8. $\underset{-1}{NH_2OH} \longrightarrow \underset{+1}{N_2O}$

∴ V.f. of NH_2OH = 2

∴ Eq wt = M/2

9. $8KMnO_4 + 3Na_2S_2O_3 + H_2O \rightarrow 2KOH + 8MnO_2 + 3Na_2SO_4 + 3K_2SO_4$

10.



$BiO_3^- + Mn^{2+} \longrightarrow Bi^{3+} + MnO_4^-$

(i) $2e + 6H^+ + BiO_3^- \longrightarrow Bi^{3+} + 3H_2O$

(ii) $4H_2O + Mn^{2+} \longrightarrow MnO_4^- + 8H^+ + 5e$

(i) × 5 + (ii) × 2, we get $14H^+ + 5BiO_3^- + 5Mn^{2+} \longrightarrow 5Bi^{3+} + 2MnO_4^- + 7H_2O$
Hence, (2) is the correct balanced reaction.

11. m.eq. of H_2SO_4 = m.eq. of NaOH

$$\frac{98\times1.84\times10}{98} \times 2 \times 10 = 2 \times V_1$$

$V_1 = 184$ mL

12. $$\text{Eq. mass} = \frac{\text{Molecular weight}}{\text{Change in oxidation No. of Mn}} = \frac{\text{Mol. wt.}}{4-2} = \frac{\text{Mol. wt.}}{2}$$

(O.N. of Mn in $MnSO_4$ = +2; O.N. of Mn in MnO_2 = +4).

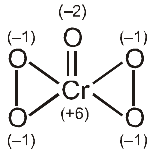
13. (1) Equilivalents of $H_2C_2O_4.2H_2O$ in 10 mL = Equivalents of NaOH

$$\left(\frac{6.3}{126/2}\times\frac{1000}{250}\right) \times \frac{10}{1000} = 0.1 \times V \text{ (in litre)}$$

$\therefore$ V = 0.04 L = 40 mL.

14. O_3 will oxidise H_2O_2 into oxygen, hence radioacitve oxygen of H_2O_2 will go only in oxygen, not in water.
Half reactions : $O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$; $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

16.



17. 70% by weight means
70 g of orthophosphoric acid is present in 100 g acid

$$N = \frac{w}{\text{Eq. wt.}}\times\frac{1000}{V_{(cc)}}$$

w = 70 g

$$\text{Eq. wt.} = \frac{\text{mol. mass}}{\text{no. replacable H} - \text{atoms}} = \frac{98}{3}$$

$$V = \frac{\text{mass}}{\text{density}} = \frac{100}{1.54}$$

$$N = \frac{70\times3\times1000\times1.54}{98\times100} = 33\ N$$

18. Normality of a mixture (N) = $\dfrac{N_1V_1+N_2V_2}{V_1+V_2}$

Normality(N_1) of H_2SO_4 = molarity × basicity = 0.2 × 2 = 0.4 N
$N_2 = 0.2 \times 1 = 0.2$ N
$V_1 = 100$ mL, $V_2 = 200$ mL

$$N = \frac{0.4\times100+0.2\times200}{100+200} = \frac{40+40}{300} = \frac{80}{300} = 0.2670\text{ N}$$

Normality of mixture of acid and base(N')

$$(N') = \frac{N_1V_1 \sim N_2V_2}{V_1+V_2}$$

19. $eq_{acid} = eq_{base}$ (VF = 1 for both)

$CHCl_2COOH + NH_3 \longrightarrow CHCl_2COONH_4$

From reaction, m.moles of NH_3 = m.moles of dichloroacetic acid = 100

$\therefore$ Moles of $NH_3 = \frac{100}{1000} = 0.1$

21. $HNO_3 + NH_4^+ \longrightarrow N_2 + NO_2$

V.F. of HNO_3 = (5 – 4) = 1

V.F. of NH_4^+ = [0 – (–3)] = 3

so molar ratio of HNO_3 and NH_4^+ is 3 : 1.

1 mole $(NH_4)_2SO_4$ is found to contain 2 mole of NH_4^+

So, required moles of HNO_3 is 3 × 2 = 6 mole.

22. $Ca(HCO_3)_2 + CaO \longrightarrow 2CaCO_3\downarrow + H_2O$

$\frac{324}{162} = n_{CaO} = 2$

23. meq H_2O_2 = meq I_2

$N \times 5 = \frac{0.508\times2}{254}\times1000$ or Normality = 0.8 N

Volume strength = 5.6 × N = 5.6 × .8 = 4.48 V.

24. (HCl, HNO_3, H_3PO_2, H_3BO_3) H_2SO_4, H_2SO_3, H_3PO_3, $H_4P_2O_5$ are diprotic. HCl, HNO_3, H_3PO_2, H_3BO_3 are monoprotic.

PART 2

1. Equivalent of $K_2Cr_2O_7$ = equivalent of N_2H_4

also equivalent of $KMnO_4$ = equivalent of N_2H_4

So, equivalent of $K_2Cr_2O_7$ = equivalent of $KMnO_4$

$0.1 \times 6 \times V_1 = 0.3 \times 5 \times V_2$

so V_2 **= 2/5 V_1**

2. (A) Explanation : No. of meq of H^+ = 10 × 1 + 20 × 2 = 50 [$\because H_2SO_4$, N = 2 M]

No. of meq of OH^- = 30 × 1 = 30

No. of meq of H^+ left unreacted = 50 – 30 = 20 meq

Hence , (A) is correct, (B), (C) and (D) are ruled out.

3. meq. of $KMnO_4$ = meq of H_2O_2

$30 \times \frac{1}{12} = 20 \times N' \Rightarrow N' = \frac{30}{12\times20} = \frac{1}{8}N$

$\therefore$ strength = N′ × equivalent mass = $\frac{1}{8} \times 17 = 2.12$ g/L.

4. $5As_2S_3 + 28KMnO_4 + H^+ \longrightarrow 10H_3AsO_4 + 28Mn^{2+} + SO_4^{2-}$

m.moles of $KMnO_4 = 50 \times 0.1 = 5$

28 m.moles of $KMnO_4 \longrightarrow$ 5 m.moles of As_2S_3

$\therefore$ 1 m.mole of $KMnO_4 \longrightarrow$ 5/28 m.moles of As_2S_3

$\therefore$ 5 m.mole of $KMnO_4 \longrightarrow \frac{5 \times 5}{28}$ m.moles of As_2S_3

Mass of $As_2S_3 = x = 246 \times \frac{5 \times 5}{28} \times 10^{-3} = 0.22$ g

5. S undergoes increase in oxidation number from +2 to +2.5, while I undergoes decrease in oxidation number from 0 to –1.

6. Normality = Molarity × v.f. $\therefore$ 1M H_3PO_4 = 3N H_3PO_4

7. $MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

$\Rightarrow$ 1 mole of MnO_4^- accepts 5 mole of e^-

1/5 mole of MnO_4^- accepts 1 mole of e^-

$\Rightarrow$ 0.2 mole of MnO_4^- accepts 1 mole of e^-

$\Rightarrow$ 0.6 mole of MnO_4^- accepts 3 mole of e^-

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

$\Rightarrow$ 1 mole of Fe^{2+} will liberate 1 mole of e^-

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

$\Rightarrow$ 1 mole of $Cr_2O_7^{2-}$ will accept 6 moles of e^-

1 mole of $FeC_2O_4 \longrightarrow Fe^{3+} + CO_2 + 3e^-$

$\Rightarrow$ 1 moles of ferrous oxalate gives 3 moles of e^-

$\Rightarrow$ 0.2 moles of $KMnO_4$ = 1/5 moles of $KMnO_4$ oxidises 1 mole of Fe^{2+} ion. (Tallies with statement A)

0.6 moles of $KMnO_4$ = 3/5 moles of $KMnO_4$ will oxidise 1 mole of ferrous oxalate (Tallies with statement C)

1 mole of $K_2Cr_2O_7$ will oxidise 2 moles of ferrous oxalate. (Tallies with statement D)

Hence ,(A) , (C) , (D) are correct while (B) is incorrect.

9. (A) Formula of silver chromate (VI) will be Ag_2CrO_4

(B) Minimum mass of zinc required for reduction of 0.1 mole of Cr^{3+} to Cr^{2+} = $\frac{0.1}{2}$ moles of Zn

(v.f. of Zn = 2 & v.f. of Cr^{3+} = 1) $= \frac{6.54}{2}$ g = 3.27 g

(C) $CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-}$

in both ions, chromium is in +6 oxidation state.

(D) Given reaction is correct.

13. Lets mole of $FeSO_4 = x$

Now, $KMnO_4$ oxidises only $FeSO_4$

equivalent of $FeSO_4$ = equivalent of $KMnO_4$

$x \times 1 = \frac{100}{1000} \times 2 \times 5 \Rightarrow x = 1$

14. moles of iodine = moles of chlorine = $\frac{80 \times 0.2}{2} \times 10^{-3} = 8 \times 10^{-3}$

so required % = $\frac{8 \times 71 \times 10^{-3}}{7.1} \times 100\% = 8\ \%$

15. Hyponitrous acid = $H_2N_2O_2$ $\therefore$ x = 2

Basicity of Boric acid = y = 1

$\therefore$ x + y = 2 + 1 = 3.

16. $NH_2OH \longrightarrow N_2O$

(–1) (+1) oxidation number of nitrogen.

$\therefore$ Vf = change in oxidation number of nitrogen = 2.

17. Necessary equations :

$KBrO_3 + KI \longrightarrow I_2 + Br^-$

$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + NaI$

equivalent of I_2 = equivalent of $KBrO_3$ = 12×10^{-2}

equivalent of $Na_2S_2O_3$ = equivalent of I_2

$$M \times 1 \times \frac{40}{1000} = 12 \times 10^{-2}$$

so molarity = 3 M.

18. $\underset{}{KI} + \underset{\substack{v.f = 2\\ moles\\ = x.}}{O_3} \longrightarrow \underset{v.f = 2}{I_2} + H_2O + O_2.$

$\underset{v.f = 2}{I_2} + \underset{\substack{M = 2\\ V = 1L\\ v.f = 1}}{Na_2S_2O_3} \longrightarrow I^- + Na_2S_4O_6$

eq of O_3 = eq of I_2 = eq of hypo

$\Rightarrow$ $2 \times x = 2$

x = 1 mole

$\Rightarrow$ weight % of $O_3 = \dfrac{1 \times 48}{1 \times 48 + 1 \times 32} \times 100$

$= \dfrac{3}{5} \times 100 = 60\%$ Ans. $= \dfrac{60}{10} = 6.$

PART - 4

2. $4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 6H_2O + 7O_2$ (Balanced reaction)

$\therefore$ 1 mole CrO_5 produces 7/4 moles of O_2.

3. wt of metal = 0.28 – 0.14 gm. = 0.14 gm

wt.of substance = wt. of oxygen

equivalent of substance = equivalent of oxygen

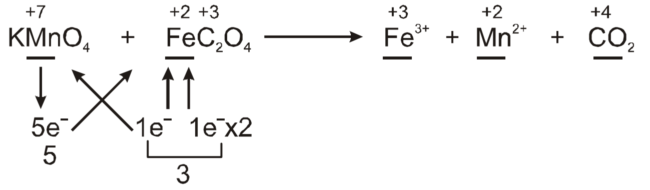
i.e. $\dfrac{w_{(sub.)}}{E_A} = \dfrac{w_{(oxygen)}}{E_O}$

$E_A = E_O = \dfrac{32}{4} = 8$

For SO_2

$E_{Sulphur} = \dfrac{32}{4} = 8$

4.



$\overset{+7}{KMnO_4} + \overset{+2\ +3}{FeC_2O_4} \longrightarrow \overset{+3}{Fe^{3+}} + \overset{+2}{Mn^{2+}} + \overset{+4}{CO_2}$

$3KMnO_4 + 5FeC_2O_4 \longrightarrow$ Products
by mole-mole analysis.

$$\frac{{}^{n}KMnO_4}{3} = \frac{{}^{n}FeC_2O_4}{5}$$

${}^{n}KMnO_4 = \frac{3}{5} \times 1$ moles.

5. Eq. of $Hg_5(IO_6)_2$ = Eq. of I_2 = Eq. of $Na_2S_2O_3$

∴ (moles of $Hg_5(IO_6)_2$) × 16 = 0.004 × 1

∴ moles of $Hg_5(IO_6)_2 = 2.5 \times 10^{-4}$.

6. In presence of phenoplhthalein,

$\frac{1}{2}$ meq. of Na_2CO_3 = meq. of HCl

$2 \times 40 \times 0.05 \times \frac{1}{2} = x \times 0.05$

∴ x = 40 mL
with M.O.
Meq. of Na_2CO_3 + Meq. of $NaHCO_3$ = Meq. of HCl
$2 \times 40 \times 0.05 + 40 \times 0.05 = y \times 0.05$
y = 120 mL
∴ (y – x) = 80 mL

7. During oxidation of H_2O_2, O–O bond is not broken.

8. The hardness of water is estimated by simple titration of ethylene diamine tetra acetate (EDTA) solution.EDTA forms stable complexes with the metal ions present in the hard water since stability constants of calcium and magnesium complexes of EDTA are different, even the selective estimation of these ions is possible.

9. m.eq of $(NH_4)_2SO_4$ + m.eq of H_2SO_4 = m.eq of NaOH

(m.moles × 2) + $(0.1 \times 10 \times \frac{250}{25}) = 0.2 \times 100$

∴ m.mole of $(NH_4)_2SO_4$ = 5

wt. of $(NH_4)_2SO_4 = \frac{5}{1000} \times 132 = 0.66$ g

∴ % of $(NH_4)_2SO_4 = \frac{0.66}{0.7} \times 100 = 94.28\ \% \approx 94.3\ \%$

10. $BrO_3^- + 6I^- \longrightarrow 3I_2 + Br^-$
moles of I_2 = 3 × moles of $KBrO_3$
∴ moles of I_2 = 0.02 × 3 = 0.06
Eq of I_2 = Eq of Hypo
0.06 × 2 = 0.1 ×V
V = 1.2 L = 1200 mL.

11. meq of H_2SO_4 = meq of NaOH + meq of Na_2CO_3

$$N \times 25 = 0.5 \times 50 + \frac{0.265}{106/2} \times 10^3$$

or $N = 1.2$

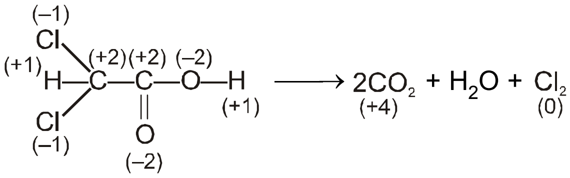
In original H_2SO_4 solution

$N_1V_1 = N_2V_2$

or $N_1 \times 10 = 1.2 \times 100$

or $N_1 = 12\ N$

12.



∴ v.f. of dichloroacetic acid = 2 (4 – 2) + 2 (0 – (– 1)) = 6

m.eq. of dichloroacetic acid = m.eq. of oxidising agent = 600

∴ m.moles of dichloroacetic acid = $\frac{600}{6}$ = 100

$$CHCl_2COOH + NH_3 \longrightarrow CHCl_2COONH_4$$

From reaction, m.moles of NH_3 = m.moles of dichloroacetic acid = 100

∴ Moles of $NH_3 = \frac{100}{1000} = 0.1$

13.

	$C + O_2 \longrightarrow$	CO	+	CO_2	......(i)
t = 0	0.1	–		–	
t = t	0	x		(0.1 – x)	

	$5CO + I_2O_5 \longrightarrow$	$5CO_2$	+	I_2	......(ii)
t = 0	x				
t = t	0			x/5	

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

∴ moles of I_2 liberated = $\frac{1}{2}$ × moles of hypo consumed = $\frac{1}{2} \times 120 \times 10^{-3} \times 0.1 = 60 \times 10^{-4}$

So, $x = 5 \times 60 \times 10^{-4} = 0.03$ moles (from reaction (ii) : 5 × mole of I_2 = mole of CO)

So, % of C forming CO = $\frac{0.03 \times 12}{1.2} \times 100 = 30\%$

14. KOH + Na_2CO_3

a m.moles b m.moles

m.eq. of KOH + m.eq. of Na_2CO_3 (v.f. = 1) = m.eq. of HCl (in presence of phenolphthalein)

$$a \times 1 + b \times 1 = 15 \times \frac{1}{20}$$

∴ a + b = 0.75 ...(i) (in presence of phenolphthalein)

m.eq. of KOH + m.eq. of Na_2CO_3 (v.f. = 2) = m.eq. of HCl (in presence of methyl orange)

$$1 \times a + 2 \times b = 25 \times \frac{1}{20}$$

∴ a + 2 × b = 1.25 ...(ii) (in presence of methyl orange)

by solving (i) & (ii), a = 0.25 m.moles.

∴ mass of KOH = $\frac{0.25}{1000} \times 56 = 0.014$ g

16. Redox changes are :

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

$O_2^{2-} \longrightarrow O_2 + 2e^-$

∴ Eq. wt. of $H_2O_2 = \frac{34}{2}$

Now m.eq. of $KMnO_4$ = m.eq. of H_2O_2

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

N = **0.588 N**

17. Assuming new normality of original H_2O_2 solution = X

After dilution to 100 mL of 10 mL of this solution, New normality will be (say X_1)

∴ $X \times 10 = X_1 \times 100$

$X_1 = \frac{X}{10}$ .... (i)

10 mL of this dilute solution is titrated with 25 mL, 0.0245 M $KMnO_4$ solution.

So, $N_1V_1 = N_2V_2$

$\frac{X}{10} \times 10 = 0.0245 \times 5 \times 25$

X = 3.0625 N

So, volume strength of original H_2O_2 solution = X × 5.6 = 3.0625 × 5.6 = 17.15 V

18. At phenolphthalein end point

eq. of Na_2CO_3 + eq. of NaOH = eq. of HCl used

Let x mole of Na_2CO_3 and y mole of NaOH present in 25 mL solution

$x \times 1 + y \times 1 = 19.5 \times 0.995 \times 10^{-3}$

$x + y = 19.4 \times 10^{-3}$ .... (i) (The v.f. of Na_2CO_3 is 1 when phenolphthalein is used)

At Methyl orange (MeOH) end point,

eq. of Na_2CO_3 + eq. of NaOH = eq. of HCl used

$x \times 2 + y \times 1 = 25 \times 0.995 \times 10^{-3}$

$2x + y = 24.875 \times 10^{-3}$ .... (ii) (The v.f. of Na_2CO_3 is 2 when methyl orange (MeOH) is used)

On solving eq. (1) and (2),

$x = 5.475 \times 10^{-3}$ and $y = 13.925 \times 10^{-3}$

or wt. of Na_2CO_3 in 25 mL = $5.475 \times 10^{-3} \times 106$

wt. of Na_2CO_3 in 1 litre = $\frac{5.475 \times 10^{-3} \times 106}{25} \times 1000$ = **23.2 g Ans.**

wt. of NaOH in 25 mL solution = $13.925 \times 10^{-3} \times 40$

wt. of NaOH in 1 litre = $\frac{13.925 \times 10^{-3} \times 40}{25} \times 1000$ = **22.28 g Ans.**

19. $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

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

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

∴ meq. of MnO_2 = meq of $Na_2C_2O_4$ = 10 × 0.2 × 2 = 4

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

Now, $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 \downarrow + K_2SO_4 + 2H_2O$

Since MnO_2 is derived from $KMnO_4$ and $MnSO_4$ both, thus it is better to proceed by mole concept millimoles of $KMnO_4$ = millimoles of MnO_2 × (2/5) = 4/5

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

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

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

20. In presence of Hph indicator
m. eq. of HCl = m. eq. of Na_2CO_3 + m.eq. of NaOH
$30 \times 0.1 = (a \times 1) + (a \times 1)$
$\therefore a = 1.5$
In presence of MeOH indicator
m. eq. of H_2SO_4 = m. eq. of Na_2CO_3 + m. eq. of NaOH
$0.15 \times 2 \times V = (a \times 2) + (a \times 1)$
V = 15 ml

21. In presence of MeOH indicator, velence factor of $Na_2CO_3 = 2$
Equivalent of HCl = Equivalent of Na_2CO_3
NV = mole × V.F
$1\ V = x \times 10^{-3} \times 2$
$V = 2x \times 10^{-3}$ L
= 2x ml

22. Equivalent of HCl = Equivalent of (NaOH + Na_2CO_3 + $NOHCO_3$]
$1 \times V = [x \times 10^{-3} \times 1] + [Y \times 10^{-3} \times 2] + [Z \times 10^{-3} \times 1]$
$V = [x + 2Y + Z] \times 10^{-3}$ L
V = [X + 2Y + Z] ml

23. In presence of phenophthalein indicator valence factor of Hph = 1
Equivalents of HCl = Equivalent of Na_2CO_3
$N_1V_1 = N_2V_2$
For HCl $N_1 = M_1$ and Na_2CO_3 $N_2 = N_2$ $M_1 V_1 = M_2V_2$
$0.1 \times 100 = N_2 \times 25$
$M_2 = 0.4$

Reaction is $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

in moles of Na_2CO_3 = MV
$= 0.4\ 018 \times 25 \times 10^{-3}$
= moles of $NaHCO_3$

$$\text{molarity of } HCO_3^- = \frac{\text{Moles of } NaHCO_3}{\text{Volume}} = \frac{0.4 \times 25 \times 10^{-3} \times 1000}{125} = 0.08$$

24. (A) Eq of Sn^{2+} = Moles × v.f. = 3.5 × 2 = 7.
Eq of MnO_4^- = Moles × v.f. = 1.2 × 5 = 6.
Since MnO_4^- (O.A) is the LR, so the amount of oxidant available decides the number of electron transfer.
Also, electron involved per mole of OA (5) > electron involved per mole of RA (2).
(B) Eq of $H_2C_2O_4$ = Moles × v.f. = 8.4 × 2 = 16.8.
Eq of MnO_4^- = Moles × v.f. = 3.6 × 5 = 18.
Since $H_2C_2O_4$ (RA) is the LR, so the amount of reductant available decides the number of electron transfer.
Also, electron involved per mole of OA (5) > electron per mole of RA (2).
(C) Eq of $S_2O_3^{2-}$ = Moles × v.f. = 7.2 × 1 = 7.2.
Eq of I_2 = Moles × v.f. = 3.6 × 2 = 7.2.