EQUIVALENT CONCEPT & TITRATIONS CONTENTS

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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.

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Equivalent Concept & Titrations

Section (A): Classical Concept of Equivalent weight / Mass, Equivalent weight, n-factor and Normality for Acid, Base and Precipitate 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.
$$2Mg + O_2 \longrightarrow 2MgO$$

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

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

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

$$AI \qquad + \qquad \quad \frac{3}{2} \, CI_2 {\longrightarrow} AICI_3$$

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

111.5 g chlorine reacts with 27 g of Al.

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

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

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

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.

Valency factor calculation:

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



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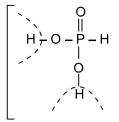
Solved Examples

Ex.-1 HCI .

H₂SO₄

H₃PO₄

H₃PO₃



{see there are only two replaceable H+ions}

Sol.

Valency factor \rightarrow

3

(Assume 100% dissicoiation)

Eq. wt. (E)

M/1

M/2

2

M/3M/2

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 -

Ex-2.

NaOH,

Sol.

KOH 1 1

 $v.f. \rightarrow$ M/1Ea. wt. \rightarrow 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 PH₄₊, NH₄₊ 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. O

Solved Examples -

Ex-3.

 $2NaOH + H_2SO_4 \longrightarrow Na_2 SO_4 + 2H_2O$

Acid Base

Sol. Valency factor of base = 1

Here, two molecule of NaOH replaced 2H+ ion from the H2 SO4. Therefore, each molecule of NaOH replaced only one H^+ ion of acid, so v.f. = 1.

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

Solved Examples

NaOH + H₂SO₄ -----> NaHSO₄ + H₂O Ex-4.

Base Acid

Sol. Valency factor of acid = 1

> Here, one of molecule of H₂SO₄ replaced one OH⁻ from NaOH. Therefore, valency factor for H₂SO₄ is one

$$\therefore \qquad \text{Eq. wt. of } \mathsf{H}_2\mathsf{SO}_4 = \frac{\mathsf{Mol.wt}}{\mathsf{1}}$$

Equivalent Concept & Titration



Salts:

- (a) In non-reacting condition
- Valency factor = Total number of positive charge or negative charge present in the compound.

Solved Examples

Ex-5. Na₂ CO₃, Fe₂(SO₄)₃, FeSO_{4.7}H₂O **Sol.** V.f. 2
$$2 \times 3 = 6$$
 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

- Na₂CO₃ + HCl ---- NaHCO₃ + NaCl Ex-6.
- Sol. It is an acid base reaction, therefore valency factor for Na₂CO₃ is one while in non-reacting condition, it will be two.

Section (B): Equivalent weight, n-factor and Normality for Oxidant and Reductant

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

In case of redox change, v.f. = Total change in oxidation number per molecule.

Solved Examples.

- $KMnO_4 + H_2O_2 \longrightarrow Mn^{2+} + O_2$ Ex-7
- Mn in KMnO₄ is going from +7 to +2, so change in oxidation number per molecule of KMnO₄ is 5. So the Sol. valency factor of KMnO₄ is 5 and equivalent weight is $\frac{M}{5}$

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 = $\frac{W}{F}$

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

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

- Normality (N) = $\frac{W \times 1000}{E \times V}$
- **Relations between Normality and Molarity:**

Normality (N) = Molarity x Valency factor

- $N \times V$ (in mL) = $M \times V$ (in mL) \times n or
- milliequivalents = millimoles x n or

-Solved Examples -

Calculate the normality of a solution containing 15.8 g of KMnO₄ in 50 mL acidic solution. Ex-8.

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

Here
$$W = 15.8 \text{ g}$$
, $V = 50 \text{ mL}$ $E = \frac{\text{molar mass of KMnO}_4}{\text{Valency factor}} = 158/5 = 31.6$
So, normality = 10 N

- Calculate the normality of a solution containing 50 mL of 5 M solution of K₂Cr₂O₇ in acidic medium.
- Sol. Normality (N) = Molarity \times valency factor = 5 x 6 = 30 N



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Section (C): Equivalent Concept for Acid Base Titration and Precipitation Reactions 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) $aA + bB \rightarrow mM + nN$; meg of A = meg of B = meg of M = m.eg. of N
- (ii) In a compound M_xN_y: meg of $M_xN_y = meg$ of M = meg of N

Solved Examples

Ex-10. Find the number of moles of KMnO₄ needed to oxidise one mole Cu₂S in acidic medium.

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

Sol. From law of equivalence.

equivalents of Cu₂S = equivalents of KMnO₄

moles of $Cu_2S \times v.f. = moles of kMnO_4 \times v.f.$

 $1 \times 8 = \text{moles of KMnO}_4 \times 5 \implies \text{moles of KMnO}_4 = 8/5$

(:. v.f. of $Cu_2S = 2(2-1) + 1(4-(-2)) = 8$ and v.f. of $KMnO_4 = 1(7-2) = 5$)

Ex-11. The number of moles of oxalate ions oxidized by one mole of MnO₄- ion in acidic medium are :

(C) $\frac{3}{5}$

(A) $\frac{5}{2}$ (B) $\frac{2}{5}$ Equivalents of $C_2O_4{}^{2-}$ = equivalents of MnO₄-Sol.

 $x(mole) \times 2 = 1 \times 5$

($\dot{}$ 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.a.

 $5e^{-} + 8H^{+} + MnO_{4}^{-} \longrightarrow Mn^{2+} + 2H_{2}O \qquad \therefore \qquad \text{Eq.wt of } MnO_{4}^{-} = \frac{\text{Mol. wt. of } MnO_{4}^{-}}{5}$ $3e^{-} + 2H_{2}O + MnO_{4}^{-} \longrightarrow MnO_{2} + 4OH^{-} \qquad \qquad \text{Eq.wt of } MnO_{4}^{-} = \frac{\text{Mol. wt. of } MnO_{4}^{-}}{3}$

e.g.

Thus, the number of equivalents of MnO₄ 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 KMnO₄ 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 KMnO4 participates. e.g. if KMnO₄ forms Mn²⁺, normality = 0.1 x 5 = 0.5 N. This same sample of KMnO₄, if employed in a reaction giving MnO₂ as product (Mn in +4 state), will have normality $0.1 \times 3 = 0.3$ 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, KIO₃ reacts with KI to liberate iodine and liberated lodine is titrated with standard hypo solution. The reactions are:

 $IO_3^- + I^- \longrightarrow I_2$ (i)

(ii) $I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$

meg of hypo = meg of I_2 = meg of IO_3^- = meg of I^-

meg of hypo = meg of IO_3^- . ٠.

This is wrong. Note that I_2 formed by equation (i) has v.f. = 5/3 & in equation (ii) has v.f. = 2.

v.f. of I2 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.



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Solved Examples

- **Ex-12** How many millilitres of 0.02 M KMnO₄ solution would be required to exactly titrate 25 mL of 0.2 M Fe(NO₃)₂ solution in acidic medium ?
- Sol. Method -1: Mole concept method

Starting with 25 mL of 0.2 M Fe2+, we can write:

Millimoles of $Fe^{2+} = 25 \times 0.2$...

and in volume V (in milliliters) of the KMnO₄,

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,

$$\frac{\text{m.moles of MnO}_{4}^{-}}{1} = \frac{\text{m.moles of Fe}^{2+}}{5}$$

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

∴ V = 50 mL.

Method -2: Equivalent Method:

At the equivalence point,

milliequivalents of MnO₄⁻ = milliequivalents of Fe²⁺

$$M_1 \times vf_1 \times V_1 = M_2 \times vf_2 \times V_2$$

$$0.02 \times 5 \times V_1 = 0.2 \times 1 \times 25 \qquad (\because MnO_4^- \longrightarrow Mn^{2+} \; ; \; v.f. = 5, \; Fe^{2+} \longrightarrow Fe^{3+} \; ; \; v.f. = 1)$$

 \therefore $V_1 = 50 \text{ mL}.$

Section (D): Equivalent Concept for Redox reactions, KMnO₄ / K₂Cr₂O₇ v/s Reducing Agents & their Redox Titration

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, K₂Cr₂O₇, AgNO₃, CuSO₄, 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, H₂SO₄, I₂, KMnO₄ 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.



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Type of Titrations :

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

Some Common Redox Titrations

Table of Redox Titrations: (Excluding Indometric / Indimetric titrations)

S.No.	Estimation	By titrating	Reactions	Relation*between	
S.NO.	of	with	neactions	OA and RA	
1	Fe ²⁺	MnO ₄ -	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	$5Fe^{2+} \equiv MnO_4^-$	
•	- 0	1011104	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. of $Fe^{2+} = M/1$	
2	Fe ²⁺	Cr ₂ O ₇ ²⁻	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$	
	-	G12O7-	G12O7	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	Eq.wt. of $Cr_2O_7^{2-} = M/6$
3	C ₂ O ₄ ² -	MnO ₄ -	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$5C_2O_4^{2-} \equiv 2MnO_4^{-1}$	
3	G 2 O 4	IVII 1O4	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. of $C_2O_4^{2-} = M/2$	
4	H ₂ O ₂	MnO ₄ -	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$	$5H_2O_2 \equiv 2MnO_4^-$	
4	H2O2	IVII 1O4	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq.wt. of $H_2O_2 = M/2$	
5	A 0 - O -	MnO.=	$As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$	Eq. ust. of Ac.O. M/4	
5	As ₂ O ₃	MnO₄¯	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	Eq. wt. of $As_2O_3 = M/4$	
6	AsO ₃ ³⁻	DrO	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$	Eq. wt. of $AsO_3^{3-} = M/2$	
0	ASU3°	BrO₃⁻	$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$	Eq.wt. of $BrO_3^- = M/6$	

Permanganate Titrations:

- KMnO₄ is generally used as an oxidising agent in acidic medium generally provided by dilute H₂SO₄.
- KMnO₄ works as self indicator persistent pink color is the indication of end point.
- Mainly used for estimation of Fe²⁺, oxalic acid ,oxalates, H₂O₂ etc.

Solved Examples

Write the balanced reaction of titration of KMnO₄ Vs oxalic acid in presence of H₂SO₄. Ex-13

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

Redox Changes :
$$C_2^{3+} \longrightarrow 2C^{4+} + 2e$$

$$\left(\mathsf{E}_{\mathsf{H}_2\mathsf{C}_2\mathsf{O}_4} = \frac{\mathsf{M}}{2} \right)$$

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

$$\left(E_{KMnO_4} = \frac{M}{5}\right)$$

Indicator: KMnO₄ acts as self indicator.

Ex-14 Write the balanced reaction of titration of KMnO₄ vs ferrous ammonium sulphate in presence of H₂SO₄.

Sol. Reaction:
$$2KMnO_4 + 10[FeSO_4(NH_4)_2SO_4.6H_2O] + 8H_2SO_4 \longrightarrow 5Fo_4(SO_4) + 10(NH_4)_2SO_4.6H_2O] + 8H_2SO_4 + 68H_4C$$

$$5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + K_2SO_4 + 2MnSO_4 + 68H_2O_4$$

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: KMnO₄ acts as self indicator

Section (E): lodometric/lodimetric Titration, Calculation of Available Chlorine from a sample of bleaching powder

lodometric/lodimetric Titrations:

Compound containing iodine are widely used in titrations.

(i) lodide ions can be oxidised to I₂ by suitable oxidising agent.

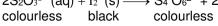
$$2I^{-}$$
 (aq) $\longrightarrow I_2$ (s) + $2e^{-}$

(ii) lodine (V) ions, IO₃-, will oxidise I- to I₂.

$$IO_3^-$$
 (aq) + $5I^-$ (aq) + $6H^+$ (aq) $\longrightarrow 3I_2$ (s) + $3H_2O$ (ℓ)

(iii) Thiosulphate ions, S₂O₃²⁻, can reduce iodine to iodide ions.

$$2S_2O_3^{2-}$$
 (aq) + I₂ (s) \longrightarrow $S_4O_6^{2-}$ + 2I⁻





Iodometric Titrations (Titration Solution is of Na₂S₂O₃.5H₂O)

0.11		tions (Titration Solution is of Na ₂ S ₂ O ₃ .5H ₂ O)	Relation between
S.No.	Estimation of	Reaction	O.A. and R.A.
1.	Τ.	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$	$I_2=2I=2Na_2S_2O_3$
1.	I ₂	or $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	Eq.wt. of $Na_2S_2O_3 = M/1$
		$2CuSO_4 + 4KI \longrightarrow 2CuI + 2K_2SO_4 + I_2$	2CuSO ₄ =I ₂ =2I=2Na ₂ S ₂ O ₃
2.	CuSO ₄	or $2Cu^{2+} + 4I^{-} \longrightarrow 2CuI + I_{2}$ white ppt	Eq.wt.of CuSO ₄ = M/1
		$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$	$CaOCl_2=Cl_2=I_2=2I=2Na_2S_2O_3$
3.	CaOCl ₂	$Cl_2 + 2KI \longrightarrow 2KCI + I_2$	
		$Cl_2 + 2I^- \longrightarrow 2CI^- + I_2$	Eq.wt. of $CaOCl_2 = M/2$
		$MnO_2 + 4HCI(conc.) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$	$MnO_2 = Cl_2 = I_2 = 2Na_2S_2O_3$
4.	MnO ₂	$Cl_2 + 2KI \longrightarrow 2KCI + I_2$	Eq.wt. of $MnO_2 = M/2$
4.	IVII IO2	or MnO ₂ + 4H ⁺ + 2Cl ⁻ \longrightarrow Mn ²⁺ + 2H ₂ O + Cl ₂	
		$Cl_2 + 2l^- \longrightarrow I_2 + 2Cl^-$	
5.	IO ₃ -	$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$
5.	103	$103 + 51 + 611 \longrightarrow 312 + 31120$	Eq.wt. of $IO_3^- = M/6$
6.	H ₂ O ₂	$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$	$H_2O_2\equiv I_2\equiv 2I\equiv 2Na_2S_2O_3$
0.	11202	11202 + 21 + 211 12 + 21120	Eq.wt. of $H_2O_2 = M/2$
7.	Cl ₂	$Cl_2 + 2l^- \longrightarrow 2Cl^- + I_2$	$CI_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$
	0.2	0.2 21	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.	CIO ⁻	$CIO^- + 2I^- + 2H^+ \longrightarrow H_2O + CI^- + I_2$	$CIO^- \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$
			Eq.wt. of OCI ⁻ = M/2 $Cr_2O_7^{2-} = 3I_2 = 6I$
10.	Cr ₂ O ₇ ²⁻	$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$	Eq.wt. of $Cr_2O_7^{2-} = M/6$
	1		$2MnO_4^- \equiv 5I_2 \equiv 10I$
11.	MnO₄ [−]	$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$	Eq.wt. of $MnO_4^- = M/5$
40	D::0 -	D.O. OTT OLL D. OY OLL O	$BrO_3^- \equiv 3I_2 \equiv 6I$
12.	BrO₃ [−]	$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$	Eq.wt. of $BrO_3^- = M/6$
13.	As(V)	$H_2AsO_4 + 2\Gamma + 3H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$	$H_3AsO_4 \equiv I_2 \equiv 2I$
13.	79(V)	$112A5O4 + 21 + 3\Pi \longrightarrow \Pi3ASO3 + \Pi2O + 12$	Eq.wt. of $H_3AsO_4 = M/2$
14.	HNO ₂	$2HNO_2 + 2I^- \longrightarrow I_2 + 2NO + H_2O$	$2HNO_2 \equiv I_2 \equiv 2I$
17.	11102	21 11 102 21	Eq.wt. of $HNO_2 = M/1$
15.	HCIO	$HCIO + 2I^- + H^+ \longrightarrow CI^- + I_2 + H_2O$	HCIO=I ₂ =2Na ₂ S ₂ O ₃
19.		, , , , , , , , , , , , , , , , , , , ,	Eq.wt. of HCIO = M/2

Iodimetric Titrations

	iodinictric ritrations		
S.No.	Estimation of	Reaction	Relation between O.A. and R.A.
1.	H ₂ S (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 ₂ H ₄	$N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$	$N_2H_4 = 2I_2 = 4I$ Eq.wt. of $N_2H_4 = M/4$



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Solved Examples

Ex-15. The sulphur content of a steel sample is determined by converting it to H₂S gas, absorbing the H₂S in 10 mL of 0.005 M I₂ and then back titrating the excess I₂ with 0.002 M Na₂S₂O₃. If 10 mL Na₂ S₂O₃ is required for the titration, how many milligrams of sulphur are contained in the sample?

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

Sol. Used millimoles of I_2 = (m.moles of I_2 taken initially) $-\frac{\text{m.moles of hypo used}}{2}$

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

= 0.04 = millimoles of H₂S

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

Calculation of available chlorine from a sample of bleaching powder:

The weight of available Cl₂ released from the given sample of bleaching powder on reaction with dilute acids or CO₂ is called available chlorine.

$$\begin{split} &\text{CaOCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{Cl}_2 \\ &\text{CaOCl}_2 + 2\text{HCI} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{Cl}_2 \\ &\text{CaOCl}_2 + 2\text{CH}_3\text{COOH} \longrightarrow \text{Ca}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{O} + \text{Cl}_2 \\ &\text{CaOCl}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{Cl}_2 \end{split}$$

Method of determination:

$$\begin{array}{lll} \text{CaOCl}_2 & + & 2\text{CH}_3\text{COOH} \longrightarrow \text{Ca}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{O} + \text{Cl}_2 \\ \text{(Sample of bleaching powder)} \\ \text{Cl}_2 + 2\text{KI} & \longrightarrow 2\text{KCI} + \text{I}_2 \\ \text{I}_2 & + & 2\text{Na}_2\text{S}_2\text{O}_3 & \xrightarrow{\text{Starch as indicator}} & \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \\ \text{V.f.} & -2 & \text{V.f.} & -1 \\ \end{array}$$

End point is indicated by disappearance of blue colour.

Let M = Molarity of hypo (Na₂S₂O₃) solution

 \therefore millimoles of Cl₂ produced = m.moles of l₂ used by hypo

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

mass of Cl₂ produced
$$= \frac{M \times V \times 10^{-3}}{2} \times 71$$
$$= 35.5 \times M \times V \times 10^{-3}$$

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

where W = amount of belaching powder taken in g.

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

Solved Examples

Ex-16 3.55 g sample of bleaching powder suspended in H₂O 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.

So. % of
$$Cl_2 = \frac{3.55 \times 0.2 \times 80}{3.55} = 16\%$$



:.

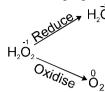
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Section (F) : Volume strength of H_2O_2 , Hardness of water Hydrogen peroxide (H_2O_2)

H₂O₂ 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 : $2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$

$$v.f = 2$$

Volume strength of H₂O₂: Strength of H₂O₂ is represented as 10V, 20 V, 30 V etc.

20V H₂O₂ means one litre of this sample of H₂O₂ on decomposition gives 20L of O₂ gas at STP.

Decomposition of H₂O₂ is given as:

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

1 mole
$$\frac{1}{2}$$
 × 22.4 L O₂ at STP

• Molarity of $H_2O_2(M) = \frac{\text{Volume strength of } H_2O_2}{11.2}$

Strength (in g/L): Denoted by S

Strength = Molarity × Mol. wt = Molarity × 34

Hardness of water (Hard water does not give lather with soap)

Temporary hardness - due to bicarbonates of Ca & Mg

Permanent hardness - due to chlorides & sulphates of Ca & Mg. 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 : CaCl₂ + Na₂CO₃ → CaCO₃ + 2NaCl
- (c) By ion exchange resins: $Na_2R + Ca^{2+} \longrightarrow CaR + 2Na^{+}$
- (d) By adding chelating agents like (PO₃⁻)₃ etc.

Measurement of Hardness:

Hardness is measured in terms of ppm (parts per million) of CaCO₃ or equivalent to it.

Hardness in ppm =
$$\frac{\text{mass of CaCO}_3}{\text{Total mass of solution}} \times 10^6$$



Solved Examples

- **Ex-17** 0.00012% MgSO₄ and 0.000111% CaCl₂ is present in water. What is the measured hardness of water and millimoles of washing soda required to purify water 1000 L water?
- **Sol.** Basis of calculation = 100 g hard water

MgSO₄ = 0.00012 g =
$$\frac{0.00012}{120}$$
 mole

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

: equivalent moles of CaCO₃ =
$$\left(\frac{0.00012}{120} + \frac{0.000111}{111}\right)$$
 mole

$$\therefore \qquad \text{mass of CaCO}_3 = \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \times 100 = 2 \times 10^{-4} \,\text{g}$$

Hardness (in terms of ppm of CaCO₃) =
$$\frac{2 \times 10^{-4}}{100} \times 10^{6} = 2 \text{ ppm}$$

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

 $NaSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$

$$\therefore \qquad \text{Required Na}_{2}\text{CO}_{3} \text{ for 100g of water} = \left(\frac{0.00012}{120} + \frac{0.000111}{111}\right) \text{mole}$$

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

$$\therefore \qquad \text{Required Na}_2\text{CO}_3 \text{ for 1000 litre water} = \frac{2 \times 10^{-6}}{100} \times 10^6 = \frac{2}{100} \text{ mole} \left(\because \text{ d} = 1 \text{g/mL}\right)$$

$$=\frac{20}{1000}$$
 mole = 20 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 SO₃ in oleum = 80(y-100)/18

Solved Examples

- **Ex-18** What volume of water is required (in mL) to prepare 1 L of 1 M solution of H₂SO₄ (density = 1.5g/mL) by using 109% oleum and water only (Take density of pure water = 1 g/mL).
- **Sol.** 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 $9/109 \times 98 = 8.09$ 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) CH₃COOH
- (ii) NaH₂PO₄
- (iii) H₃BO₃

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) K₂SO₄.Al₂(SO₄)₃.24H₂O
- (ii) CaCO₃

Ans. (i) 8

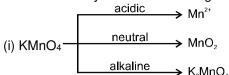
(ii) 2



Equivalent Concept & Titration /



4. Find the valency factor for following redox reactions :



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

(iii)
$$C_2O_4^{2-} \longrightarrow CO_2$$

Ans.

(iv)
$$Fe^{2+} \longrightarrow Fe^{2+}$$

- 5. Calculate the normality of a solution obtained by mixing 50 mL of 5 M solution of K₂Cr₂O₇ and 50 mL of 2 M K₂Cr₂O₇ in acidic medium.
- **Sol.** v.f. of $K_2Cr_2O_7 = 6$

so
$$N_f = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} = \frac{5 \times 6 \times 50 + 2 \times 6 \times 50}{50 + 50} = 21 \text{ N}$$

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

(iii) 2:

Sol. 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 KMnO₄ in acidic medium is :

(A) 5/2

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 KMnO₄ are needed to oxidise a mixture of 1 mole of each FeSO₄ & FeC₂O₄ in acidic medium?

(A) 4/5

Sol. Eq. of KMnO₄ = Eq. of FeSO₄ + Eq. of FeC₂O₄

moles of KMnO₄ \times 5 = moles of FeSO₄ \times 1 + moles of FeC₂O₄ \times 3

∴ moles of KMnO₄ = 4/5

9. A sample of hydrazine sulphate [N₂H₆SO₄] was dissolved in 100 mL water. 10 mL of this solution was treated with excess of FeCl₃ Sol. Ferrous ions formed were estimated and it required 20 mL of M/50 KMnO₄ 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 KMnO₄

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

 $v.f. of N_2H_6SO_4 = 4$

so, weight of N₂H₆SO₄ in 1 L solution =
$$\frac{2 \times 10^{-3} \times 1000}{4 \times 10} \times 130 = 6.5 \text{ g}.$$

- **10.** Write the balanced redox reaction and calculate the equivalent weight of oxidising agent and reducing agent for titration of K₂Cr₂O₇ Vs Ferrous ammonium sulphate.
- **Ans.** The reaction : $6[FeSO_4(NH_4)_2SO_4.6H_2O] + K_2Cr_2O_7 + 7H_2SO_4$ —

$$3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 6(NH_4)_2SO_4 + 43H_2O_4$$

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



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Equivalent Concept & Titration



- One litre of acidified KMnO₄ solution containing 15.8 g KMnO₄ is decolorized by passing sufficient SO₂. If SO₂ is produced by FeS₂, what is the amount of FeS₂ required to give desired SO₂?
- Ans. 15 g.
- v.f. of $KMnO_4 = 5 \& v.f.$ of $SO_2 = 2$ Sol.

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

$$\frac{15.8}{158/5}$$
 = moles of SO₂ × 2

- SO. moles of $SO_2 = 1/4$
- Now. applying POAC on S, we get:

$$2 \times \text{mole}$$
 of FeS₂ = $1 \times \text{moles}$ of SO₂

so, moles of FeS₂ =
$$\frac{1}{4} \times \frac{1}{2} = \frac{1}{8}$$

so, weight of FeS₂ =
$$\frac{1}{8}$$
 × 120 = 15 g.

12. An aqueous solution containing 0.1 g KIO₃ (formula weight = 214) and an excess of KI was acidified with HCI. The liberated I2 consumed 45 mL of thiosulphate. The molarity of sodium thiosulphate solution is:

The reaction involved is :
$$IO_{3}^{-} + I^{-} + H^{+} \longrightarrow I_{2} + H_{2}O$$

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

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

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

Now, Moles of KIO₃ =
$$\frac{0.1}{214}$$

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

Now, Moles of Na₂S₂O₃ =
$$2 \times 3 \times \frac{0.1}{214}$$

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

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

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

- Calculate the percentage of available chlorine in a sample of 3.55 g of bleaching powder which was 13. 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.
$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

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

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

In 25 mL solution, moles of Na₂S₂O₃ =
$$\frac{20}{1000} \times \frac{0.125}{1} = 25 \times 10^{-4}$$

So, moles of
$$I_2 = \frac{1}{2} \times \text{moles of Na}_2S_2O_3$$

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

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

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

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



Exercise-1

Marked questions are recommended for Revision.

PART - I: SUBJECTIVE QUESTIONS

Section (A): Classical Concept of Equivalent weight / Mass, Equivalent weight, n-factor and Normality for Acid, Base and Precipitate

- **A-1.** Determine the equivalent weight of the following ions:
 - (a) Na+
- (b) Al³⁺
- (c) NO+
- (d) CI-

- (e) CO₃²⁻
- (f) SO₄²-
- (g) PO₄3-
- **A-2.** Determine the equivalent weights of the following salts :
 - (a) NaCl
- (b) K₂SO₄
- (c) Ca₃(PO₄)₂
- **A-3.** 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?

Section (B): Equivalent weight, n-factor and Normality for Oxidant and Reductant

- **B-1.** A mixture of CuS (molecular weight = M₁) and Cu₂S (molecular weight = M₂) is oxidised by KMnO₄ (molecular weight = M₃) in acidic medium, where the product obtained are Cu²⁺, Mn²⁺ and SO₂. Find the equivalent weight of CuS, Cu₂S and KMnO₄ respectively.
- **B-2.** Determine the equivalent weight of the following oxidising and reducing agents :
 - (a) KMnO₄ (reacting in acidic medium MnO₄⁻ → Mn²⁺)
 - (b) KMnO₄ (reacting in neutral medium MnO₄ $^- \longrightarrow$ MnO₂)

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

- **C-1.** 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.
- **C-2.** A dilute solution of H₂SO₄ is made by adding 5 mL of 3N H₂SO₄ to 245 mL of water. Find the normality and molarity of the diluted solution.
- C-3.≥ What volume at NTP of gaseous ammonia will be required to be passed into 30 cm³ of 1 N H₂SO₄ solution to bring down the acid strength of the latter to 0.2 N?

Section (D): Equivalent Concept for Redox reactions, KMnO₄ / K₂Cr₂O₇ v/s Reducing Agents & their Redox Titration

- **D-1.** 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.
- **D-2.** It requires 40 mL of 1 M Ce⁴⁺ to titrate 20 mL of 1M Sn²⁺ to Sn⁴⁺. What is the oxidation state of the Cerium in the product?
- **D-3.** 25 mL of a solution of Fe²⁺ ions was titrated with a solution of the oxidizing agent $Cr_2O_7^{2-}$. 50 mL of 0.01 M K₂Cr₂O₇ solution was required. What is the molarity of the Fe²⁺ solution?
- **D-4.** How many mL of 0.3M K₂Cr₂O₇ (acidic) is required for complete oxidation of 5 mL of 0.2 M SnC₂O₄ solution.



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Section (E): lodometric/lodimetric Titration, Calculation of Available Chlorine from a sample of Bleaching Powder

- E-1. 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 H₂SO₄. After the reaction was complete, the excess Mohr salt required 30 mL of 0.1 M KMnO₄ for oxidation. The % of available Cl₂ approximately is (mol wt = 71)
- **E-2.** ★ A mixture containing As₂O₃ and As₂O₅ required 20 mL of 0.05 N iodine solution for titration. The resulting solution is then acidified and excess of KI was added. The liberated iodine required 1.116 g hypo (Na₂S₂O₃.5H₂O) for complete reaction. Calculate the mass of the mixture. The reactions are:

$$As_2O_3 + 2I_2 + 2H_2O \longrightarrow As_2O_5 + 4H^+ + 4I^-$$

 $As_2O_5 + 4H^+ + 4I^- \longrightarrow As_2O_3 + 2I_2 + 2H_2O_3$

(Atomic weight : As = 75)

Section (F): Volume strength of H₂O₂, Hardness of water

- 20 ml of H_2O_2 after acidification with dil H_2SO_4 required 30 ml of $\frac{N}{12}$ KMnO₄ for complete oxidation. F-1. Detemine the strength of H₂O₂ solution.
- F-2. A 100 mL sample of water was treated to convert any iron present to Fe²⁺. Addition of 25 mL of 0.002 M K₂Cr₂O₇ resulted in the reaction:

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

The excess K₂Cr₂O₇ was back-titrated with 7.5 mL of 0.01 M Fe²⁺ solution. Calculate the parts per million (ppm) of iron in the water sample.

- F-3. By which reason temporary and permanent hardness occur?
- F-4. Define two method by which we can soften the water sample.

PART - II: ONLY ONE OPTION CORRECT TYPE

Section (A): Classical Concept of Equivalent weight / Mass, Equivalent weight, n-factor and Normality for Acid, Base and Precipitate

A-1. 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)
$$\frac{x}{v} \times 8$$

(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-2. Equivalent wt. of H₃PO₄ 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

3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. Equivalent A-3. weidht of the metal is:

(A) 33.25

(B) 3.325

(C) 12

(D) 20

Section (B): Equivalent weight, n-factor and Normality for Oxidant and Reductant

B-1.≥ An ion is reduced to the element when it absorbs 6 × 10²⁰ electrons. The number of equivalents of the ion is:

(A) 0.1

(B) 0.01

(C) 0.001

(D) 0.0001



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Equivalent Concept	&	Titration
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=9000	entent conteept of in this	/			
B-2.3	When N ₂ is converted into (A) 1.67 (eight of nitrogen will be : (C) 3.67	(D) 4.67	
B-3.	In the ionic equation 2K will be:	+BrO ₃ - + 12H+ + 10e	\longrightarrow Br ₂ + 6H ₂ O + 2K ⁺ , †	the equivalent weight of KBrO ₃	
	(A) M/5 (where M = molecular we	B) M/2 ight of KBrO ₃)	(C) M/6	(D) M/4	
Section	on (C) : Equivalent C	oncept for Acid Ba	ase Titration and Pr	ecipitation Reactions	
C-1.	If one mole of H ₂ SO ₄ read (A) 98	cts with one mole of Na B) 49	OH, equivalent weight of (C) 96	H ₂ SO ₄ will be : (D) 48	
C-2.	containing 0.125 g of pure	e Na ₂ CO ₃ :	will be required for com	plete reaction with a solution (D) 32.6 mL	
C-3.æ	One litre of a solution cor In what volume ratio mus	rtains 18.9 g of HNO₃ a	nd one litre of another so	olution contains 3.2 g of NaOH.	
Section	on (D) : Equivalent 0 Agents & their Redo		≀ reactions, KMnO₄	/ K ₂ Cr ₂ O ₇ v/s Reducing	
D-1.	If equal volumes of 0.1 Macidic medium, then Fe ²⁺ (A) more by KMnO ₄ (C) equal in both cases		K ₂ Cr ₂ O ₇ solutions are allowed to oxidise Fe ²⁺ to Fe ³⁺ in (B) more by K ₂ Cr ₂ O ₇ (D) cannot be determined.		
D-2.æ	Which of the following sol (A) 25 mL of 0.1 M KMnC (C) 25 mL of 0.6 M KMnC)4	ize 25 mL of an acid solution of 0.1 M iron (II) oxalate: (B) 25 mL of 0.2 M KMnO ₄ (D) 15 mL of 0.1 M KMnO ₄		
D-3.æ	the experiment, 1.68 × oxidation number of A aft	10^{-3} moles of $K_2Cr_2O_7$ er oxidation is :	were used for 3.36 ×	d by $Cr_2O_7^{2-}$ in acid medium. In 10^{-3} moles of ABD. The new	
	. ,	,	(C) n – 3	(D) +n	
D-4.	The number of moles of c (A) 5/2	oxalate ions oxidized by B) 2/5	one mole of MnO ₄ – ion (C) 3/5	in acidic medium is : (D) 5/3	
	on (E) : lodometric/lo le of Bleaching Powo		n, Calculation of Av	ailable Chlorine from a	
E-1.	sample (Take formula of	bleaching powder as Ca	aOCl ₂) ?	in a given bleaching powder	
	(A) 52.9% (B) 55.9 %	(C) 58%	(D) 60%	
E-2.>	copper (I) by iodide ions.	$2Cu^{2+} + 4I^{-} \longrightarrow 2C$	CuI + I2	where copper(II) is reduced to I iodine, then the percentage of	
	copper in the sample will (A) 31.75 % ((C) 53 %	(D) 37 %	
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Section (F): Volume strength of H₂O₂, Hardness of water

- F-1. A substance which participates readily in both acid-base and oxidation-reduction reactions is :
 - (A) Na₂ CO₃
- (B) KOH
- (C) KMnO₄
- (D) H₂ C₂ O₄
- **F-2.** A fresh H₂O₂ 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
- F-3.2 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
- **F-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 CaCO₃ 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
 - (A) 4.1 g H₂SO₃
 - (B) 4.9 g H₃PO₄
 - (C) 4.5 g oxalic acid (H₂C₂O₄)
 - (D) 5.3 g Na₂CO₃

- Column II
- (p) 200 mL of 0.5 N base is used for complete neutralization
- (q) 200 millimoles of oxygen atoms
- (r) Central atom is in its highest oxidation number
- (s) May react with an oxidising agent

Exercise-2

marked questions are recommended for Revision.

PART - I: ONLY ONE OPTION CORRECT TYPE

- 1.a 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. Oxalic acid, $H_2C_2O_4$, reacts with paramagnet ion according to the balanced equation $5H_2C_2O_4$ (aq) + $2MnO_4$ ⁻ (aq) \implies 2 Mn^{2+} (aq) + 10 CO_2 (g) + 8 H_2O (l). The volume in mL of 0.0162 M KMnO₄ 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
- 3. \times x mmol of KMnO₄ react completely with y mmol of MnSO₄ in presence of fluoride ions to give MnF₄ quantitatively. Then :
 - (A) x = y
- (B) 4x = y
- (C) x > y
- (D) x < y
- 1 mol each of H₃PO₂, H₃PO₃ and H₃PO₄ 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
- 5. 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
- **6.** \searrow 28 NO₃⁻ + 3As₂S₃ + 4H₂O \longrightarrow 6AsO₄³⁻ + 28NO + 9SO₄²⁻ + 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) $\frac{M}{28}$

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Equivalent Concept & Titration

- 7. If 25 mL of a H₂SO₄ solution reacts completely with 1.06 g of pure Na₂CO₃, what is the normality of this acid solution :
 - (A) 1 N
- (B) 0.5 N
- (C) 1.8 N
- (D) 0.8 N
- **8.** 125 mL of 63% (w/v) H₂C₂O₄.2H₂O 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) alkalin
- 9.5 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 KMnO₄ 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) $Z^{2+} \rightarrow Z^{4+}$
- 10. How many litres of Cl_2 at STP will be liberated by the oxidation of NaCl with 10 g KMnO₄ in acidic medium: (Atomic weight: Mn = 55 and K = 39)
 - (A) 3.54
- (B) 7.08
- (C) 1.77
- (D) None of these
- 11. № One gram of Na₃AsO₄ is boiled with excess of solid KI in presence of strong HCI. 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]

- (A) 48.1 mL
- (B) 38.4 mL
- (C) 24.7 mL
- (D) 30.3 mL
- 12. 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+i} ions] (Atomic masses : V = 51, O = 16, I = 127)

- (A) 0.11
- (B) 0.22
- (C) 0.055
- (D) 0.44
- **13.** During the disproportionation of lodine 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
- 14. If 1 mL of a KMnO₄ solution react with 0.140 g Fe²⁺ and if 1 mL of KHC₂O₄. H₂C₂O₄ solution react with 0.1mL of previous KMnO₄ solution, how many millilitres of 0.20 M NaOH will react with 1 mL of previous KHC₂O₄. H₂C₂O₄ solution in which all the protons (H⁺) are ionisable?
 - (A)15/16 mL
- (B) 13/16
- (C) 11/14
- (D) None of these

PART - II: SINGLE AND DOUBLE VALUE INTEGER TYPE

- 1. How many equivalents of Mg would have to react in order to liberate 4 N_A electrons? (Mg $-2e^- \rightarrow Mg^{2+}$)
- 2. A certain weight of pure CaCO₃ is made to react completely with 20 mL of a HCl solution to give 224 mL of CO₂ 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 H₃PO₄ 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:

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



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Equivalent Concept & Titration



- 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.a An oxide of a metal contains 40% oxygen, by weight. What is the equivalent weight of the metal?
- 8. In the following reaction, $3\text{Fe} + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$, 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 K₂C₂O₄.3H₂C₂O₄.4H₂O can be oxidized by MnO₄⁻ in acid medium. Calculate the volume of (in mL) 1 M KMnO₄ reacting in acid solution with 5.08 gram of the acid oxalate.
- 11. In the following reaction, SO₂ acts as a reducing agent:

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

Find the equivalent weight of SO₂.

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

1. In the titration of K₂Cr₂O₇ and ferrous sulphate, following data is obtained :

V₁ mL of K₂Cr₂O₇ solution of molarity M₁ requires V₂ mL of FeSO₄ solution of molarity M₂.

Which of the following relations is/are true for the above titration:

(A) $6 M_1 V_1 = M_2 V_2$

(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 MnO₄⁻ ion can oxidise 5 moles of Fe²⁺ ion in acidic medium.
 - (B) 1 mole of Cr₂ O₇²⁻ ion can oxidise 6 moles of Fe²⁺ ion in acidic medium.
 - (C) 1 mole of Cu₂S can be oxidised by 1.6 moles of MnO₄- ion in acidic medium.
 - (D) 1 mole of Cu₂S can be oxidised by 1.33 moles of Cr₂O₇²⁻ ion in acidic medium.
- **3.** Which of the following samples of reducing agents is /are chemically equivalent to 25 mL of 0.2 N KMnO₄ to be reduced to Mn²⁺ and water :
 - (A) 25 mL of 0.2 M FeSO₄ to be oxidized to Fe³⁺
 - (B) 50 mL of 0.1 M H₃AsO₃ to be oxidized to H₃AsO₄
 - (C) 25 mL of 0.1 M H₂O₂ to be oxidized to H⁺ and O₂
 - (D) 25 mL of 0.1 M SnCl₂ to be oxidized to Sn^{4+}
- **4.** To a 25 ml H₂O₂ 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 H₂O₂ present in 25 ml solution is 0.102 g
 - (B) The molarity of H₂O₂ solution is 0.12 M
 - (C) The weight of H₂O₂ present in 1 L of the solution is 0.816 a
 - (D) The volume strength of H₂O₂ 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 KHC₂O₄ (potassium acid oxalate) required to reduce 100 mL of 0.02 M KMnO₄ 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



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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 = $\frac{\text{Molecular mass of acid}}{\text{Basicity of acid}}$

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 = $\frac{\text{Molecular mass of base}}{\text{Aciditiy of base}}$

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 = $\frac{\text{Molecular mass of oxidising agent}}{\text{Number of electrons gained by one molecule}}$
- (b) Oxidation number concept : Equivalent mass of oxidising agent = $\frac{\text{Molecular mass of oxidising agent}}{\text{Total change in oxidation number per molecule of oxidising agent}}$
- 1. Equivalent mass of Ba(MnO₄)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 K₂Cr₂O₇ 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 K₂Cr₂O₇ needed to oxidise the above volume of H₂O₂ solution is :
 - (A) 3.6 g
- (B) 0.8 g
- (C) 4.2 g
- (D) 0.98 g
- **6.** The volume of O₂ at STP that would be liberated by above H₂O₂ solution on disproportionation is:
 - (A) 56 mL
- (B) 112 mL
- (C) 168 mL
- (D) 224 mL



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Comprehension #3

Answer Q.7, Q.8 and Q.9 by appropriately matching the information given in the three columns of the following table.

Equivalent weight = $\frac{\text{Molecular weight / Atomic weight}}{\text{n-factor}}$ n-factor is very important in redox as well as non-

redox reactions.

In general n-factor of acid/base is number of moles of H⁺/OH⁻ furnished per mole of acid/base. n-factor of reactions is number of moles of electrons lost or gained per mole of reactant columns 1, 2, 3 contain reactions, n-factor & equivalent weight respectively.

Column-1			Column-2		Column-3
(I)	$MnO_4^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$	(i)	1	(P)	158
(II)	$MnO_4^- \longrightarrow MnO_4^{-2}$	(ii)	1 <u>0</u>	(Q)	96
(III)	$Br_2 + OH^- \longrightarrow BrO_3^- + Br^-$	(iii)	3	(R)	34
(IV)	$H_2O_2 \longrightarrow O_2 + H_2O$	(iv)	2	(S)	52.6

- 7. For KMnO₄ in strong basic medium correct combination is -
 - (A) (I) (ii) (R)
- (B) (II) (i) (P)
- (C) (II) (iii) (S)
- (D) (I) (iv) (Q)
- 8. For KMnO₄ in neutral medium correct combination is -
 - (A) (I) (iii) (Q)
- (B) (II) (i) (R)
- (C) (I) (iii) (S)
- (D) (II) (iii) (R)
- 9. For a disproportionation reaction the only correct combination is -
 - (A) (I) (ii) (R)
- (B) (II) (ii) (Q)
- (C) (IV) (i) (S)
- (D) (III) (ii) (Q)

Exercise-3

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

1.	In basic medium, I^- is oxidised by MnO_4^- . In this process, I^- changes to :	[JEE 2
----	---	--------

[JEE 2004, 3/144]

(A) IO_3^-

(B) I₂

(C) IO₄-

(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 Na₂S₂O₃ 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 : $I^- + CIO_3^- + H_2SO_4 \longrightarrow CI^- + HSO_4^- + I_2$

The correct statement(s) in the balanced equation is/are:

[JEE (Advanced) 2014, 3/120]

- (A) Stoichiometric coefficient of HSO₄ is 6.
- (B) lodide is oxidized.

(C) Sulphur is reduced.

(D) H₂O is one of the products.



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^{*} Marked Questions may have more than one correct option.

5. To measure the quantity of MnCl₂ dissolved in an aqueous solution, it was completely converted to KMnO₄ using the reaction.

 $MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCI$ (equation not balanced).

Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared. The quantity of $MnCl_2$ (in mg) present in the initial solution is ____.

(Atomic weights in g mol⁻¹ : Mn = 55, Cl = 35.5)

[JEE (Advanced) 2018, 3/120]

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

JEE(MAIN) OFFLINE PROBLEMS

1.	When $KMnO_4$ acts as an oxidising agent and ultimately forms MnO_4^{2-} , MnO_4^{2-}	$_{2}$, Mn $_{2}$ O $_{3}$ 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 CrO₄²⁻.

[AIEEE 2003, 3/225]

(2) Cr oxidises in the oxidation state +7 from CrO₄²⁻.

(3) Cr+3 and Cr₂O₇2- will be formed.

(4) Cr₂O₇²⁻ and H₂O 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 KMnO₄ solution in the presence of H₂SO₄. 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 Mn²⁺.

(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 : $xMnO_4^- + yC_2O_4^{2-} + zH^+ \longrightarrow xMn^{2+} + 2yCO_2 + \frac{z}{2}H_2O_4^{2-}$

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%



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JEE(MAIN) ONLINE PROBLEMS

1.		•	es H ₂ O ₂ acts as a red	ent depending upon the nature of the lucing agent in acid medium ? 014 Online (12-04-14), 4/120]
	(1) MnO ₄ -	(2) Cr ₂ O ₇ ²⁻	(3) SO ₃ ²⁻	(4) KI
2.	Permanent hardness (1) Treatment with w (3) Ion exchange me	•	d by: [JEE(Main) (2) Boiling (4) Calgon's metho	2015 Online (10-04-15), 4/120]
3.	was absorbed in 60		ution. The excess sulp age of nitrogen in the	s method and the ammonia evolved phuric acid required 20 mL of M/10 compound is: ain) 2015 Online (10-04-15), 4/120]
	(1) 24	(2) 5	(3) 10	(4) 3
4.	aqueous solution is	:	[JEE(Mai	se that furnishes 0.04 mole of OH $^-$ in \mathbf{n}) 2016 Online (10-04-16), 4 /120]
	(1) 400 mL	(2) 600 mL	(3) 200 mL	(4) 80 mL
5.	For standardizing Na (1) Sodium tetrabora	aOH solution, which of the	<u> </u>	n) 2018 Online (16-04-18), 4/120]
	(3) Oxalic acid		(4) dil. HCl	mam danate
6.	The temporary hards (1) CaCl ₂	ness of water is due to : (2) Ca(HCO ₃) ₂	[JEE(Mai (3) NaCl	n) 2019 Online (09-01-19), 4/120] (4) Na ₂ SO ₄
7.	producing one mole	cule of CO2 is :	[JEE(Mair	the number of electrons involved in a) 2019 Online (10-01-19), 4/120]
	(1) 5	(2) 1	(3) 2	(4) 10
8.		ICI solution requires 30 m equired to titrate 30 mL o	f 0.2 M aqqueous NaC	bonate solution. What is the volume OH solution? n) 2019 Online (11-01-19), 4/120]
	(1) 12.5 mL	(2) 75 mL	(3) 50 mL	(4) 25 mL
9.	The hardness of wat (molar mass of CaS	. ,	•	ontaining 10 ⁻³ M CaSO ₄ is : n) 2019 Online (12-01-19), 4/120]
	(1) 10 ppm	(2) 50 ppm	(3) 90 ppm	(4) 100 ppm
10.	The volume strength	n of 1M H ₂ O ₂ is: (Molar ma	•	ol ^{–1}) n) 2019 Online (12-01-19), 4/120]
	(1) 11.35	(2) 22.4	(3) 16. 8	(4) 5.6

Answers

EXERCISE - 1

PART - I

A-1. (a) 23; (b) E = 9; (c) E = 30; (d) E =
$$\frac{35.5}{1}$$
; (e) E = 30; (f) E = 48; (g) E = 31.67

A-2. (a)
$$E = 58.5$$
 or $E = 58.5$; (b) $E = 87$ or $E = 87$; (c) $E = 51.67$ or $E = 51.67$

A-3. 20.1 **B-1.**
$$\frac{M_1}{6}$$
, $\frac{M_2}{8}$, $\frac{M_3}{5}$ **B-2.** (a) 31.6; (b) 52.67 **C-1.** 72.61

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

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

$$\text{or} \qquad \text{By Slaked lime}: \qquad \qquad \text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 \ + 2\text{H}_2\text{O}$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$$

(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

PART - III

(A - p,s); (B - q,r); (C - p,q,s); (D - r)

EXERCISE - 2

PART - I

1.	(A)	2.	(A)	3.	(D)	4.	(D)	5.	(A)
• • •	(* ')		(* 1)	O.	(0)	••	(0)	0.	(' ')

PART - II

1.

Equ	ivalent Conc	ept & Titr	ration /						—————————————————————————————————————	
	PART - III									
1.	(AC)	2.	(ABCD)	3.	(ACD)	4.	(ABD)	5.	(ABCD)	
6.	(AB)									
				PA	RT - IV					
1.	(C)	2.	(B)	3.	(C)	4.	(C)	5.	(D)	
6.	(B)	7.	(B)	8.	(C)	9.	(D)			
				EXEF	RCISE - 3					
				PA	ART - I					
1.	(A)	2.	(D)	3.	(C)	4.*	(ABD)	5.	126 mg	
				PA	ART - II					
			JEE(MA	IN) OF	FLINE PRO	BLEMS				
1.	(3)	2.	(4)	3.	(4)	4.	(2)	5.	(3)	
6.	(3)	7.	(2)							
			JEE(M	AIN) ON	ILINE PRO	BLEMS				
1.	(4)	2.	(2)	3.	(3)	4.	(3)	5.	(3)	
6.	(2)	7.	(2)	8.	(4)	9.	(4)	10.	(1)	

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Additional Problems for Self Practice (APSP)

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

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Ti	ime : 1 Hr. Max.			Marks : 120
Impor 1. 2. 3. 4.	Each question is allotted Candidates will be awa question. ¼ (one fourth deduction from the total There is only one cor	sts of 30 questions. The lead 4 (four) marks for corrected marks as stated at h) marks will be deducte score will be made if no rect response for each as wrong response and	bove in Instructions No. d for indicating incorrect response is indicated fo question. Filling up mo	3 for correct response of each response of each question. No r an item in the answer sheet. ore than one response in any se will be deducted accordingly
1.		$0_3 + 4Cl_2 + 5H_2O \longrightarrow Na_1$ $0_3 + 4Cl_2 + 5H_2O \longrightarrow Na_2$ $0_3 $	$_{12}SO_4 + H_2SO_4 + 8HCI,$ molecular weight of Na ₂ S (3) M/1	S ₂ O ₃) (4) M/2
2.	In the reaction, 2CuSO ₂ the equivalent weight of (1) 79.75	$_1$ + 4KI \longrightarrow 2Cu ₂ I ₂ + I ₂ + CuSO ₄ will be : (2) 159.5	- 2K ₂ SO ₄ (3) 329	(4) None of these
3.	100 milli moles of dich form ammonium dichlor (1) 0.0167		COOH) can neutralize ho	ow many moles of ammonia to (4) 0.6
4.	The number of moles of (1) 5/2	f ferrous oxalate oxidised (2) 2/5	by one mole of KMnO ₄ (3) 3/5	in acidic medium is : (4) 5/3
5.	How many moles of Kl acidic medium : (1) 4/5	MnO_4 are needed to oxide (2) 5/4	idise a mixture of 1 mol	e of each FeSO ₄ & FeC ₂ O ₄ in (4) $5/3$
6.			10.2 mL of a dilute H_2SO ution in order to make it ϵ (3) 90.2 mL	4 solution. The volume of water exactly N/10. (4) 290.2 mL
7.	HNO_3 oxidises NH_4^+ ior mole of $(NH_4)_2SO_4$ is : (1) 4	ns to nitrogen and itself (gets reduced to NO ₂ . Th	e moles of HNO ₃ required by 1 (4) 2
8.	The mass of oxalic acid (1) 4.5 g	crystals (H ₂ C ₂ O ₄ .2H ₂ O) (2) 6.3 g	required to prepare 50 n (3) 0.63 g	nL of a 0.2 N solution is : (4) 0.45 g
9.	When HNO ₃ is converted (1) M/2 (M = molecular weight of	(2) M/1	nt weight of HNO ₃ will be (3) M/6	e : (4) M/8
10.	In the conversion NH_2O (1) $M/4$ ($M = molecular weight of$	(2) M/2	ent weight of NH2OH will (3) M/5	be : (4) M/1
11.		O required to remove ha om of potassium chloride (2) 4		ater having 324 ppm of calcium (4) 2



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Equi	vateni Concept & Hiro	<u>iiion</u> /		
12.		H ₂ O ₂ liberates 0.508 g oume strength at STP is : (2) 1.12 V	of I_2 from an acidified K (3) 4.48 V	I solution. The strength of H_2O_2 (4) 8.96 V
13.	When hypo solution is (1) Na ₂ S ₂ O ₃ is convert (3) KMnO ₄ is converte		n then (2) Na ₂ S ₂ O ₃ is converted (4) KMnO ₄ is converted	
14.	(1) $5BiO_{3}^{-} + 22H^{+} + M$ (2) $5BiO_{3}^{-} + 14H^{+} + 2M$ (3) $2BiO_{3}^{-} + 4H^{+} + Mn$	equations is a balanced on $^{2+}$ \longrightarrow $5Bi^{3+}$ + $7H_2O$ + Mn^{2+} \longrightarrow $5Bi^{3+}$ + $7H_2O$ + $2H_2O$	+ MnO4 ⁻ + 2MnO4 ⁻ MnO4 ⁻	
15.		ncid solution (specific gr of 2 N NaOH solution req (2) 92 mL		98% by weight of pure acid. e acid. (4)184 mL
16.	The equivalent mass $(1) \text{ Mn}_2\text{O}_3$	of MnSO ₄ is half its molec (2) MnO ₂	cular mass when it is con (3) MnO ₄ -	verted to : (4) MnO ₄ ²⁻
17.		f 6.3 g of oxalic acid dihy neutralise 10 mL of this : (2) 20 mL		mL. The volume of 0.1 N NaOH (4) 4 mL
18.	In the reaction H ₂ O ₂ ¹⁸ (1) water	+ O ₃ → water + oxygen, r (2) oxygen	radioactivity will be show (3) both (1) & (2)	n by which of the product : (4) none of these
19.		of the following acids HCI, HNO ₃ , H ₂ SO ₄ , H ₂ S (2) 7		mol of NaOH, under required D ₂ , H ₄ P ₂ O ₅ , H ₃ BO ₃ (4) 9
20.	CrO ₅ has structure as	0		
	(1) 4	of chromium in the above (2) 5	e compound is : (3) 6	(4) 0
21.	The normality of ortho(1) 11 N	ohosphoric acid having p (2) 22 N	urity of 70% by weight ai (3) 33 N	nd specific gravity 1.54 is : (4) 44 N
22.	The normality of mixtu (1) 0.0267	re obtained by mixing 100 (2) 0.2670	0 mL of 0.2 M H ₂ SO ₄ and (3) 1.0267	d 200 mL of 0.2 M HCl is : (4) 1.1670
23.	The reagent commonly (1) oxalic acid (3) sodium citrate	y used to determine hard	ness of water titrimetrica (2) disodium salt of ED (4) sodium thiosulphate)ŤA
24.	HCI. When phenoplhth		r, x mL HCl is used. In a	.2H ₂ O) is titrated against 0.05 M separate titration of same using (4) 180 mL
25.	In the following reaction The radioactive oxyge (1) H ₂ O (3) both	n 2MnO ₄ - + 5H ₂ O ₂ 18 + 6H n will appear in :	$H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O$ (2) O_2 (4) above reaction doe	
26.		lar mixture of Na ₂ CO ₃ an t completely with the abo (2) 157.8 mL		th 0.1 NHCI. The milliliters of 0.1 (4) 295.5 mL



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- **27.** Which of the following is not a redox reaction?
 - (1) KCN + Fe(CN)₂ \longrightarrow K₄ [Fe(CN)₆]
- (2) $Rb + H_2O \longrightarrow RbOH + H_2$

(3) $H_2O_2 \longrightarrow H_2O + O$

- (4) $CuI_2 \longrightarrow CuI + I_2$
- **28.** Equivalent weight of chlorine molecule in the equation is :

$$3 \text{ Cl}_2 + 6 \text{ NaOH} \longrightarrow 5 \text{ NaCl} + \text{NaClO}_3 + 3 \text{ H}_2\text{O}$$

- (1)42.6
- (2) 35.5
- (3)59.1
- (4)71

- **29.** $Cr_2O_7^{2-} \xrightarrow{H^+} Cr^{3+}$, Eq. wt of $Cr_2O_7^{2-}$ is :
 - (1) mol. wt./6
- (2) mol.wt./3
- (3) mol.wt./4
- (4) mol.wt./1
- 30. One mole of acidified $K_2Cr_2O_7$ on reaction with excess KI will liberate mole (s) of I_2 .
 - (1) 6

- (2) 1
- (3)7
- (4) 3

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

PART-II: NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

- 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, KMnO₄ 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:

[NSEC-2000]

- (A) 31.6
- (B) 63.2
- (C) 126.4
- (D) 158
- 3. When 25 g of Na₂SO₄ is dissolved in 10³ 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 hydrochloric acid
- 5. The volume of water which must be added to 0.4 dm³ of 0.25 N oxalic acid in order to make it exactly decinormal is:
 - (A) 0.2 dm³
- (B) 0.4 dm³
- (C) 0.6 dm³
- (D) 0.8 dm³
- The quantity of electricity required to reduce $0.05 \text{ mol of MnO}_{4^-}$ to Mn^{2_+} in acidic medium would be (A) 0.01 F (B) 0.05 F (C) 0.15 F (D) 0.25 F [NSEC-2003]
- 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 it 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 its equivalent weight.
- 8. The normality of '20 volume' H₂O₂ solution is

[NSEC-2005]

- (A) 2.0
- (B) 2.5
- (C) 3.0
- (D) 3.5



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9.	required will be		prepare 100 ml of 2 N	•	tion, the weight [NSEC-2006]
	(A) 6.4 g	(B) 1.6 g	(C) 3.2 g	(D) 0.8 g	
10.		below, which statement	is true?		[NSEC-2007]
	2Fe + 3CdCl₂ ← 2F (A) Fe is the oxidizing a (C) Cd is the reducing a	agent	(B) Cd undergoes oxida (D) Fe undergoes oxida		
11.	, ,		ion according to the bala Mn^{2+} (aq) + $10CO_{2(g)}$ + 8		jiven below :
	solution?		re required to react with)208 M H ₂ C ₂ O ₄ [NSEC-2008]
	(A) 13.5 mL	(B) 18.5 mL	(C) 33.8 mL	(D) 84.4 mL	
12.	will be 0.2 N?		0 ml of a 0.205 N solution		esulting solution [NSEC-2008]
	(A) 40 mL	(B) 50 mL	(C) 100 mL	(D) 20 mL	
13.	$2MnO_4^-(aq) + 6H^+(aq)$		e ion according to the ba $O_2(g) + 8 H_2O(I)$. The vol $M H_2C_2O_4$ solution is (C) 33.8		0162 M KMnO ₄ [NSEC-2011]
14.	,	()	oncentration. The fluorid	()	
• ••	will be				[NSEC-2012]
	(A) 200	(B) 400	(C) 500	(D) 800	
15.	[Fe(C ₂ O ₄)] in acidic sol	ution is	eded to react completely		ferrous oxalate [NSEC-2012]
	(A) 1	(B) 2/5	(C) 3/5	(D) 4/5	
16.	= = :	$H^+ \to 2Mn^{2+} + 5O_2 + 8H_2C$)		
	II. $H_2O_2 + Ag_2O \rightarrow 2AQ$		otion in		INCEC 20141
	(A) oxidising in I and re (C) reducing in I as well		(B) reducing in I and ox (D) oxidising in I as wel		[NSEC-2014]
17.			f the density of the solution	on is 1.54 g cm∹	
	the H ₃ PO ₄ solution requ (A) 90mL	uired to prepare 1L of IN (B) 45mL	solution is. (C) 30mL	(D) 23mL	[NSEC-2015]
18.	The unbalanced equati	on for the reaction of P_4	S_3 with nitrate in aqueous	acidic medium	is given below.
		H ₃ PO ₄ + SO ₄ ²⁻ + NO			
	The number of mol of v (A) 18	vater required per mol of (B) 8/3	P ₄ S ₃ is (C) 8	(D) 28	[NSEC-2015]
19.			$H^+ \rightarrow 2Mn^{2+} + 10CO_2 +$	8H ₂ O, 20 mL o	
	react quantitatively with (A) 20 mL of 0.1 M oxa (C) 50 mL of 0.25 M ox	late	(B) 40 mL of 0.1 M oxa (D) 50 mL of 0.1 M oxa		[NSEC-2015]
20			. ,		propotod LICI
20.			d with 500 mL of 0.1 M F neutralization. Identify th (C) Sr		[NSEC-2016]
21.	diluted solution require		3. 10.0 cm ³ of this acid is um hydroxide solution for		
	(A) 98	(B) 38	(C) 19	(D) 49	[



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

Reagent added	Observation
dil. HCl	No change
aq. Na₂CO₃	White precipitate
Aq. Na ₂ SO ₄	No change

The water sample is likely to contain

[NSEC-2018]

(A) Ba²⁺

(B) Cu²⁺

(C) Li+

(D) Mg²⁺

23. An ion exchange resin, RH₂ can replace Ca²+ in hard water as RH₂ + Ca²+ → RCa²+ + 2H⁺. When a 1.0 L hard water sample was passed through the resin, all H⁺ ions were replaced by Ca²+ ions and the pH of eluted water was found to be 2.0. The hardness of water (as ppm of Ca²+) in the sample of water treated is [NSEC-2018]

(A) 50

(B) 100

(C) 125

(D) 200

PART - III: HIGH LEVEL PROBLEMS (HLP)

SUBJECTIVE QUESTIONS

- 1. A solution contains a mixture of Na₂CO₃ 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.
- 2. Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of KMnO₄ (20mL) acidified with dilute H₂SO₄. The same volume of the KMnO₄ solution is just decolourised by 10 mL of MnSO₄ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO₂. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H₂SO₄. Write the balanced equations involved in the reactions and calculate the molarity of H₂O₂.

[JEE 2001, 5/100]

ONLY ONE OPTION CORRECT TYPE

3.	0./ g of (NH ₄) ₂	SO ₄ sample was boiled	with 100 mL of 0.2	? N NaOH solution till a	all the NH₃ gas is
	evolved. The re	sulting solution was dilut	ed to 250 mL. 25 mL	_ of this solution was ne	utralized using 10
	mL of a 0.1 N H	2SO ₄ solution. The perce	ntage purity of the (N	IH ₄) ₂ SO ₄ sample is :	
	(A) 94.3	(B) 50.8	(C) 47.4	(D) 79.8	

4. A mixture of 0.02 mole of KBrO₃ and 0.01 mole of KBr was treated with excess of KI and acidified. The volume of 0.1 M Na₂S₂O₃ solution required to consume the liberated iodine will be :

(A) 1000 mL

(B) 1200 mL

(C) 1500 mL

(D) 800 mL

5. 10 mL of a H₂SO₄ 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 Na₂CO₃ for complete neutralization. The normality of original H₂SO₄ solution is :

(A) 12 N

(B) 11 N

(C) 3 N

(D) 0.275 N

- 6. Dichloroacetic acid (CHCl₂ COOH) is oxidised to CO₂, H₂O and Cl₂ 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
- 1.2 g of carbon is burnt completely in oxygen (limited supply) to produce CO and CO₂. 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%
- **8.** 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



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Equivalent Concept & Titration



- **9.** Phenolphthalein is not a good indicator for titrating :
 - (A) NaOH against oxalic acid

(B) NaOH against HCI

(C) Ferrous sulphate against KMnO₄

- (D) NaOH against H₂SO₄
- **10.** A 1 g sample of H₂O₂ solution containing x % H₂O₂ by mass requires x cm³ of a KMnO₄ solution for complete oxidation under acidic conditions. Calculate the normality of KMnO₄ solution.

(A) 0.588 N

(B) 0.294 N

(C) 0.882 N

(D) 0.735 N

11. A solution of H₂O₂ labelled as '20 V' was left open. Due to this some, H₂O₂ decomposed and volume strength of the solution decreased. To determine the new volume strength of the H₂O₂ 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 KMnO₄ solution under acidic condition. Calculate the volume strength of the H₂O₂ solution.

(A) 15.00 V

(B) 17.15 V

(C) 20.00 V

(D) 12.30 V

SINGLE AND DOUBLE VALUE INTEGER TYPE

12. If a mixture of Na₂CO₃ 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 H₂SO₄ used in the separate titration of same mixture in presence of methyl orange indicator.

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time: 1 Hr. Max. Marks: 66

Important Instructions

A. General:

- 1. The test is of 1 hour duration.
- 2. The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format:

- Each part consists of five sections.
- 4. Section-1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- 5. Section-2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- 6. Section 3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- 7. Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- 8. Section 5 contains 1 multiple choice questions. Question has two lists (list-1: P, Q, R and S; List-2: 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme:

- 9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (-1) mark will be awarded.
- 10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
- 11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.



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SECTION-1: (Only One option correct Type)

This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

- 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 KMnO₄ needed for same oxidation in acidic medium will be:
 - (A) $\frac{2}{5}$ V₁
- (B) $\frac{5}{2}$ V₁
- (C) 113 V₁
- (D) can not be determined
- 2. Hg₅ (IO₆)₂ oxidizes KI to I₂ in acid medium and the other product containing iodine is K₂HgI₄. If the I₂ liberated in the reaction requires 0.004 mole of Na₂S₂O₃, the number of moles of Hg₅ (IO₆)₂ that have reacted is :
 - $(A) 10^{-3}$
- (B) 10⁻⁴
- (C) 2.5×10^{-4}
- (D) 2.5×10^{-2}
- 3. 10 mL of 1 N HCl is mixed with 20 mL of 1 M H₂SO₄ and 30 mL of 1 M NaOH. The resultant solution has :
 - (A) 20 meg of H⁺ ions

(B) 20 meq of OH-

(C) 0 meg of H+ or OH-

- (D) 30 milli moles of H+
- 4. 20 mL of H_2O_2 after acidification with dilute H_2SO_4 required 30 mL of N/12 KMnO₄ 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
- 5. x gram of pure As_2S_3 is completely oxidised to respective highest oxidation states by 50 mL of 0.1 M hot acidified KMnO₄, 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
- 6. During the titration of a mixture of Na₂CO₃ and NaHCO₃ 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
- 7. 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

Section-2: (One or More than one options correct Type)

This section contains 5 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

- 8. 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) I₂ gets reduced to I-

- (D) I₂ gets oxidised to I-
- **9.** Which of the following relations is/are correct for solutions?
 - (A) 3 N Al₂(SO₄)₃ = 0.5 M Al₂(SO₄)₃
 - (B) 3 M H₂SO₄ = 6 N H₂ SO₄
 - (C) 1 M H_3 $PO_4 = 1/3$ N H_3PO_4
 - (D) 1 M Al₂ (SO₄)₃ = 6 N Al₂(SO₄)₃
- **10.** Which of the following statements is/are correct:
 - (A) 0.2 moles of KMnO₄ will oxidise one mole of ferrous ions to ferric ions in acidic medium.
 - (B) 1.5 moles of KMnO₄ 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 KMnO₄ 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.

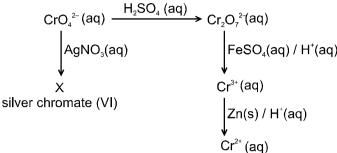


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- H₂C₂O₄ and NaHC₂O₄ behave as acids as well as reducing agents. Which are the correct statements?
 (A) equivalent weight of H₂C₂O₄ and NaHC₂O₄ are equal to their molecular weights when behaving as reducing agents.
 - (B) 100 ml of 1 (N) solution of each is neutralised by equal volume of 1 (M) Ca(OH)2
 - (C) 100 ml of (N) solution H₂C₂O₄ 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) KMnO₄
- **12.** 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 Ag₂CrO₄.
- (B) The minimum mass of zinc required to reduce 0.1 mole of Cr³⁺ to Cr²⁺ is 6.54 g.
- (C) The conversion of CrO₄²⁻ into Cr₂O₇²⁻ 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 FeSO₄.

Section-3: (One Integer Value Correct Type.)

This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

- **13.** A 3 mole mixture of FeSO₄ and Fe₂(SO₄)₃ required 100 mL of 2M KMnO₄ solution in acidic medium. Find the mole of FeSO₄ in the mixture.
- 14. A 7.1 g sample of bleaching powder suspended in H₂O 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 NH₂OH 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 KBrO₃ (converted to Br⁻), requiring 40 mL $Na_2S_2O_3$ solution. What is the molarity of $Na_2S_2O_3$ solution ? (Molar mass of KBrO₃ = 167 g mol⁻¹)
- 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 $\frac{x}{10}$.

SECTION-4: Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)



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Paragraph for Questions 19 to 21

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 (ℓ)

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).

19. How many mI of 1N HCl are required for X milimoles of Na₂CO₃ with methyl orange indicator

(A) X ml

(B) 2 X ml

(C) 3 X ml

(D) 4X ml

20. How many ml of 1N HCl are required for X milimoles of NaOH + Y milimoles of Na₂CO₃ + Z milimoles of NaHCO₃ 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

21. 25 ml of Na₂CO₃ solution requires 100ml of 0.1M HCl to reach end point with phenolphthalein indicator. Molarity of HCO₃- ions in the resulting solution is

(A) 0.008 M

(B) 0.04M

(C) 0.16M

(D) 0.08M

SECTION-5: Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct.

22. 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-l		List-II						
(1)	Sn ⁺² + MnO ₄ ⁻ (acidic)	(n)	Amount of oxidant available decides the number of						
(A)	3.5 mole 1.2 mole	(p)	electrons transfer						
(D)	H ₂ C ₂ O ₄ + MnO ₄ ⁻ (acidic)	(a)	Amount of reductant available decides the number of						
(B)	8.4 mole 3.6 mole	(q)	electrons transfer						
(C)	S ₂ O ₃ ⁻² + I ₂	(r)	Number of electrons involved per mole of oxidant > Number						
(C)	7.2 mole 3.6 mole	(r)	of electrons involved per mole of reductant						
(D)	Fe ⁺² + Cr ₂ O ₇ ⁻² (acidic)	(c)	Number of electrons involved per mole of oxidant < Number						
(D)	9.2 mole 1.6 mole	(s)	of electrons involved per mole of reductant.						

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

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



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APSP Answers

				PA	RT - I				
1.	(2)	2.	(2)	3.	(2)	4.	(4)	5.	(1)
6.	(1)	7.	(3)	8.	(3)	9.	(4)	10.	(2)
11.	(4)	12.	(3)	13.	(1)	14.	(2)	15.	(4)
16.	(2)	17.	(1)	18.	(2)	19.	(1)	20.	(3)
21.	(3)	22.	(2)	23.	(2)	24.	(1)	25.	(2)
26.	(2)	27.	(1)	28.	(1)	29.	(1)	30.	(4)
				PAI	RT - II				
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)				
				PAF	RT - III				
1.	Na ₂ CO ₃ =	23.2 g/L, Na	aOH = 22.28 (g/L.		2.	0.1 M		
3.	(A)	4.	(B)	5.	(A)	6.	(B)	7.	(D)
8.	(A)	9.	(C)	10.	(A)	11.	(B)	12.	15
				PAF	RT - IV				
1.	(A)	2.	(C)	3.	(A)	4.	(A)	5.	(D)
6.	(A)	7.	(D)	8.	(BC)	9.	(ABD)	10.	(ACD)
11.	(CD)	12.	(ACD)	13.	1	14.	8	15.	3
16.	2	17.	3	18.	6	19.	(B)	20.	(D)
21.	(D)	22.	(A) - p, r;	(B) – q, r ; ((C) – p, q, r ;	(D) – q, r.			

APSP Solutions

PART - I

1. $\operatorname{Na_2 \overset{+2}{S}_2 O_3} \longrightarrow \operatorname{Na_2} \overset{+6}{S} O_4$

the total change in oxidation number = $4 \times 2 = 8$

$$\therefore \qquad \qquad \mathsf{E}_{\mathsf{Na}_2\mathsf{S}_2\mathsf{O}_3} = \frac{\mathsf{mol.\ wt.}}{\mathsf{V.\ f}} \ = \frac{\mathsf{M}}{\mathsf{8}}$$

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

CHCl₂COOH + NH₃ -----> CHCl₂COONH₄

From reaction, m.moles of NH₃ = m.moles of dichloroacetic acid = 100

$$\therefore$$
 Moles of NH₃ = $\frac{100}{1000}$ = 0.1

4. Equivalents of FeC_2O_4 = equivalents of KMnO₄

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

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

5. Equivalent of KMnO₄ = equivalent of FeSO₄ + equivalent of FeC₂O₄

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

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

6. meg of $Na_2CO_3 = meg$ 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 $V_f = 890.2 \text{ mL}$

 \therefore Volume of H₂O mixed = 890.2 – 400 = 490.2 mL

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

V.F. of
$$HNO_3 = (5-4) = 1$$

V.F. of
$$NH_{4^+} = [0 - (-3)] = 3$$

so molar ratio of HNO₃ and NH₄+ is 3:1.

1 mole (NH₄)₂SO₄ is found to contain 2 mole of NH₄+

So, required moles of HNO₃ is $3 \times 2 = 6$ mole.

8. $H_2C_2O_4$. $2H_2O = 2 + 24 + 64 + 36 = 126$ and Equivalent wt. $= \left\lceil \frac{126}{2} \right\rceil$

$$0.2 = \frac{W \times 1000}{\left(\frac{126}{2}\right) \times 50}$$

∴
$$W = 0.63 g$$

- 9. $HNO_3 \longrightarrow NH_3 : V.f. \text{ of } HNO_3 = 8$ Eq. wt. = M/8.
- 10. $NH_2OH \longrightarrow N_2O$ -1 +1 $\therefore V.f. \text{ of } NH_2OH = 2$ $\therefore Eq \text{ wt } = M/2$
- 11. $Ca(HCO_3)_2 + CaO \longrightarrow 2CaCO_3 \downarrow + H_2O$ $\frac{324}{162} = n_{CaO} = 2$
- 12. $meq H_2O_2 = meq I_2$ $N \times 5 = \frac{0.508 \times 2}{254} \times 1000 \text{ or Normality} = 0.8 \text{ N}$ $Volume \text{ strength} = 5.6 \times N = 5.6 \times .8 = 4.48 \text{ V}.$
- 13. $8KMnO_4 + 3Na_2S_2O_3 + H_2O \rightarrow 2KOH + 8MnO_2 + 3Na_2SO_4 + 3K_2SO_4$
- Reduction $BiO_{3}^{-} + Mn^{2^{+}} \longrightarrow Bi^{3^{+}} + MnO_{4}^{-}$ Oxidation
 (i) $2e + 6H^{+} + BiO_{3}^{-} \longrightarrow Bi^{3^{+}} + 3H_{2}O$
 - (ii) $4H_2O + Mn^{2+} \longrightarrow MnO_4^- + 8H^+ + 5e$
 - (i) \times 5 + (ii) \times 2, we get 14 H⁺ + 5 BiO₃⁻ + 5Mn²⁺ \longrightarrow 5Bi³⁺ + 2MnO₄⁻ + 7 H₂O Hence, (2) is the correct balanced reaction.
- 15. m.eq. of H₂SO₄ = m.eq. of NaOH $\frac{98 \times 1.84 \times 10}{98} \times 2 \times 10 = 2 \times V_1$ $V_1 = 184 \text{ mL}$
- 16. 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 MnSO₄ = +2; O.N. of Mn in MnO₂ = +4).
- 17. (1) Equilivalents of $H_2C_2O_4.2H_2O$ in 10 mL = Equivalents of NaOH $\left(\frac{6.3}{126/2} \times \frac{1000}{250}\right) \times \frac{10}{1000} = 0.1 \times V \text{ (in litre)}$ $\therefore \qquad V = 0.04 \text{ L} = 40 \text{ mL}.$
- 18. O₃ will oxidise H₂O₂ into oxygen, hence radioacitve oxygen of H₂O₂ will go only in oxygen, not in water. Half reactions: O₃ + 2H⁺ + 2e⁻ \longrightarrow O₂ + H₂O ; $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$
- **19.** (HCl, HNO₃, H₃PO₂, H₃BO₃) H₂SO₄, H₂SO₃, H₃PO₃, H₄P₂O₅ are diprotic. HCl, HNO₃, H₃PO₂, H₃BO₃ are monoprotic.
- 20. $\bigcup_{\substack{(-1) \\ (-1) \\ (-1)}}^{(-2)} \bigcup_{\substack{(-1) \\ (+6)}}^{(-2)} \bigcup_{\substack{(-1) \\ (-1)}}^{(-1)}$



21. 70% by weight means

70 g of orthophosphoric acid is present in 100 g acid

$$\begin{split} N &= \frac{w}{Eq. \ wt.} \times \frac{1000}{V_{(cc)}} \\ w &= 70 \text{ g} \\ Eq. \ wt. = \frac{mol. \ mass}{no. \ replacable \ H-atoms} = \frac{98}{3} \\ V &= \frac{mass}{density} = \frac{100}{1.54} \\ N &= \frac{70 \ \times \ 3 \ \times \ 1000 \ \times \ 1.54}{98 \ \times \ 100} = 33 \ N \end{split}$$

22. Normality of a mixture (N) =
$$\frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

Normality(N₁) of H₂SO₄ = molarity × basicity = $0.2 \times 2 = 0.4 \text{ N}$

$$N_2 = 0.2 \times 1 = 0.2 \text{ N}$$

$$V_1 = 100 \text{ mL}, V_2 = 200 \text{ mL}$$

$$N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} = \frac{40 + 40}{300} = \frac{80}{300} = 0.2670 \text{ N}$$

Normality of mixture of acid and base (N')

$$(N') = \frac{N_1 V_1 \sim N_2 V_2}{V_1 + V_2}$$

- 23. 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.
- 24. In presence of phenoplhthalein,

$$\frac{1}{2}$$
 meq. of Na₂CO₃ = meq. of HCl

$$2 \times 40 \times 0.05 \times \frac{1}{2} = X \times 0.05$$

$$\therefore x = 40 \text{ mL}$$

with M.O.

Meg. of Na₂CO₃ + Meg. of NaHCO₃ = Meg. of HCl

$$2 \times 40 \times 0.05 + 40 \times 0.05 = y \times 0.05$$

$$y = 120 \text{ mL}$$

$$\therefore$$
 (y - x) = 80 mL

- **25.** During oxidation of H_2O_2 , O-O bond is not broken.
- **26.** Suppose the molecules of Na₂CO₃ and NaHCO₃ in a mixture are 'a'. milli-equivalent of HCI

$$N_1V_1 + N_2V_2 = NV$$

$$a \times 2 \times 1000 + a \times 1 \times 1000 = 0.1 \text{ V}$$

 $3a = 10^{-4} \text{ V}$ (i)

 $[:: N = basicity/acidity \times M]$

wt. of $Na_2CO_3 + wt.$ of $NaHCO_3 = 1$ g

(\therefore wt. of mixture = 1 g)

$$\Rightarrow$$
 a × 106 + a × 84 = 1

$$a = 5.26 \times 10^{-3}$$
(ii)

From Eqs. (i) and (ii) we have $3 \times 5.26 \times 10^{-3} = 10^{-4} \text{V} \implies \text{V} = 157.8 \text{ mL}$

27. KCN + Fe $(CN)_2 \longrightarrow K_4[Fe(CN)_6]$ This is not redox reaction.

28.
$$Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$$
; v.f. of $Cl_2 = \frac{2 \times 10}{2 + 10} = \left(\frac{5}{3}\right)$

$$\therefore$$
 Eq. wt. of Cl₂ = $\frac{71}{5/3}$ = 42.6

29. Valency factor of $Cr_2O_7^{2-} = 6$

Equivalent weight =
$$\frac{\text{molecular weight}}{\text{v.f}} = \frac{\text{molecular weight}}{6}$$

30. $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ (v.f.=6) (v.f.=2)

Equivalents of $K_2Cr_2O_7$ = equivalents of I_2

$$1 \times 6 = \text{moles of } I_2 \times 2$$

Moles of $I_2 = 3$

PART - III

1. At phenolphthalein end point

eq. of Na₂CO₃ + eq. of NaOH = eq. of HCl used

Let x mole of Na₂CO₃ 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 Na₂CO₃ is 1 when phenolphthalein is used)

At Methyl orange (MeOH) end point,

eq. of Na₂CO₃ + 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 Na₂CO₃ 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 Na₂CO₃ in 25 mL = $5.475 \times 10^{-3} \times 106$

wt. of Na₂CO₃ 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.

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

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

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

 \therefore meg. of MnO₂ = meg of Na₂C₂O₄ = 10 × 0.2 × 2 = 4

$$\therefore$$
 millimoles of MnO₂ = $\frac{4}{2}$ = 2

$$\begin{bmatrix} Mn^{4+} + 2e \rightarrow Mn^{2+} \\ \therefore Valency & factor & of & MnO_2 = 2 \end{bmatrix}$$

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 $MnO_2 \times (2/5) = 4/5$

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

$$\therefore \text{ millimoles of H}_2O_2 = \text{millimoles of KMnO}_4 \times \frac{5}{2} = \frac{4}{5} \times \frac{5}{2} = 2$$

$$\therefore \qquad \qquad M_{H_2O_2} \; \times 20 = 2 \quad \text{ or } \quad M_{H_2O_2} \; = \textbf{0.1 M}$$

Equivalent Concept & Titration



m.eq of $(NH_4)_2 SO_4 + m.eq$ of $H_2 SO_4 = m.eq$ of NaOH

(m.moles × 2) + (0.1 × 10 ×
$$\frac{250}{25}$$
) = 0.2 × 100

m.mole of $(NH_4)_2 SO_4 = 5$

wt. of
$$(NH_4)_2 SO_4 = \frac{5}{1000} \times 132 = 0.66 g$$

- % of $(NH_4)_2 SO_4 = \frac{0.66}{0.7} \times 100 = 94.28 \% \approx 94.3 \%$
- 4. $BrO_3^- + 6l^- \longrightarrow 3l_2 + Br^-$

moles of
$$I_2 = 3 \times \text{moles of KBrO}_3$$

∴ moles of
$$I_2 = 0.02 \times 3 = 0.06$$

Eq of $I_2 = \text{Eq of Hypo}$
 $0.06 \times 2 = 0.1 \times \text{V}$

$$V = 1.2 L = 1200 mL$$

meq of H_2SO_4 = meq of NaOH + meq of Na₂CO₃ 5.

$$N \times 25 = 0.5 \times 50 + \frac{0.265}{106/2} \times 10^3$$

or
$$N = 1.2$$

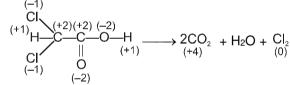
In original H₂SO₄ solution

$$N_1V_1 = N_2V_2$$

or
$$N_1 \times 10 = 1.2 \times 100$$

or
$$N_1 = 12 N$$

6.



- v.f. of dichloroacetic acid = 2(4-2) + 2(0-(-1)) = 6m.eq. of dichloroacetic acid = m.eq. of oxidising agent = 600
- m.moles of dichloroacetic acid = $\frac{600}{6}$ = 100 ∴.

From reaction, m.moles of NH₃ = m.moles of dichloroacetic acid = 100

$$\therefore$$
 Moles of NH₃ = $\frac{100}{1000}$ = 0.1

7. t = 0

$$t = 0$$
 0.1 $t = t$ 0 x $(0.1 - x)$

$$5CO + I_2O_5 \longrightarrow 5CO_2 + I_2 \qquad(ii)$$

$$t = 0 \qquad x$$

$$t = t \qquad 0$$

$$\begin{array}{ccc} & 0 & & x/5 \\ & & I_2 + 2Na_2S_2O_3 & \longrightarrow & Na_2S_4O_6 + 2Na_1 \end{array}$$

moles of I₂ liberated =
$$\frac{1}{2}$$
 × moles of hypo consumed = $\frac{1}{2}$ × 120 × 10⁻³ × 0.1 = 60 × 10⁻⁴

So,
$$x = 5 \times 60 \times 10^{-4} = 0.03$$
 moles (from reaction (ii) : $5 \times$ mole of $I_2 =$ mole of CO)

So, % of C forming CO =
$$\frac{0.03 \times 12}{1.2} \times 100 = 30\%$$

8. **KOH**

Na₂CO₃

a m.moles

b m.moles

m.eq. of KOH + m.eq. of Na₂CO₃ (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

(in presence of phenolphthalein) ...(i)

m.eq. of KOH + m.eq. of Na₂CO₃ (v.f. = 2) = m.eq. of HCl (in presence of methyl orange)

$$1 \times a + 2 \times b = 25 \times \frac{1}{20}$$

 $a + 2 \times b = 1.25$

(in presence of methyl orange)

by solving (i) & (ii), a = 0.25 m.moles.

: mass of KOH =
$$\frac{0.25}{1000} \times 56 = 0.014 \text{ g}$$

10. 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

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

$$N = 0.588 N$$

11. Assuming new normality of original H₂O₂ solution = X

After dilution to 100 mL of 10 mL of this solution, New normality will be (say X₁)

$$\therefore X \times 10 = X_1 \times 100$$

$$X_1 = \frac{X}{10}$$

.... (i)

10 mL of this dilute solution is titrated with 25 mL, 0.0245 M KMnO₄ 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 = $X \times 5.6 = 3.0625 \times 5.6 = 17.15 \text{ V}$

12. In presence of Hph indicator

m. eq. of HCl = m. eq. of Na₂CO₃ + m.eq. of NaOH

$$30 \times 0.1 = (a \times 1) + (a \times 1)$$

∴
$$a = 1.5$$

In presence of MeOH indicator

m. eq. of $H_2SO_4 = m$. eq. of $Na_2CO_3 + m$. eq. of NaOH

$$0.15 \times 2 \times V = (a \times 2) + (a \times 1)$$

$$V = 15 \text{ ml}$$

2.

PART - IV

Equivalent of K₂Cr₂O₇ = equivalent of N₂H₄ 1.

also equivalent of KMnO₄ = equivalent of N₂H₄

So, equivalent of K₂Cr₂O₇ = equivalent of KMnO₄

$$0.1 \times 6 \times V_1 = 0.3 \times 5 \times V_2$$
 : so $V_2 = 2/5 V_1$
Eq. of Hg₅ (IO₆)₂ = Eq. of I₂ = Eq. of Na₂S₂O₃

- (moles of Hg₅ (IO₆)₂) \times 16 = 0.004 \times 1 ∴.
- moles of Hg₅ (IO₆)₂ = 2.5×10^{-4} . ∴.



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Equivalent Concept & Titration



3. (A) Explanation : No. of meq of $H^+ = 10 \times 1 + 20 \times 2 = 50$ [:: H_2SO_4 , N = 2 M] No. of meq of $OH^- = 30 \times 1 = 30$

No. of meq of H⁺ left unreacted = 50 - 30 = 20 meq Hence, (A) is correct, (B), (C) and (D) are ruled out.

4. meq. of $KMnO_4 = meq$ of H_2O_2

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

- ∴ strength = N' × equivalent mass = $\frac{1}{8}$ × 17 = 2.12 g/L.
- 5. $5As_2S_3 + 28KMnO_4 + H^+ \longrightarrow 10H_3AsO_4 + 28Mn^{2+} + SO_4^{2-}$ m.moles of $KMnO_4 = 50 \times 0.1 = 5$

28 m.moles of KMnO₄ \longrightarrow 5 m.moles of As₂S₃

- ∴ 1 m.mole of KMnO₄ \longrightarrow 5/28 m.moles of As₂S₃
- $\therefore \qquad 5 \text{ m.mole of KMnO}_4 \longrightarrow \frac{5 \times 5}{28} \text{ m.moles of As}_2S_3$

Mass of As₂S₃ = x = 246 ×
$$\frac{5 \times 5}{28}$$
 × 10⁻³ = 0.22 g

7. $4CrO_5 + 6H_2SO_4 \longrightarrow 2Cr_2 (SO_4)_3 + 6H_2O + 7O_2$ (Balanced reaction)

∴ 1 mole CrO₅ produces 7/4 moles of O₂.

- 8. S undergoes increase in oxidation number from +2 to +2.5, while I undergoes decrease in oxidation number from 0 to -1.
- 9. Normality = Molarity \times v.f. \therefore 1M H₃PO₄ = 3N H₃ PO₄
- **10.** $MnO_4^- + 5e^- + 8 H^+ \longrightarrow Mn^{2+} + 4 H_2O$

 \Rightarrow 1 mole of MnO₄⁻ accepts 5 mole of e⁻

- 1/5 mole of MnO₄- accepts 1 mole of e-
- \Rightarrow 0.2 mole of MnO₄⁻ accepts 1 mole of e⁻
- \Rightarrow 0.6 mole of MnO₄⁻ accepts 3 mole of e⁻

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

⇒ 1 mole of Fe²⁺ will liberate 1 mole of e⁻

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

- \Rightarrow 1 mole of Cr₂O₇²⁻ will accept 6 moles of e⁻
 - 1 mole of FeC₂O₄ \longrightarrow Fe³⁺ + CO₂ + 3 e⁻
- ⇒ 1 moles of ferrous oxalate gives 3 moles of e⁻

(A) Formula of silver chromate (VI) will be Ag₂ CrO₄

 \Rightarrow 0.2 moles of KMnO₄ = 1/5 moles of KMnO₄ oxidises 1 mole of Fe²⁺ ion. (Tallies with statement A) 0.6 moles of KMnO₄ = 3/5 moles of KMnO₄ will oxidise 1 mole of ferrous oxalate. (Tallies with statement C)

1 mole of K₂Cr₂O₇ will oxidise 2 moles of ferrous oxalate. (Tallies with statement D) Hence ,(A) , (C) , (D) are correct while (B) is incorrect.

- -- ,() , () , () -- -- -- -- -- () -- --
- **(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 Cr³⁺ = 1) =
$$\frac{6.54}{2}$$
 g = 3.27 g

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

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

(D) Given reaction is correct.



12.

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13. Lets mole of $FeSO_4 = x$

Now, KMnO₄ oxidises only FeSO₄

equivalent of FeSO₄ = equivalent of KMnO₄

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

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

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

15. Hyponitrous acid = $H_2N_2O_2$

Basicity of Boric acid = y = 1

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

16. $NH_2OH \longrightarrow N_2O$

(-1)

oxidation number of nitrogen.

∴ x = 2

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 KBrO₃ = 12×10^{-2}

equivalent of Na₂S₂O₃ = equivalent of I₂

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

so molarity = 3 M.

18. $O_3 \longrightarrow I_2 + H_2O + O_2$. ΚI

v.f = 2v.f = 2

moles

$$I_2$$
 + $Na_2S_2O_3 \longrightarrow I^- + Na_2S_4O_6$

$$v.f = 2$$
 $M = 2$

$$V = 1L$$

$$v.f = 1$$

eq of O_3 = eq of I_2 = eq of hypo

$$\Rightarrow$$
 2 × x = 2

$$x = 1$$
 mole

$$\Rightarrow \qquad \text{weight \% of O}_3 = \frac{1 \times 48}{1 \times 48 + 1 \times 32} \times 100$$

$$=\frac{3}{5}\times 100 = 60\%$$
 Ans. $=\frac{60}{10} = 6$.

Ans. =
$$\frac{60}{10}$$
 = 6.

19. In presence of MeOH indicator, velence factor of Na₂CO₃ = 2

Equivalent of HCI = Equivalent of Na₂CO₃

$$NV = mole \times V.F$$

$$1 \text{ V} = \text{x} \times 10^{-3} \times 2$$

$$V = 2x \times 10^{-3} L = 2x ml$$

20. Equivalent of HCl = Equivalent of (NaOH + Na₂CO₃ + NOHCO₃]

$$1 \times V = [x \times 10^{-3} \times 1] + [Y \times 10^{-3} \times 2] + [Z \times 10^{-3} \times 1]$$

$$V = [x + 2Y + Z] \times 10^{-3} L$$

$$V = [X + 2Y + Z] mI$$

Equivalent Concept & Titration



21. In presence of phenophthalein indicator valence factor of Hph = 1

Equivalents of HCI = Equivalent of Na₂CO₃

 $N_1V_1 = N_2V_2$

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 Na₂CO₃ + HCl ---- NaHCO₃ + NaCl

in moles of Na₂CO₃ = MV

 $= 0.4018 \times 25 \times 10^{-3}$

= moles of NaHCO3

molarity of HCO₃⁻ =
$$\frac{\text{Moles of NaHCO}_3}{\text{Volume}} = \frac{0.4 \times 25 \times 10^{-3} \times 1000}{125} = 0.08$$

22. (A) Eq of Sn^{2+} = Moles × v.f. = $3.5 \times 2 = 7$.

Eq of $MnO_4^- = Moles \times v.f. = 1.2 \times 5 = 6$.

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 MnO₄⁻ = Moles \times v.f. = 3.6 \times 5 = 18.

Since H₂C₂O₄ (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 l_2 = Moles × v.f. = 3.6 × 2 = 7.2.

Since $S_2O_3^{2-}$ (RA) and I_2 (OA) both completely get consumed, so both the amount of reductant and oxidant decides the number of electron transfer.

Also, electron involved per mole of OA (2) > electron involved per mole of RA (1).

(D) Eq of Fe²⁺ = Moles \times v.f. = 9.2 \times 1 = 9.2.

Eq of $Cr_2O_7^{2-}$ = Moles × v.f. = 1.6 × 6 = 9.6.

Since Fe²⁺ (RA) is the LR, so the amount of reductant available decides the number of electron transfer.

Also, electron involved per mole of OA (6) > electron involved per mole RA (1).

