



CLASSROOM STUDY
PACKAGE

CHEMISTRY

REDOX &
EQUIVALENT
CONCEPTS

JEE EXPERT

Redox & equivalent Concepts

CONTENTS

THEORY	-	1 - 35
EXERCISE-I	-	36 - 38
EXERCISE-II	-	39 - 41
EXERCISE-III (Sections-A)	-	42 - 43
EXERCISE-III(Sections - B)	-	43 - 44
EXERCISE-IV	-	45 - 47
ANSWER KEY	-	48 -51

Redox & equivalent Concepts

1. REDOX REACTIONS :

A chemical reaction is a process that leads to the transformation of one set of chemical substances to another substance. Classically, chemical reactions encompass changes that strictly involve the motion of electron in the forming and breaking of chemical bonds. The concept of electron transfer can easily explain in the redox reactions in the case of ionic substances. However, for covalent compounds we use a new term oxidation number to explain oxidation and reduction or redox reactions. Redox reactions are the chemical reactions which involve both oxidation as well as reduction simultaneously. In fact oxidation and reduction go hand in hand.

2. OXIDATION AND REDUCTION :

2.1 Classical concept :

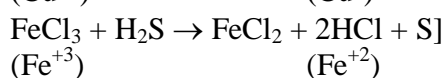
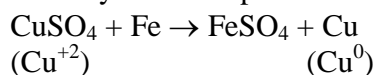
(A) Oxidation :

- (i) Oxidation is a chemical reaction in which oxygen is added
 $2\text{HNO}_2 + \text{O}_2 \rightarrow 2\text{HNO}_3$; $2\text{CH}_3\text{CHO} + \text{O}_2 \rightarrow 2\text{CH}_3\text{COOH}$
- (ii) Hydrogen is removed i.e. hydrogen becomes less
 $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$; $\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
- (iii) Electronegative element is added
 $2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3$; $2\text{Sb} + 3\text{Cl}_2 \rightarrow 2\text{SbCl}_3$
- (iv) Electropositive element is removed
 $2\text{NaI} + \text{H}_2\text{O}_2 \rightarrow 2\text{NaOH} + \text{I}_2$;

(B) Reduction

- (i) Addition of Hydrogen.
 $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$, $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
- (ii) Loss of Oxygen.
 $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3$ $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Cr} + \text{Al}_2\text{O}_3$
- (iii) Addition of electropositive element.
 $2\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$ $\text{CuCl}_2 + \text{Cu} \rightarrow \text{Cu}_2\text{Cl}_2$
- (iv) Loss of electronegative element decreases.
 $2\text{FeCl}_3 + \text{H}_2 \rightarrow 2\text{FeCl}_2 + 2\text{HCl}_2$ $\text{PbS} + \text{H}_2 \rightarrow \text{Pb} + \text{H}_2\text{S}$

- (v) Valency of electropositive element decreases.

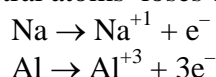


2.2 Modern Concept :

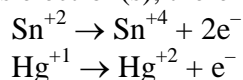
(A) Oxidation

The reaction in which an element or an atom or an ion or molecule loses electron(s) is called oxidation. Illustrative examples in various cases are given below

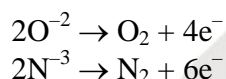
- (i) **Neutral atoms :** When a neutral atoms loses electron(s), it gets converted to a positive ion



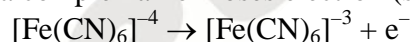
- (ii) **Cation :** When an anion loses electron(s), there is an increase in its positive charge.



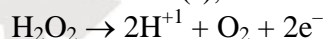
- (iii) **Anion** : When an anion loses electron(s) equal to its negative charge, it gets converted to a neutral atoms.



- (iv) **Complex Anion :** When a complex anion loses electron (s), its negative charge decreases.



- (v) **Molecule :** When a molecule loses electron(s), It breaks up into its constituents.



In oxidation reactions - positive charge increases and negative charge decreases .

(B) Reduction

The reaction in which an element or an atom or an ion (positive or negative) or molecule accepts electron(s), is called reduction. Illustrative examples in various cases are given below.

- (i) **Neutral Atom :** When a neutral element or atom accepts electron(s), it get converted into an anion



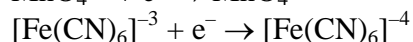
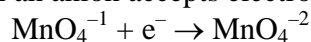
- (ii) **Cation** : When a cation accepts electron(s) equal to its charge, it gets converted into a neutral atoms



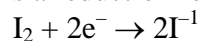
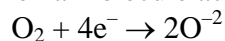
- (iii)** Similarly, when a cation accepts electron(s) than, its positive charge decreases. For example



(iv) **Anion** : When an anion accepts electron(s) its negative charge increases.



(v) **Molecule** : When a molecule accepts electron(s), it is a reduction reaction.



In reduction reactions - Positive charge decreases and negative charge increases .

3. Oxidation Number (O.N.) :

Definition :

Oxidation number of an element in a particular compound represents the number of electrons lost or gained by an element during its change from free state into that compound or Oxidation number of an element in a particular compound represents the extents of oxidation or reduction of an element during its change from free state into that compound.

Oxidation number is given positive sign if electrons are lost. Oxidation number is given negative sign if electrons are gained. Oxidation number represents real charge in case of ionic compound however, in covalent compounds it represents for imaginary charge.

3.1 Rule for deriving Oxidation number :

Following arbitrary rules have been adopted to derive Oxidation Number of elements on the basis of periodic properties of elements .

1. In uncombined state or free state, Oxidation Number of an element is zero.
2. In combined state Oxidation Number of
 - a. F is always -1
 - b. O is -2; In peroxides (-O-O-) it is -1. However in F_2O , it is +2
 - c. H is 1; In ionic hydrides it is -1.
 - d. metals is always positive.
 - e. alkali metals (IA e.g. Li, Na, K, Rb, Cs, Fr) is always +1.
 - f. alkaline earth metals (IIA e.g. Be, Mg, Ca, Sr, Ba, Ra) is always +2.
 - g. halogens in halides is always -1.
 - h. sulphur in sulphides in always -2.
3. The algebraic sum of all the Oxidation Number of elements in a compound is equal to zero. e.g. K_2MnO_4 $2 \times \text{Oxidation Number of K} + \text{Oxidation Number of Mn} + 4 (\text{Oxidation Number of O}) = 0$
4. The algebraic sum of all the Oxidation Numbers of elements in a radical is equal to net charge on that radical
e.g. $\text{C}_2\text{O}_4^{2-}$. $2 \times \text{Oxidation Number of C} + 4 (\text{Oxidation Number of O}) = -2$.

5. Variable oxidation number is most commonly shown by transition elements as well as by p-block elements.

Transition elements : Fe(+2 & +3), Cu(+1 & +2), Mn(+7, +6, +5, +4, +3, +2) etc.

p-block elements : As (+3 & +5); Sb(+3 & +5), Sn(+2 & +4) etc.

Group No.	Outer shell configuration	Common Oxidation Number
1	ns^1	0, +1
2	ns^2	0, +2
13	ns^2np^1	0, +1, +3
14	ns^2np^2	0, ± 1 , ± 2 , ± 3 , ± 4
15	ns^2np^3	0, ± 1 , ± 3 , +5
16	ns^2np^4	0, ± 2 , +4, +6
17	ns^2np^5	0, ± 1 , +3, +5, +7
18	ns^2np^6	0, (usually)

3.2 Exceptions

- Oxidation Number of Cl in Cl_2O is +1, because Cl acts as an electropositive elements in this
- Oxidation Number of Cl in ClF_3 = + 3
- Oxidation Number of Cl in $KClO_3$ = + 5
- Oxidation Number of I in IF_7 = + 7
- Oxidation Number of I in IF_5 = + 5
- Oxidation Number of Cl in Cl_2O_7 = + 7
- Oxidation Number of Cl in $HClO$ = + 1
- Oxidation Number of Cl in $HClO_2$ = + 3
- Oxidation Number of Cl in $HClO_3$ = + 5
- Oxidation Number of Cl in $HClO_4$ = + 7

3.3 Oxidation Number of radicals

Oxidation Number of radicals is equal to charge present on them. For example,

- Oxidation Number of sulphite (SO_3^{-2}), sulphate (SO_4^{-2}) thiosulphate ($S_2O_3^{-2}$), oxalate ($C_2O_4^{-2}$), carbonate (CO_3^{-2}), sulphite (S^{-2}) is equal to charge (-2) present on each of them.
- Oxidation Number of each of the anions, Cl^- , Br^- , I^- , NO_3^- , CN^- , OH^- , SCN^- , CH_3COO^- and HCO_3^- is -1 .
- Oxidation Number of each of the anions. PO_4^{-3} , BO_4^{-3} , AsO_4^{-3} . (Arsenate) and AsO_3^{-3} is -3 .
- Oxidation Number of each of the cations, CH_3^+ , NH_4^+ , Na^+ , K^+ is +1.
- Oxidation Number of each of the cations, Ca^{+2} , Mg^{+2} , Sr^{+2} and Fe^{+2} is +2.
- Oxidation Number of Al in $[Al(H_2O)_6]^{+3}$ is +3.

3.4 Oxidation no. of S element

1.	S in H_2S	$2(1) + x = 0$	$+2 + x = 0$	$x = -2$
2.	S in SO_2	$x + 2(-2) = 0$	$x - 4 = 0$	$x = +4$
3.	S in SO_4^{-2}	$x + 4(-2) = -2$	$x - 8 = -2$	$x = +6$
4.	S in SO_3^{-2}	$x + 3(-2) = -2$	$x - 6 = -2$	$x = +4$
5.	S in SF_6	$x + 6(-1) = 0$	$x - 6 = 0$	$x = +6$
6.	S in H_2SO_3	$2(-1) + x + 3(-2) = 0$	$+2 + x - 6 = 0$	$x = +4$

3.5 Oxidation no. if P element

1. Oxidation number of P in $P_4 = 0$
2. P in OP_4^{-3} : $x + 4(-2) = -x - 8 = -3$, $x = +5$
3. P in $NaHPO_2$: $1(1) + 1(1) + 2(-2) = 0 + 1 + 1 + x - 4 = 0$, $x = +2$
4. P in H_3PO_3 : $3(+1) + x + 3(-2) = 0 + 3 + x - 6 = 0$, $x = +3$
5. P in Na_2HPO_4 : $2(1) + 1(1) + x + 4(-2) = 0 + 2 + 1 + x - 8 = 0$, $x = +5$
6. P in $Mg_2P_2O_7$: $2(2) + 2x + 7(-2) = 0 + 4 + 2x - 14 = 0$, $2x = 10$, $x = +5$

3.6 Oxidation Number of Cr in its various compounds

1. Cr in CrO : $x - 2 = 0$, $x = +2$
2. Cr in Cr_2O_3 : $2x - 6 = 0$, $x = +3$
3. Cr in $CrSO_4$: $x - 2 = 0$, $x = +2$
4. Cr in $Cr_2(SO_4)_3$: $2x - 6 = 0$, $x = +3$
5. Cr in CrO_2Cl_2 : $2x - 6 = 0$, $x = +3$
6. Cr in $K_2Cr_2O_7$: $2 + 2x - 14 = 0$, $x = +6$
7. Cr in K_2CrO_4 : $2 + x - 8 = 0$, $x = +6$
8. Cr in $Cr_2O_7^{-2}$: $2x - 14 = -2$, $2x = 12$
9. Cr in CrO_4^{-2} : $x - 8 = -2$, $x = +6$
10. Cr in $Cr(NH_3)_4SO_4$: $x - 2 = 0$, $x = +2$ (Here, Oxidation Number of NH_3 is zero)
11. Oxidation Number of Cr in $[Cr(NH_3)_4]^{+2}$: $x = +2$
12. Oxidation Number of Cr in Na_2CrO_4 : $+2 + x - 8 = 0$, $x = +6$
13. Oxidation Number of Cr in $Cr(CO)_6$: $x = 0$ (Oxidation Number of Cr = 0)

3.7 Oxidation Number of Mn in its compounds :

1. Mn in MnO : $x - 2 = 0$, $x = +2$
2. Mn in Mn_2O_3 : $2x - 6 = 0$, $x = +3$
3. Mn in $MnSO_4$: $x - 2 = 0$, $x = +2$
4. Mn in $Mn_2(SO_4)_3$: $2x - 6 = 0$, $x = +3$
5. Mn in K_2MnO_4 : $+2 + x - 8 = 0$, $x = +6$
6. Mn in $KMnO_4$: $+1 + x - 8 = 0$, $x = +7$
7. Mn in $Mn(CO)_{10}$: $x + 10(0) = 0$, $x = 0$
8. Mn in MnO_4^- : $x - 8 = -1$, $x = +7$
9. Mn in $Mn(C_2O_4)_2 \cdot 2H_2O$: $x - 4 = 0$, $x = +4$

3.8 Comparison of Valency and Oxidation Number

Valency of an element represents the power or capacity of the element to combine with the other element. The valency of an element is numerically equal to the number of hydrogen atoms or chlorine atoms or twice the number of oxygen atoms that combine with one atom of that element. It is also equal to the number of electrons lost or accepted or shared by the atoms of an element.

In some cases (mainly in the case of electrovalent compounds), valency and oxidation number are the same but in other cases they may have different values. The difference between the two have been tabulated.

S.No.	Valency	Oxidation Number (State)
1.	It is the combining capacity of the element. No Plus or minus sign is attached to it.	Oxidation number is the charge (real or imaginary) present on the atom of the element when it is in combination. It may have plus or minus sign.
2.	Valency of an element is usually fixed.	Oxidation number of an element may have different values. It depends on the nature of compound in which it is present.
3.	Valency is always a whole number	Oxidation number of the element may be a whole number or fractional.
4.	Valency of the element is never zero except in noble gases.	Oxidation number of the element may be zero.

In the following compounds of carbon, the oxidation number varies from -4 to $+4$ but valency of carbon is 4 in all the compounds.

Compound	CH ₄	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
Oxidation number of carbon	-4	-2	0	$+2$	$+4$

4. OXIDATION AND REDUCTION IN TERMS OF OXIDATION NUMBER :

- Oxidation :** Chemical process involving increase in oxidation number.
- Reduction :** Chemical process involving decrease in oxidation number.
- Oxidising agent :** substance which undergoes decrease in oxidation number of one or more of its element.
- Reducing agent :** Substance which undergoes increase in oxidation number of one or more of its elements.
- List of same common oxidising agents.**

Reagent	Chemical change	Element changing O.N.	Change in O.N.
F ₂	$F_2 \rightarrow 2F^-$	F	$0 \rightarrow -1$
O ₃	$O_3 \rightarrow H_2O$	O	$0 \rightarrow -2$
H ₂ O ₂	$H_2O_2 \rightarrow H_2O$	O	$-1 \rightarrow -2$
KMnO ₄ /H ₂ SO ₄	$MnO_4^{-1} \rightarrow Mn^{+2}$	Mn	$+7 \rightarrow +2$
KMnO ₄ /KOH	$MnO_4^- \rightarrow MnO_4^{2-}$	Mn	$+7 \rightarrow +6$
KMnO ₄ /H ₂ O	$MnO_4^- \rightarrow MnO_2$	Mn	$+7 \rightarrow +4$
Conc. HNO ₃	$HNO_3 \rightarrow NO_2$	N	$+5 \rightarrow +4$
K ₂ Cr ₂ O ₇ /H ₂ SO ₄	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	Cr	$+6 \rightarrow +3$
KIO ₃ /HCl	$IO_3^- \rightarrow I^-$	I	$+5 \rightarrow -1$

6. List of some common reducing agents :

Reagent	Chemical change	Element changing O.N.	Change in O.N.
Metal atoms	$M \rightarrow M^{n+}$	M	$0 \rightarrow +n$
Alkali metals	$M \rightarrow M^+$	M	$0 \rightarrow +1$
Carbon	$C \rightarrow CO_2$	C	$0 \rightarrow +4$
S_8	$S_8 \rightarrow SO_2$	S	$0 \rightarrow +4$
$S_2O_3^{2-}$	$S_2O_3^{2-} \rightarrow S_4O_6^{2-}$	S	$+2 \rightarrow +2.5$
KI	$I^- \rightarrow I_2$	I	$1 \rightarrow 0$
$C_2O_4^{2-}$	$C_2O_4^{2-} \rightarrow CO_2$	C	$+3 \rightarrow +4$
H_2S	$H_2S \rightarrow S$	S	$-2 \rightarrow 0$

7. Metal ions in their lowest oxidation states such as Fe^{2+} , Sn^{2+} , Cu^+ , etc., also act as reducing agents.

Common Oxidising and Reducing Agents.

Oxidising agent	Effective Change	Decrease in O.N.
$KMnO_4$ in acid solution	$MnO_4^- \rightarrow Mn^{2+}$	5
$KMnO_4$ in alkaline solution	$MnO_4^- \rightarrow MnO_2$	3
$K_2Cr_2O_7$ in acid solution	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	3
dilute HNO_3	$NO_3^- \rightarrow NO$	3
concentrated HNO_3	$NO_3^- \rightarrow NO_2$	1
concentrated H_2SO_4	$SO_4^{2-} \rightarrow SO_2$	2
manganese (IV)oxide	$MnO_2 \rightarrow Mn^{2+}$	2
chlorine	$Cl \rightarrow Cl^-$	1
KIO_3 in dilute acid	$IO_3^- \rightarrow I$	5
KIO_3 in concentrated acid	$IO_3^- \rightarrow I^-$	6

Reducing agent	Effective change	Increase in O.N.
iron (ii) salts (acid)	$Fe^{2+} \rightarrow Fe^{3+}$	1
tin (ii) salts (acid)	$Sn^{2+} \rightarrow Sn^{4+}$	2
sulphites (acid)	$SO_3^{2-} \rightarrow SO_4^{2-}$	2
hydrogen sulphide	$S^{2-} \rightarrow S$	2
iodides (dilute acid)	$I^- \rightarrow I$	1
iodides (concentrated acid)	$I^- \rightarrow I^+$	2
metals, e.g. Zn	$Zn \rightarrow Zn^{2+}$	2
hydrogen	$H \rightarrow H^+$	1

Special cases of ON : Apart from above discussed molecules there are some special cases due to peroxide linkage or covalent or coordinate bond, the following rules are generally used.

4.1 Type I

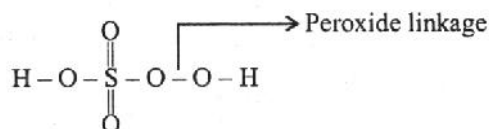
In molecules containing peroxide linkage in addition to element-oxygen bonds. For example,

- (i) Oxidation number of S in H_2SO_5
(Permonosulphuric acid or Caro's acid)

By usual method; H_2SO_5

$$2 \times 1 + x + 5 \times (-2) = 0 \text{ or } x = +8$$

But this cannot be true as maximum oxidation number for S cannot exceed +6. Since S has only 6 electrons in its valence shell. This exceptional value is due to the fact that two oxygen atoms in shows peroxide linkage as shown below,



Therefore the evaluation of o.n. of sulphur here should be made as follows,

$$\begin{array}{ccccccc} 2 \times (+1) & + & x & + & 3 \times (-2) & + & 2 \times (-1) \\ \text{(for H)} & & \text{(for S)} & & \text{(for O)} & & \text{(for O-O)} \\ \text{or} & & 2 + x - 6 - 2 = 0 & & \text{or} & & x = +6. \end{array}$$

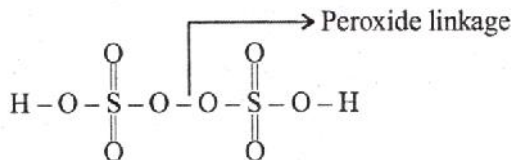
- (ii) Oxidation number of S in $\text{H}_2\text{S}_2\text{O}_8$
(Peroxidisulphuric acid or Marshall's acid)

By usual method; $\text{H}_2\text{S}_2\text{O}_8$

$$1 \times 2 + 2x + 8(-2) = 0$$

$$2x = +16 - 2 = 14 \text{ or } x = +7$$

Similarly Caro's acid, Marshall's acid also has a peroxide linkage so that in which S shows +6 oxidation state.



Therefore the evaluation of oxidation state of sulphur should be made as follow,

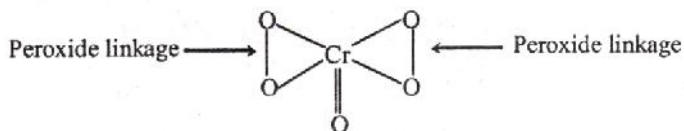
$$\begin{array}{ccccccc} 2 \times (+1) & + & 2 \times (x) & + & 6 \times (-2) & + & 2 \times (-1) = 0 \\ \text{(for H)} & & \text{(for S)} & & \text{(for O)} & & \text{(for O-O)} \\ \text{Or } 2 + 2x - 12 - 2 = 0 & & \text{or} & & x = +6. \end{array}$$

- (iii) Oxidation number of Cr in CrO_5
(Blue perchromate)

By usual method CrO_5 ; $x - 10 = 0$ or $x = +10$

This cannot be true as maximum O.N. of Cr cannot be more than +6. Since Cr has only five electrons in 3d orbitals and one electron in 4s orbital. This exceptional value is due to the fact that four oxygen atoms in CrO_5 are in peroxide linkage.

The chemical structure of CrO_5 is



Therefore, the evaluation of oxidation number of Cr should be made as follows

$$\begin{array}{l}
 x + 1 \times (-2) + 4(-1) = 0 \\
 \text{(for Cr)} \quad \quad \quad \text{(for O)} \quad \quad \text{(for O-O)} \\
 \text{or} \quad \quad \quad x - 2 - 4 = 0 \text{ or } x = +6.
 \end{array}$$

4.2 Type II

In molecules containing covalent and coordinate bonds, following rules are used for evaluating the oxidation numbers of atoms.

- (i) For each covalent bond between dissimilar atoms the less electronegative element is assigned the oxidation number of +1 while the atom of the more electronegative elements is assigned the oxidation number of -1.
- (ii) In case of a coordinate-covalent bond between similar or dissimilar atoms but the donor atom is less electronegative than the acceptor atom, an oxidation number of +2 is assigned to the donor atom and an oxidation number of -2 is assigned to the acceptor atom.

Conversely, if the donor atom is more electronegative than the acceptor atom, the contribution of the coordinate bond is neglected. Examples,

- (a) Oxidation number of C in $\text{HC} \equiv \text{N}$ and $\text{HN} \equiv \text{C}$

The evaluation of oxidation number of C cannot be made directly by usual rules since no standard rule exists for oxidation number of N and C

- (i) Oxidation number of carbon in $\text{H}-\text{N} \equiv \text{C}$

The contribution of coordinate bond is neglected since the bond is directed from a more electronegative N atom (donor) to a less electronegative carbon atoms (acceptor).

Therefore the oxidation number of N in $\text{HN} \equiv \text{C}$ remains -3 as it has three covalent bonds.

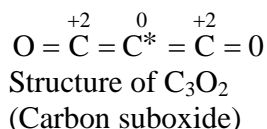
$$\begin{array}{l}
 1 \times (+1) + 1 \times (-3) + x = 0 \\
 \text{(for H)} \quad \quad \quad \text{(for N)} \quad \quad \text{(for C)} \\
 \text{Or} \quad \quad \quad 1 + x - 3 = 0 \text{ or } x = +2
 \end{array}$$

- (ii) Oxidation number of carbon in $\text{HC} \equiv \text{N}$

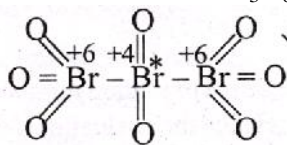
In $\text{HC} \equiv \text{N}$, N is more electronegative than carbon, each bond gives an oxidation number of -1 to N. There are three covalent bonds, the oxidation number of N in is taken as -3

$$\text{Now } \text{HC} \equiv \text{N} \therefore +1 + x - 3 = 0 \Rightarrow x = +2$$

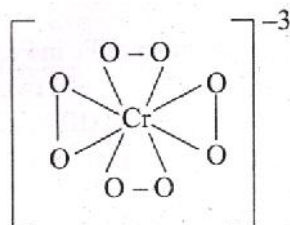
- (b) Oxidation number of carbon in C_3O_2



- (c) Oxidation number of Br in
- Br_3O_8

Structure of Br_3O_8 (tribromooctaoxide)

- (d) Oxidation number of Cr in
- $\text{K}_3[\text{CrO}_8]$



$$x - 8 = -3$$

$$x = 5$$

4.3 Type III

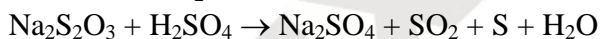
In a molecule containing two or more atoms of same or different elements in different oxidation states.

- (i) Oxidation number of S in
- $\text{Na}_2\text{S}_2\text{O}_3$

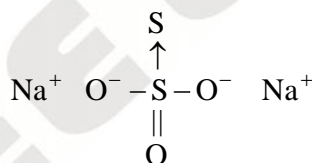
By usual method

$$\therefore 2 \times (+1) + 2 \times x + 3(-2) = 0 \text{ or } 2 + 2x - 6 = 0 \text{ or } x = 2.$$

But this is unacceptable as the two sulphur atoms in $\text{Na}_2\text{S}_2\text{O}_3$ cannot have the same oxidation number because on treatment with dil. H_2SO_4 , one sulphur atom is precipitated while the other is oxidised to SO_2 .



In this case, the oxidation number of sulphur is evaluated from concepts of chemical bonding.

The chemical structure of $\text{Na}_2\text{S}_2\text{O}_3$ is

Due to the presence of a co-ordinate bond between two sulphur atoms, the acceptor sulphur atom has oxidation number of -2 whereas the other S atom gets oxidation number of +2.

$$2 \times (+1) + 3 \times (-2) + x \times 1 + 1 \times (-2) = 0$$

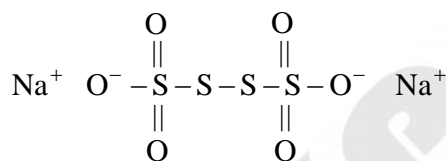
(for Na) (for O) (for S) (for coordinate S)

$$\text{or } +2 - 6 + x - 2 = 0 \text{ or } x = +6$$

Thus two sulphur atoms in $\text{Na}_2\text{S}_2\text{O}_3$ have oxidation number of -2 and +6.

- (ii) Oxidation number of chlorine in CaOCl_2 (bleaching powder)
In bleaching powder, $\text{Ca}(\text{OCl})\text{Cl}$, the two Cl atoms are in different oxidation states i.e. one Cl^- having oxidation number of -1 and the other as OCl -having oxidation number of +1.
- (iii) Oxidation number of N in NH_4NO_3
By usual method $\text{N}_2\text{H}_4\text{O}_3$; $2x + 4 \times (+1) + 3 \times (-1) = 0$
 $2x + 4 - 3 = 0$ or $2x = +1$ (wrong)
No doubt NH_4NO_3 has two nitrogen atoms but one N has negative oxidation number (attached to H) and the other has positive oxidation number (attached to O). Hence the evaluation should be made separately for NH_4^+ and NO_3^-

$$\begin{array}{ll} \text{NH}_4^+ & x + 4 \times (+1) = +1 \text{ or } x = -3 \\ \text{NO}_3^- & x + 3 \times (-2) = -1 \text{ or } x = +5. \end{array}$$
- (iv) Oxidation number of Fe in Fe_3O_4
In Fe_3O_4 , Fe atoms are in two different oxidation states. Fe_3O_4 can be considered as an equimolar mixture of FeO [iron (II) oxide] and Fe_2O_3 [iron (III) oxide]. Thus in one molecule of Fe_3O_4 , two Fe atoms are in +3 oxidation state and one Fe atom is in +2 oxidation state.
- (v) Oxidation number of S in sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$)
Its structure can be represented as follows,



The two S-atoms which are linked to each other have oxidation number zero. The oxidation number of other S-atoms can be calculated as follows

Let oxidation number of S is x.

$$\begin{array}{lll} 2 \times x & + & 2 \times 0 + 6 \times (-2) = -2 \\ \text{(for S)} & \text{(for S-S)} & \text{(for O)} \end{array}$$

$$X = +5.$$

Illustration :1

Determine Oxidation number of the element underlined in each of the following"

- (a) $\underline{\text{Fe}}\text{SO}_4$ (NH_4) $\underline{\text{S}}$ O_4 . $6\text{H}_2\text{O}$:
 (b) $\underline{\text{Fe}}_{0.94}\text{O}$:
 (c) $\text{Na}_2[\underline{\text{Fe}}(\text{CN})_5\text{NO}]$:
 (d) $\text{FeNO}(\text{H}_2\text{O})_5\underline{\text{S}}$ O_4 :

Sol. :

- (a) Put sum of Oxidation Number of $\text{SO}_4 = -2$
 Sum of Oxidation Numbers in $(\text{NH}_4)_2\text{SO}_4 = 0$
 Sum of Oxidation Numbers in $\text{H}_2\text{O} = 0$
 $X + (-2) + 0 + 0 = 0$;

$$\begin{array}{l} [(\text{NH}_4)_2\text{SO}_4 \text{ is a complete molecule}] \\ [\text{H}_2\text{O} \text{ is complete molecule}] \\ \therefore \quad x = +2 \end{array}$$

- (b) $x \times 0.94 + (-2) = 0$;

$$x = 200/94$$

(c) NO in iron complexes has NO^+ nature.

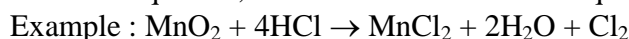
$$\begin{array}{ccccccc} \text{Thus } 2 \times 1 & + & x & + & 5 \times (-1) & + & 1 = 0 \\ \text{(for Na)} & & \text{(for Fe)} & & \text{(for CN)} & & \text{(for NO)}; \end{array} \quad \therefore x = +2$$

$$\text{(d) } x + 1 + 5 \times 0 + (-2) = 0; \quad \therefore x = +1$$

5. BASIC TERMS

5.1 Molecular equations :

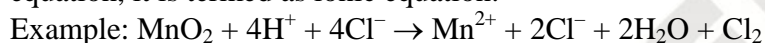
When the reactants and products involved in a chemical change are written in molecular forms in the chemical equation, it is termed as molecular equation.



In above example the reactants and products have been written in molecular forms, thus the equation is termed as molecular equation

5.2 Ionic equations :

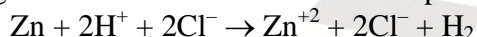
When the reactants and products involved in a chemical change are ionic compounds, these will be present in the form of ions in the solution. The chemical change is written in ionic forms in chemical equation, it is termed as ionic equation.



In above example the reactants and products have been written in ionic forms, thus the equation is termed as ionic equation .

5.3 Spectator Ions :

Species that are present in the solution but not take part in the reaction and are also omitted while writing the net ionic reaction are called spectator ions or bystander ions.



In this reaction ions are omitted and are called as spectator ions and appear on the reactant as well as product side.

5.4 Oxidising agent :

The substance (atom, ion or molecule) that gains electrons and is thereby reduced to a low valency state is called as oxidising agent.

5.5 Reducing agent :

The substance that loses electrons and is thereby oxidised to a higher valency state is called a reducing agent.

6. TYPES OF REDOX REACTIONS

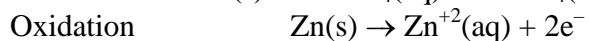
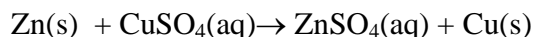
6.1 Direct and Indirect redox reaction :

Direct redox reaction : When both oxidation and reduction reactions occurs in same vessel

Indirect Redox reactions : When oxidation and reduction reactions occur in different vessels.

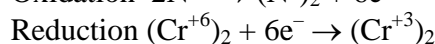
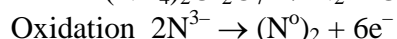
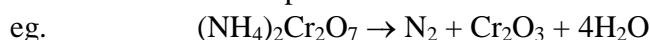
6.2 Inter molecular redox reactions

Two substances react one of them is oxidant and other is reductant.



6.3 Intra-molecular redox reactions

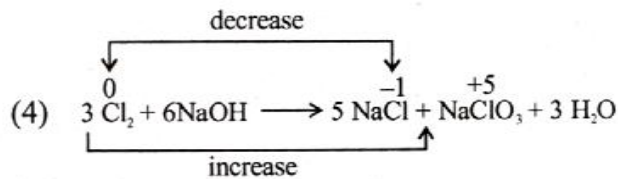
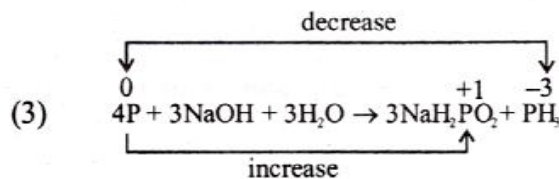
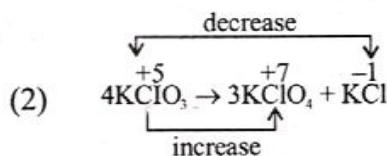
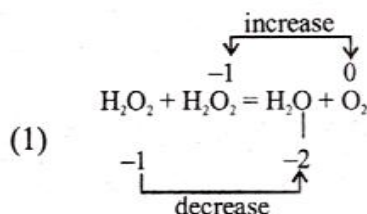
One element of a compound is oxidised and other element of the same compound is reduced.



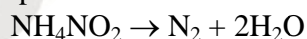
6.4 Disproportionation

One and the same substance may act simultaneously as an oxidising agent and as a reducing agent with the result that a part of its gets oxidised to a higher state and rest of it is reduced to lower state of oxidation. Such a reaction, in which a substance undergoes simultaneous oxidation and reduction is called disproportionation and the substance is said to disproportionate.

Following are the some examples of disproportionation



6.5 Comproportionation reaction



Nitrogen in this compound has -3 and +3 oxidation number so it is not a definite value, so its not a disproportion reaction. It is an example of comproportionation reaction which is a case of redox reaction in which a element from two different oxidation state gets converted into a single oxidation state.

Can you identify the difference between Intra-molecular redox and disproportionation reaction .

7. OXIDISERS AND REDUCERS

- 7.1. Substances that have the ability to oxidize other substances are said to be oxidative or oxidizing and are known as oxidizing agents, oxidants, or oxidizers. Put another way, the oxidant (oxidizing agent) removes electrons from another substance; i.e., it oxidizes other substances, and is thus itself reduced. And, Because it "accepts" electrons, it is also called an electron acceptor. Oxidants are usually chemical elements or substances with elements in high oxidation states

Important oxidising agents

- (i) Molecules made up of electronegative elements.
Example : O_2 , O_3 and X_2 (halogens).
- (ii) Compounds containing an element which is in the highest oxidation state.
Example : $KMnO_4$, $K_2Cr_2O_7$, $Na_2Cr_2O_7$, CrO_3 , H_2SO_4 ,
 HNO_3 , $NaNO_3$, $FeCl_3$, $HgCl_2$, $KClO_4$, SO_3 , CO_2 , H_2O_2 etc.
- (iii) Oxides of elements, MgO , CuO , CrO_3 , CO_2 , P_4O_{10} , etc
- (iv) Fluorine is the strongest oxidising agent.

7.2 Reducers

Substances that have the ability to reduce other substances are said to be reductive or reducing and are known as reducing agents, reductants, or reducers. The reductant (reducing agent) transfers electrons to another substance; e.i., it reduces others, and is thus itself oxidized. And, because it "donates" electrons it is also called an electron donor. Electron donors can also form charge transfer complexes with electron acceptors.

Important reducing agents

- (i) All metals e.g. Na, Zn, Fe, Al, etc
- (ii) A few non-metals e.g. C, H_2 , S etc.
- (iii) Hydrides : HCl , HBr , HI , H_2S etc
- (iv) A few compounds containing an element in the lower oxidation state (ous).
Example : $FeCl_2$, $FeSO_4$, $SnCl_2$, Hg_2Cl , Cu_2O etc
- (v) Metallic hydrides e.g. NaH , LiH etc.
- (vi) Organic compounds like $HCOOH$ and $(COOH)_2$ and their salts, aldehydes, alkanes etc.
- (vii) Lithium is the strongest reducing agent in solution.
- (viii) Cesium is the strongest reducing agent in absence of water

Substances which act as oxidising as well as reducing agents

Examples : H_2O_2 , SO_2 , H_2SO_3 , HNO_2 , $NaNO_2$, Na_2SO_3 , O_3 etc.

Tips for the identification of oxidising and reducing agents :

- (i) If an element is in its highest possible oxidation state in a compound, the compound can function as an oxidising agent.
Example : $KMnO_4$, $K_2Cr_2O_7$, HNO_3 , H_2SO_4 , $HClO_4$ etc.
- (ii) If an element is in its lowest possible oxidation state in a compound, the compound can function only as a reducing agent.
 H_2S , $H_2C_2O_4$, $FeSO_4$, $Na_2S_2O_3$, $SnCl_2$ etc.

- (iii) If an element is in its intermediate oxidation state in a compound, the compound can function both as an oxidising agent as well as reducing agent.
Example : H_2O_2 , H_2SO_3 , HNO_2 , SO_2 etc.
- (iv) If a highly electronegative element is in its highest oxidation state in a compound, that compound can function as a powerful oxidising agent
Example : KClO_4 , KClO_3 , KBrO_3 , KIO_3 etc
- (v) If an electronegative element is in its lowest possible oxidation state in a compound or in free state, it can function as a powerful reducing agent.
Example : I^- , Br^- , N^{3-} , etc.

Illustration : 2

Which of the following acts as both oxidant and reductant -

- (A) HNO_3 (B) HNO_2 (C) Both HNO_3 & HNO_2 (D) Neither HNO_3 nor HNO_2

Sol : (B)

O.N. of N in HNO_2 is +3

Max. O. N. of N is + 5

Min. O.N. of N is – 3

Thus O.N. of N in HNO_2 can show an increase or decrease as the case may be. That is why HNO_2 acts as oxidant and reductant both.

O.N. of N in HNO_3 is +5, Hence it can act only as an oxidant.

8. BALANCING OF REDOX REACTIONS :

There are a number of methods for balancing oxidation - reduction reactions, two main methods are discussed below :

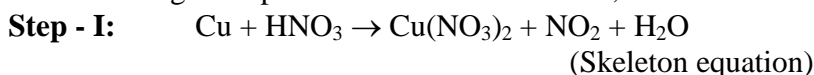
- (1) Oxidation number method (2) Ion-electron method

8.1 Oxidation number method :

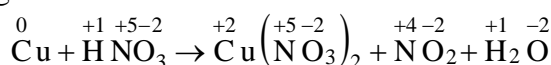
The method for balancing redox reactions by oxidation number change method was developed by Johnson. In a balanced redox reaction, total increase in oxidation number must be equal to the total decrease in oxidation number. This equivalence provides the basis for balancing redox reactions. This method is applicable to both molecular and ionic equations. The general procedure involves the following steps,

- (i) Write the skeleton equation (if not given, frame it) representing the chemical change.
- (ii) Assign oxidation numbers to the atoms in the equation and find out which atoms are undergoing oxidation and reduction. Write separate equations for the atoms undergoing oxidation and reduction.
- (iii) Find the change in oxidation number in each equation. Make the change equal in both the equations by multiplying with suitable integers. Add both the equations.
- (iv) First balance those substances which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally balance hydrogen and oxygen by putting H_2O molecules wherever needed.
The final balanced equation should be checked to ensure that there are as many atoms of each element on the right as there are on the left.
- (v) In ionic equations the net charges on both sides of the equation must be exactly the same. Use H^+ ion/ions in acidic reactions and OH^- ion/ions in basic reactions to balance the charge and number of hydrogen and oxygen atoms.

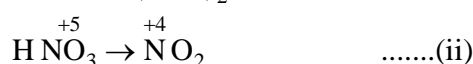
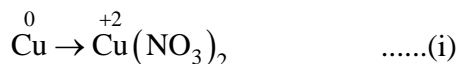
The following example illustrate the above rules,



Step - II : Writing the oxidation number of all the atoms.



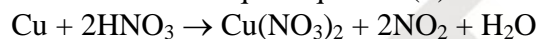
Step -III : Change in oxidation number has occurred in copper nitrogen.



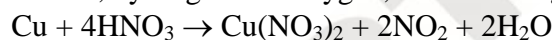
Increase in oxidation number of copper = 2 units per molecule Cu

Decrease in oxidation number of nitrogen = 1 units per molecule HNO_3

Step : IV To make increase and decrease equal equation (ii) is multiplied by 2.



Step : V Balancing nitrate ions, hydrogen and oxygen, the following equation is obtained.



This is the balanced equation.

8.2 Ion-electron method (half reaction method)

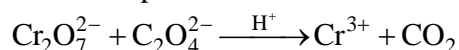
Jette and LaMev developed the method for balancing redox-reaction by ion electron method is 1927. It involves the following steps

- (i) Write down the redox reaction in ionic form.
- (ii) Split the redox reaction into two half reactions, one for oxidation and other for reduction.
- (iii) Balance each half reaction for the number of atoms of each element. For this purpose,
 - (a) Balance the atoms other than H and O for each half reaction using simple multiples.
 - (b) Add water molecules to the side deficient in oxygen and H^+ to the side deficient in hydrogen. This is down in acidic or neutral solution.
 - (c) In alkaline solution, for each excess of oxygen, add one water molecule to the same side and 2OH^- ions to the other side. If hydrogen is still unbalanced, add one OH^- ion for each excess hydrogen on the same side and one water molecule to the other side.
- (iv) Add electrons to the side deficient in electrons as to equalise the change on both sides.
- (v) Multiply one or both the half reactions by a suitable number so that number of electrons become equal in both the equations.
- (vi) Add the two balanced half reactions and cancel any term common to both sides .

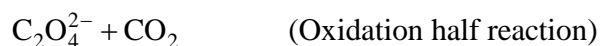
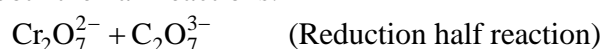
The following examples illustrate the above rules

In acidic medium

(a) consider the example



(b) Write both the half reactions.



- (c) Atoms other than H and O are balanced

$$\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$$

$$\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2$$
- (d) Balance O-atoms by the addition of H_2O to another side

$$\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

$$\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2$$
- (e) Balance H-atoms by the addition of H^+ ions to another side

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

$$\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2$$
- (f) Now, balance the charge by the addition of electrons (e^-)

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

$$\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{e}^-$$
- (g) Multiply equations by a constant to get number of electrons same on both side. In the above case second equation is multiplied by 3 and then added to first equation

$$\begin{array}{r} \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \\ 3\text{C}_2\text{O}_4^{2-} \rightarrow 6\text{CO}_2 + 6\text{e}^- \\ \hline \text{Cr}_2\text{O}_7^{2-} + 3\text{C}_2\text{O}_4^{2-} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{CO}_2 + 7\text{H}_2\text{O} \end{array}$$

In alkaline medium

- (a) Consider the reaction

$$\text{Cr}(\text{OH})_3 + \text{IO}_3^- \xrightarrow{\text{OH}^-} \text{I}^- + \text{CrO}_4^{2-}$$
- (b) Separate the two half reactions

$$\text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^{2-} \text{ (Oxidation half reaction)}$$

$$\text{IO}_3^- \rightarrow \text{I}^- \text{ (Reduction half reaction)}$$
- (c) Balance O-atoms by adding H_2O .

$$\text{H}_2\text{O} + \text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^{2-}$$

$$\text{IO}_3^- \rightarrow \text{I}^- + 3\text{H}_2\text{O}$$
- (d) Balance H-atom by adding H_2O to side having deficiency and OH^- to side having deficiency of H-atoms.

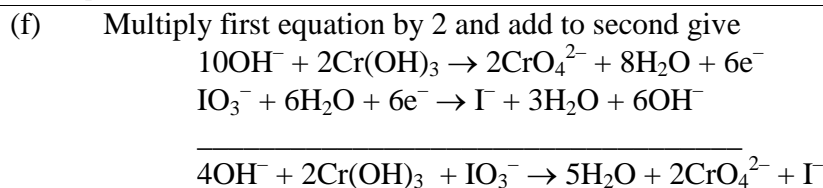
$$5\text{OH}^- + \text{H}_2\text{O} + \text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^{2-} + 5\text{H}_2\text{O}$$

$$5\text{OH}^- + \text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^{2-} + 4\text{H}_2\text{O}$$

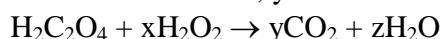
$$\text{IO}_3^- + 6\text{H}_2\text{O} \rightarrow \text{I}^- + 3\text{H}_2\text{O} + 6\text{OH}^-$$
or
$$\text{IO}_3^- + 3\text{H}_2\text{O} \rightarrow \text{I}^- + 6\text{OH}^-$$
- (e) Balance the charges by electrons

$$5\text{OH}^- + \text{Cr}(\text{OH})_3 \rightarrow \text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^-$$

$$\text{IO}_3^- + 6\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{I}^- + 3\text{H}_2\text{O} + 6\text{OH}^-$$

**Illustration : 3**

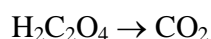
What will be the value of x, y and z in the following equation-



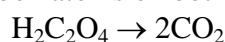
- (A) 2, 1, 2 (B) 1, 2, 2 (C) 2, 2, 1 (D) None

Sol : (B)

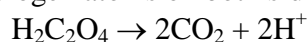
- (i) The half reaction for oxidation is ,



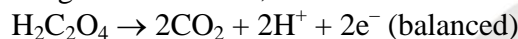
Balancing carbon atoms on both sides,



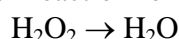
Balancing hydrogen atoms on both sides,



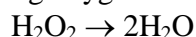
Balancing the charge on both sides,



- (ii) The half reaction for reduction is –



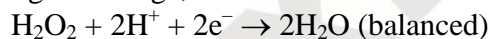
Balancing oxygen atoms on both sides,



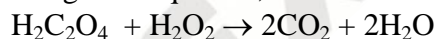
Balancing hydrogen atoms,



Balancing the charge,



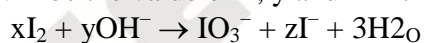
Now, adding both equation,



This is balanced equation.

Illustration : 4.

What will be the value of x, y and z in the following equation –

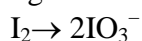


- (A) 3, 5, 6 (B) 5, 6, 3 (C) 3, 6, 5 (D) 6, 3, 5

Sol : (C)

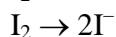


Balancing atoms of Iodine on two sides,



or $\text{I}_2 + 12\text{OH}^- \rightarrow 2\text{IO}_3^- + 6\text{H}_2\text{O}$

Balancing charge,



and $(\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-) \times 5$

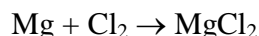
Adding, $6\text{I}_2 + 12\text{OH}^- \rightarrow 2\text{IO}_3^- + 10\text{I}^- + 6\text{H}_2\text{O}$
 or, $3\text{I}_2 + 6\text{OH}^- \rightarrow \text{IO}_3^- + 5\text{I}^- + 3\text{H}_2\text{O}$
 It is balanced equation.

9. EQUIVALENT WEIGHT :

Equivalent weight is primarily used in analytical chemistry because weighing errors are reduced. It is generally determined through the experiments. Equivalent weight is defined in various ways, depending upon the purpose of use.

(a) The equivalent weight of an element is the weight of the element that will combine with or replace directly or indirectly 1.0 gm of H, 35.5 gm of Cl or 8.0 gm of O or 108 gm of Ag.

(b) In the reaction



1 atom of Mg loses 2 electrons to become Mg^{2+} ion. If we start with 1 mole or 24 gm of Mg, we have N_A (6.023×10^{23}) number of Mg atoms which would lose $2N_A$ number of electrons and form N_A number of Mg^{2+} ions. Therefore, we get $2N_A$ number of electrons from 24 gm of Mg.

So, N_A number of electrons can be obtained from $\frac{24}{2} = 12$ gm of Mg. Thus the equivalent weight of Mg = 12.

Thus equivalent weight of an element is that weight of the element which loses or gained Avogadro number (N_A) of electrons.

(c) Equivalent weight of an element can also be calculating with the help of n factor or valency factor

$$\text{Equivalent weight of element} = \frac{\text{Atomic wt of the element}}{\text{n factor / Valency factor}}$$

Equivalent weight of compound

$$= \frac{\text{Formula wt of the compound}}{\text{n factor / Valency factor}}$$

n-Factor (n.f.) or Valency factor (v.f.) Calculation : The above use n-factor is defined for different cases as below :

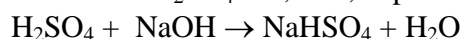
9.1 Acids

Acids are the species which furnish H^+ ions when dissolved in a solvent. For acids, n-factor is defined as the number of H^+ ions replaced by 1 mole of acid in a reaction. The n-factor for acids is not equal to its basicity ; i.e. the number of moles of replaceable H^+ atoms present in one mole of acid.

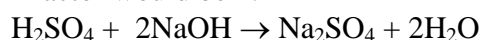
For example, n-factor of HCl = 1,

n-factor of HNO_3 = 1

n-factor of H_2SO_4 = 1, or 2, depending upon extent of reaction it undergoes.



Although one mole of H_2SO_4 has 2 replaceable H atoms but in this reaction H_2SO_4 has given only one H^+ ions, so its n-factor would be 1.



The n-factor of H_2SO_4 in this reaction would be 2.

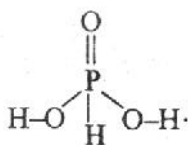
Similarly, n-factor of H_2SO_4 = 1 or 2

n-factor of H_2CO_3 = 1 or 2

n-factor of H_3PO_4 = 1 or 2 or 3

n-factor of H_3PO_3 = 1 or 2 because one of the H is not replaceable in H_3PO_3 .

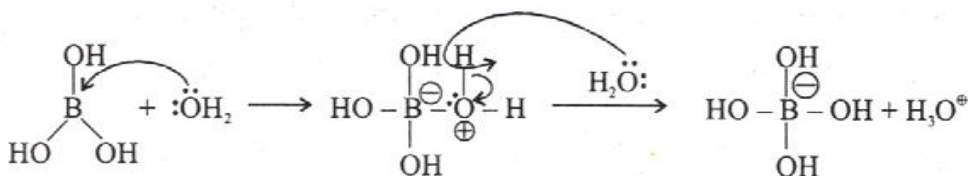
This can be seen using its structure



The H atoms which are linked to oxygen are replaceable while the H atom linked directly to central atom (P) is non replaceable.

n-factor of H_3BO_3 = 1

In H_3BO_3 , although all three H are linked to oxygen, yet all 3 H are not replaceable. Here, boron atom is electron deficient, so it acts as a Lewis acid. When H_3BO_3 is added to water, then oxygen atom of H_2O through its lone pair attack the boron atom, as follows



The net reaction is $\text{H}_3\text{BO}_3 + 2\text{H}_2\text{O} \rightarrow [\text{B}(\text{OH})_4]^- + \text{H}_3\text{O}^+$.

Thus, one mole of H_3BO_3 in solution gives only one mole of H^+ , so its n-factor is 1.

9.2 Bases

Bases are the species, which furnish OH^- ions when dissolved in a solvent. For bases, n-factor is defined as the number of OH^- ions replaced by 1 mole of bases in a reaction. The n-factor is not equal to its acidity i.e. the number of mole of replaceable OH^- ions present in 1 mole of base.

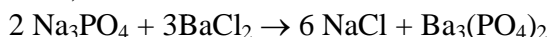
For example,

- n-factor of NaOH = 1
- n-factor of $\text{Zn}(\text{OH})_2$ = 1 or 2
- n-factor of $\text{Ca}(\text{OH})_2$ = 1 or 2
- n-factor of $\text{Al}(\text{OH})_3$ = 1 or 2 or 3
- n-factor of $\text{NH}_4(\text{OH})$ = 1

9.3 Salts

(i) When no atom undergoes change in oxidation state

The n-factor for such salt is defined as the total moles of cationic/anionic charge present in 1 mole of the salt. For the reaction,



n-factor of Na_3PO_4 in this reaction is 3

n-factor of BaCl_2 in this reaction is 2

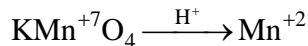
n-factor of NaCl in this reaction is 1

n-factor of $\text{Ba}_3(\text{PO}_4)_2$ in this reaction is 6

(ii) When only one atom undergoes change in oxidation state and goes in only one product

The n-factor of such salts is defined as the number of moles of electrons exchanged (lost or gained) by one mole of the salt.

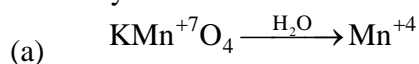
For example, let us calculate the n-factor KMnO_4 for the given chemical change.



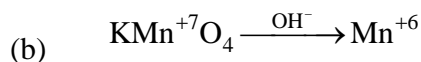
In this reaction, oxidation state of Mn changes from +7 to +2. Thus, KMnO_4 is acting as oxidising agent, since it is reduced.

$$\therefore \text{ n-factor of } \text{KMnO}_4 = |1 \times (+7) - 1 \times (+2)| = 5$$

Similarly



$$\text{ n-factor of } \text{KMnO}_4 = |1 \times (+7) - 1 \times (+4)| = 3$$



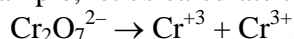
$$\text{ n-factor of } \text{KMnO}_4 = |1 \times (+7) - 1 \times (+6)| = 1$$

It can be seen that in all above chemical changes KMnO_4 is acting as oxidising agent, yet its n-factor is not same in all reactions. Thus, the n-factor of a compound is not fixed, it depends on the type and the extent of reaction it undergoes.

(iii) When only one atom undergoes change in oxidation state but goes in two products with the same oxidation state

In such case the n-factor is calculated in the same manner as in case (ii).

For example, let us calculate the n-factor of $\text{K}_2\text{Cr}_2\text{O}_7$ for the given chemical change.



In this reaction, state of Cr changes from +6 to +3 in both products.

$$\therefore \text{ n-factor of } \text{K}_2\text{Cr}_2\text{O}_7 = |2 \times (+6) - 2 \times (+3)| = 6$$

(iv) When only one atom undergoes change in oxidation state but goes in two products with different oxidation state

Consider a chemical change, $2\text{Mn}^{7+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$

Out of the two moles of Mn^{7+} , changes to mole Mn^{7+} change to Mn^{+4} by gaining 3 mole of electrons and the other mole of Mn^{7+} changes to Mn^{2+} by gaining 5 mole of electrons, so in all 8 mole of electrons are gained by 2 mole of Mn^{7+} . So each mole of Mn^{7+} has gained $8/2 = 4$ mole of electrons. Thus, 4 would be the n-factor of Mn^{7+} in this reaction.

If the reaction would have been



Out of 3 moles of Mn^{7+} , two mole of Mn^{7+} changes to Mn^{2+} by gaining 10 mole of electrons and one mole of Mn^{7+} changes to Mn^{4+} by gaining 3 mole of electrons. Thus each mole of Mn^{7+} have gained $13/3$ mole of electron. Therefore, the n-factor of Mn^{7+} in this reaction would be $13/3$.

Note that n-factor can be a fraction because it is not the number of electrons exchange but it is the number of moles of electrons exchanged which can be a fraction.

Now, if the reaction would have been $3\text{Mn}^{7+} \rightarrow \text{Mn}^{2+} + 2\text{Mn}^{4+}$. Thus, each mole of Mn^{7+} have gained $11/3$ mole of electron. Therefore, n-factor of Mn^{7+} in this reaction would be $11/3$.

Salts which react in a fashion that only one atom undergoes change in oxidation state but goes in two products with deferent state (in one product with same oxidation state and in other with different state than in the reactant)

For such reactions also, the n-factor calculation is not possible without the knowledge of balanced chemical reaction because n-factor of reactant would depend on the fact that how much of reactant underwent change to different oxidation state + y and how much of reactant remained in the same oxidation state + x

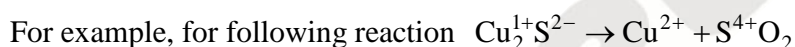
For example, if we have a chemical change as



In this reaction, 5 moles of electrons are gained by 2 moles of Mn^{+7} , so each mole of Mn^{+7} takes up $5/2$ mole of electrons. Therefore, n-factor of Mn^{+7} in this reaction would be $5/2$

- (v) **When two type of atoms in the salt undergoes change in oxidation state (Both the atoms are either getting oxidised or reduced)**

In this case, the n-factor of the salt will be the total number of mole of electrons lost or gained by one mole of the salt.



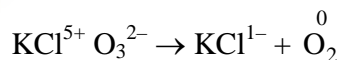
in which Cu^+ and S^{2-} both are getting oxidised to Cu^{2+} and S^{4+} respectively.

$$m \quad n\text{-factor of } \text{Cu}_2\text{S} = (1 \times 2) + (1 \times 6) = 8$$

- (vi) **When two atoms in the salt undergoes change in oxidation state (one atom is getting oxidised and the other is getting reduced)**

The n-factor of such a salt can be calculated either by taking the total number of moles of electrons gained by one mole of the salt.

For example, decomposition reaction of KClO_3 is represented as



In this reaction, O^{2-} is getting oxidised to O_2 and Cl^{5+} is getting reduced to Cl^{1-} . In each case, 6 mole of electrons are exchanged whether we consider oxidation reduction

$$n\text{-factor of } \text{KClO}_3 \text{ considering oxidation} = |3(-2) - 3(0)| = 6$$

$$\text{or } n\text{-factor of } \text{KClO}_3 \text{ considering reducing} = |1 \times (+5) - 1 \times (-1)| = 6$$

- (vii) **Salts or compounds which undergoes disproportionation reaction**

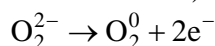
Disproportionation reactions can be divided into two types.

- (a) Disproportionation reactions in which moles of compound getting oxidised and reduced are same i.e. moles of oxidising agent and reducing agent are same. Then n-factor for such compounds is calculated

by either the number of mole of electrons lost or gained by one mole of the compound because in such a case, n-factor of the compound acting as oxidizing agent or as reducing agent would be same.

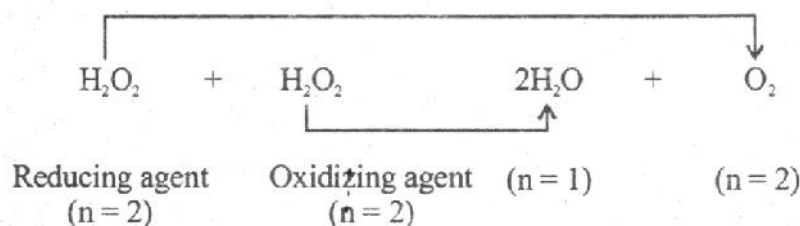
For example, $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

Out of 2 mole of H_2O_2 used in reaction, one mole of H_2O_2 gets oxidised to O_2 (oxidation state of O changes from -1 to -2). When 1 mole of H_2O_2 gets oxidised to O_2 , the half-reaction would be

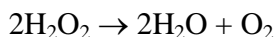


and when 1 mole of H_2O_2 gets reduced to H_2O the half-reaction would be $\text{O}_2^{2-} + 2\text{e}^- \rightarrow 2\text{O}^{2-}$

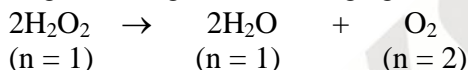
Thus, it is evident that one mole of H_2O_2 (which is either getting oxidised or reduced) will lose or gain 2 mole of electrons. Therefore, n-factor of H_2O_2 as oxidizing as well as reducing agent in this reaction is 2. Thus



Or when the reaction is written as



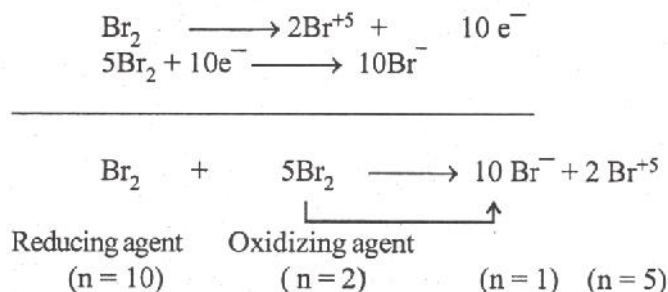
Where, H_2O_2 is not distinguished as how much of it functions as oxidizing agent and how much as reducing agent, then n-factor calculation can be done in the following manner. Find the number of electrons exchanged (lost or gained) using the balanced equation and divide it by the number of moles H_2O_2 involved in the reaction. Thus, the n-factor of H_2O_2 when the reaction is written without segregating oxidising and reducing agent is $2/2 = 1$



- (b) Disproportionation reactions in which moles of compound getting oxidised and reduced are not same.



In this reaction, the mole of electrons lost by the oxidation of some of the moles of Br_2 are same as the number of mole of electrons gained by the reduction of rest on the moles of Br_2 . Of the 6 moles of Br_2 used, one mole is getting oxidized, losing 10 electrons (as reducing agent) and 5 moles of Br_2 are getting reduced and accepts 10 moles of electron (as oxidizing agent)



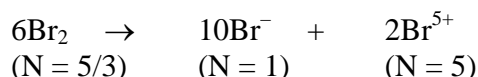
Thus, n-factor of Br_2 acting as oxidizing agent is 2 and that Br_2 acting as reducing agent has n-factor 10.

Or when the reaction is written as



Where, Br_2 is not distinguished as how much of it function as oxidizing agent and how much as reducing agent, then for calculating n-factor of compound in such reactions, first find the total number of electrons exchanged (lost or gained) using the balanced equation and divide it with the number of mole of Br_2 involved in the reaction to get the number of mole electrons exchanged by one mole of Br_2 .

In the overall reaction, the number of mole of electrons exchanged (lost or gained) is 10 and the moles of Br_2 used in the reaction are 6. Thus, each mole of Br_2 has exchanged $10/6$ or $5/3$ mole of electrons. Therefore, the n-factor of Br_2 when the reaction is written without segregation oxidising and reducing agent is $5/3$

**Illustration : 5**

In acting as a reducing agent, a piece of metal M weighing 16 grams gives up 2.25×10^{23} electrons, what is the equivalent weight of the metal

- (A) 42.83 (B) 21.33 (C) 83.32 (D) 32

Sol : (A)

N_A no of electron will removed by

$$= \frac{6.023 \times 10^{23}}{2.25 \times 10^{23}} \times 16 \text{ gm of metal M}$$

$$= 42.83 \text{ gm of metal M}$$

\therefore equivalent wt. of metal is 42.83

Illustration : 6

The equiv. wt of the salt

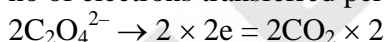
$\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (to be used as a reducing agent) is-

- (A) $\frac{\text{Mol.wt}}{1}$ (B) $\frac{\text{Mol.wt}}{2}$ (C) $\frac{\text{Mol.wt}}{3}$ (D) $\frac{\text{Mol.wt}}{4}$

Sol. (D)

Per mole of this salt contains 2 moles of $\text{C}_2\text{O}_4^{2-}$

\therefore no of electrons transferred per moles of this salt is



\therefore 'n' factor (as a reducing) of the given salt = 4

\therefore equiv. wt. of the given salt = $\frac{\text{Mol.wt}}{4}$

Illustration : 7

What weight of HNO_3 is needed to convert 62 gm of P_4 in H_2PO_4 in the reaction ?



- (A) 63 gm (B) 630 gm (C) 315 gm (D) 126 gm

Sol: (B)

$$\text{The equiv. wt. of } \text{P}_4 = \frac{31 \times 4}{5 \times 4} = \frac{31}{5}$$

$$\therefore 62 \text{ gm } \text{P}_4 = \frac{62 \times 5}{31} \text{ equiv. of } \text{P}_4$$

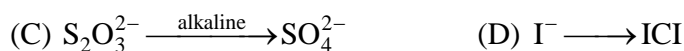
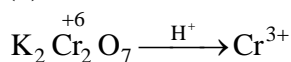
$$= 10 \text{ equiv of } \text{P}_4$$

$$\text{The equiv. wt of HNO}_3 = \frac{\text{mol. wt}}{1} = \frac{63}{1}$$

$$\therefore \text{the wt. of HNO}_3 \text{ required} \\ = 10 \times 63 = 630 \text{ gm}$$

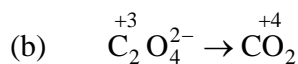
Illustration : 8

Calculate the n-factor of reactants in the given chemical changes.

**Sol.** (a)

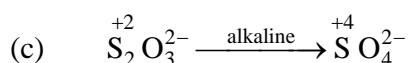
The oxidation state of Cr changes from +6 to +3

$$\therefore n = |2 \times (+6) - 2 \times (+3)| = 6$$



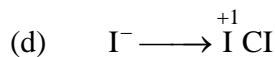
Carbon get oxidized from +3 to +4

$$\therefore n = |2 \times (+3) - 2 \times (+4)| = 2$$



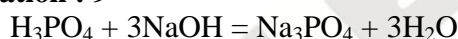
The oxidation state of sulphur changes from +2 to +6

$$\therefore n = |2 \times (+2) - 2 \times (+6)| = 8$$



I⁻ get oxidized to I⁺

$$\therefore n = |1 \times (-1) \times (+1)| = 2$$

Illustration : 9

As per the above mentioned equation what is the equivalent weight of H₃PO₄ ?

Sol : In the mentioned reaction 3 replacable H atoms present in H₃PO₄ are replaced by Na

$$\therefore \text{the } n = 3$$

$$\therefore \text{equiv. wt of H}_3\text{PO}_4 = \frac{\text{Mol. wt. of H}_3\text{PO}_4}{3} = \frac{98}{3} \text{ Ans.}$$

Illustration : 10

On heating 5×10^{-3} equiv. of $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$, 0.18 gm. of water is obtained, what is the value of x ?

Sol. Equiv. wt of $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$

$$= \frac{111 + 18x}{2} = 55.5 + 9x$$

$$\begin{aligned} m \quad & 5 \times 10^{-3} \text{ equiv of } \text{CaCl}_2 \cdot x\text{H}_2\text{O} \\ & = 5 \times 10^{-3} (55.5 + 9x) \text{ gm.} \\ & \text{Of } \text{CaCl}_2 \cdot x\text{H}_2\text{O.} \end{aligned}$$

$$\begin{aligned}
 \therefore \quad & \text{amount of water obtained} \\
 &= \frac{18x}{111+18x} \times 5 \times 10^{-3} (55 + 9x) \\
 &= 9x \times 5 \times 10^{-3} \\
 \therefore \quad & 9x \times 5 \times 10^{-3} = 0.18 \\
 \text{or} \quad & x = \frac{0.18}{9 \times 5} \times 10^3 = 4 \\
 \therefore \quad & x = 4 \text{ Ans.}
 \end{aligned}$$

10. LAW OF EQUIVALENCE

The law states that one equivalent of an element combined with one equivalent of the other, and in a chemical reaction equivalent and milli equivalent of reactants react in equal to give same no. equivalent or milli equivalent of products separately.

- (i) $aA + bB \rightarrow mM + nN$
 $\text{m.eq of A} = \text{m.eq of B} = \text{m.eq of M} = \text{m.eq. of N}$
- (ii) In a compound M_xN_y
 $\text{m.eq of } M_xN_y = \text{m.eq of M} = \text{m.eq of N}$

Illustration : 11

The number of moles of oxalate ions oxidized one mole of MnO_4^- ion in acidic medium.

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

Sol : (A)

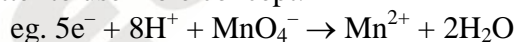
Equivalents of $\text{C}_2\text{O}_4^{2-} = \text{equivalents of } \text{MnO}_4^-$

$$x(\text{mole}) \times 2 = 1 \times 5$$

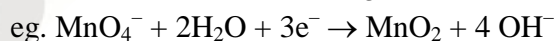
$$x = \frac{5}{2}$$

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.



$$\therefore \quad \text{Eq. wt. of } \text{MnO}_4^- = \frac{\text{MnO}_4^- (\text{mol. wt.})}{5}$$



$$\therefore \quad \text{Eq. wt. } \text{MnO}_4^- = \frac{\text{MnO}_4^-}{3}$$

Thus the no. of equivalents of MnO_4^- will be different in the above two cases but no. moles will be same.

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

11. REDOX TITRATION

Redox titration is another volumetric technique like neutralization titration, to determine the amount of a specific substance in an unknown sample. This involves oxidation-reduction reaction between the titer and titrant during titration. Oxidation-reduction reaction between ions in the solution can become the basis for the volumetric analysis, provided it fulfills the following conditions.

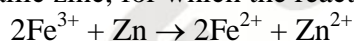
- (1) there is only one reaction under the given condition
- (2) The reaction goes essentially to completion at equivalence point
- (3) A suitable indicator (or other source) is available to locate the end point

The number of reactions fulfilling these conditions is very large. Fortunately, however the general principles involved are common to all and a limited study of only a few reactions is sufficient to give a good understanding of the whole redox analysis. Common methods of redox analysis fall in one of the following three categories :

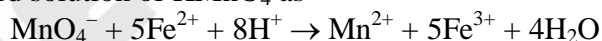
- (i) A solution of substance that is readily oxidized is treated by a standard solution of a strong oxidizing agent. Strong oxidizing agent has good affinity for electron, to ensure the completion of reaction at equivalence point. The most widely used strong oxidizing agents for volumetric analysis are MnO_4^- ion in acidic solution, $\text{Cr}_2\text{O}_7^{2-}$ ion in acidic solution, Ce^{4+} ion in acidic solution and MnO_4^- in basic solution.

In analysis of reducing agents by titration with a strong oxidizing agent, it is necessary to pre-treat the sample before the titration, to ensure that all the sought substance is reduced to its lower oxidation state and to ensure that no reducing agent other than the sought material is present in the solution in the solution.

For example : The iron sample is dissolved and the solution is treated with a strong reducing agent to convert ferric ion into ferrous ions, if present any. The commonly used reducing agent for this purpose is metallic zinc, for which the reaction is



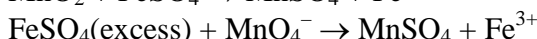
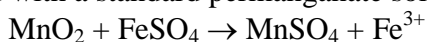
After reduction is complete, the metallic zinc is removed from the solution, which is then titrated by a standard solution of KMnO_4 as



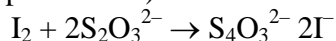
- (ii) If the test sample consists of a strong oxidizing agent, it may be analyzed by titration its solution with a solution of strong reducing agent. The reducing agents commonly used for this purpose are oxalate ion, ferrous ion, arsenious acid etc.

Sample of oxidizing agents that are not fairly soluble in water may be analyzed by reacting a known weight of the sample with a measured volume of a standard reducing agent and after the reaction is complete, back titrating the excess of reducing agent in the solution with a standard solution of oxidizing agent. A common analysis of this type is determination of MnO_2 in a sample pyrolusite. A weighed

portion of pyrolusite is treated with a measured volume of FeSO_4 and excess of FeSO_4 is then back titrated with a standard permanganate solution as



- (iii) Indirect method : Indirect titration is frequently used for the analysis of oxidizing agents. The sample is treated with a solution of KI, and the liberated iodine is titrated by a solution of sodium thiosulphate " $\text{Na}_2\text{S}_2\text{O}_3$ " (hypo solution) which reacts with iodine as



(Applications of redox Processes)

Titration based on redox processes are called redox titrations. In these titrations titrate/titrant are oxidising/ reducing agents. The calculations made in redox titrations are again based on law of chemical equivalence.

Titrate + Titrant \rightarrow Products

Meq. Of titrate = meq. Of titrant (at equivalent point),

or $N_1V_1 = N_2V_2$

Common oxidizing agents which are used in redox titration are given below :

1. Acidified KMnO_4
2. Acidified $\text{K}_2\text{Cr}_2\text{O}_7$
3. Acidified KIO_3 and KBrO_3
4. Acidified Ce^{4+} salts
5. Iodine/Iodide (iodimetry and iodometry) etc.

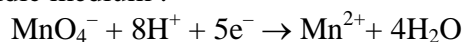
Common oxidising agents used for the preparation of standard solution

Reagent	Usual condition for use	Half-reaction	Stability of solution
Potassium permanganate (KMnO_4)	Strong acid Weakly acid or neutral strongly basic	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + \text{H}_2\text{O}$ $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$ $\text{MnO}_4^- + \text{e}^- \rightleftharpoons \text{MnO}_4^{2-}$	Solution require Occasional standardization
Quadrivalent cerium (Ce^{4+})	H_2SO_4 solution	$\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}$	Indefinitely stable
Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)	Acid solution	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	Indefinitely stable
Potassium iodate (KIO_3)	Strong solution HCl	$\text{IO}_3^- + 2\text{Cl}^- + 6\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{ICl}_2 + 3\text{H}_2\text{O}$	Stable
Potassium bromate (KBrO_3) + KBr)	Dilute acid solution	$\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightleftharpoons 3\text{Br}_2 + 3\text{H}_2\text{O}$ $\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	Indefinitely stable
Triiodide ion (I_3^-)	Neutral, dilute acid or base solution	$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	Restandardisation necessary

11.1 Titration using acidified KMnO_4

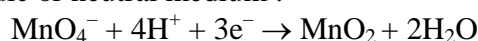
Use of KMnO_4 as oxidising agent in redox titrations was first made by F. Marguerette for the titration of Fe^{2+} ions. It is a powerful oxidant and probably the most widely used of all volumetric oxidising agents. It is readily available and colour of its solution is too intense that an indicator is not ordinarily required and MnO_4^- ions act as self indicator. Titrations of MnO_4^- are usually carried out in acid medium. The possible reactions are :

In strongly acidic medium :



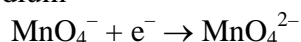
$$E = \frac{M}{5} = \frac{158}{5} = 31.6$$

In weakly acidic or neutral medium :



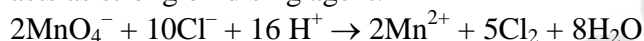
$$E = \frac{M}{3} = \frac{158}{3} = 52.6$$

In alkaline medium



$$E = \frac{M}{1} = 158$$

Among the common mineral acids H_2SO_4 , HCl and HNO_3 only H_2SO_4 is useful for providing acidic medium. HCl cannot be used since Cl^- are oxidised to Cl_2 by KMnO_4 . On the other-hand HNO_3 itself acts as strong oxidising agent.

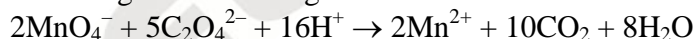


Yet KMnO_4 fulfils almost all the requirements of a good volumetric oxidising agent but it has some limitation also. The multiplicity of possible reactions at a time, cause uncertainty regarding the stoichiometric of a permanganate oxidation. Also permanganate solution have limited stability and need occasional stabilisation.

Some important titrations using KMnO_4 are given below :

(a) KMnO_4 vs. oxalic acid :

Titrant	Titrate
Oxidising	reducing
agent	agent



Reaction is slow initially and needs elevated temperature but after sometime Mn^{2+} (Product) catalyse the reaction. (Autocatalysis)

Medium : acidic (by H_2SO_4).

End point : Light pink colour of MnO_4^- solution, KMnO_4 acts as self indicator .

At equivalence point

(i) 2m- mol KMnO_4 reacts with 5 m-mol oxalic acid.

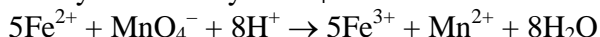
(ii) meq. Of KMnO_4 = meq. Of oxalic acid

$$N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = N_{\text{oxalic acid}} \times V_{\text{oxalic acid}}$$

$$(iii) \quad \frac{1}{2} \times M_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = \frac{1}{5} \times M_{\text{oxalic acid}} \times V_{\text{oxalic acid}}$$

(b) KMnO_4 vs. Fe^{2+} ions :

Fe^{2+} is readily oxidised by MnO_4^- to Fe^{3+} . The reaction which takes place is given below :

**Reducing agent and oxidising agent**

In the laboratory, for practical purposes ferrous ammonium sulphate is taken as a source of Fe^{2+} ions. In the determination of Fe content in iron ores, the whole iron content present in a definite amount of its solution is first converted into Fe^{2+} by using suitable reducing agent like SnCl_2 .

End point : MnO_4^- acts as self indicator and light pink colour of solution indicates end point.

At equivalent point :

(i) 1 mol MnO_4^- reacts with 5 mol Fe^{2+} .

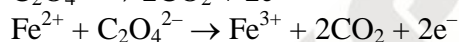
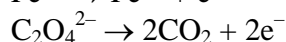
(ii) Meq. of $\text{MnO}_4^- = \text{Meq. of } \text{Fe}^{2+}$

$$\text{or } N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = N_{\text{Fe}^{2+}} \times V_{\text{Fe}^{2+}}$$

$$\text{or } 5 \times M_{\text{KMnO}_4} \times V_{\text{KMnO}_4} = M_{\text{Fe}^{2+}} \times V_{\text{Fe}^{2+}}$$

$$(\therefore N_{\text{KMnO}_4} = 5 \times M_{\text{KMnO}_4}, N_{\text{Fe}^{2+}} = M_{\text{Fe}^{2+}})$$

Note : It titration is being carried out with solution of ferrous oxalate then



$$\text{so } E_{\text{Fe-oxalate}} = \frac{M}{3} \quad (E = \text{Equivalent mass})$$

(c) Estimation of Fe^{2+} and Fe^{3+} ions in a solution :

In this estimation, the solution is titrated twice. First without reduction in which only Fe^{2+} reacts and Fe^{3+} remains unreacted. In second step same volume of solution is taken. Fe^{3+} ions are reduced to Fe^{2+} and then titrated. Here

(i) In I step : Meq. of KMnO_4 (let x) = Meq. of Fe^{2+}

(ii) In II step : Meq. KMnO_4 (y) = Meq. of Fe^{2+} + Meq. of Fe^{3+}
and Meq. of Fe^{3+} (y - x)

(d) Analysis of sample containing oxalic acid and sodium oxalate :

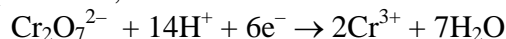
Same volume of solution are titrated separately with NaOH and KMnO_4 solution

Meq. of NaOH = Meq. of oxalic acid

and Meq. of KMnO_4 = Meq. of oxalic acid + Meq. of sodium oxalate

11.2 Titration using acidified $\text{K}_2\text{Cr}_2\text{O}_7$:

In volumetric analysis $\text{Cr}_2\text{O}_7^{2-}$ is also used commonly as oxidant yet weaker than MnO_4^- , Ce^{4+} etc. In most of its applications, it is reduced to Cr^{3+}

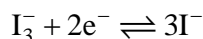


$$E_{\text{Cr}_2\text{O}_7^{2-}} = \frac{M_{\text{Cr}_2\text{O}_7^{2-}}}{6} = \frac{296}{6} = 49$$

These titrations are made in 1–2 N acid solution. In neutral or alkaline medium, it is not used. In alkaline medium orange $\text{Cr}_2\text{O}_7^{2-}$ changes to yellow CrO_4^{2-} .

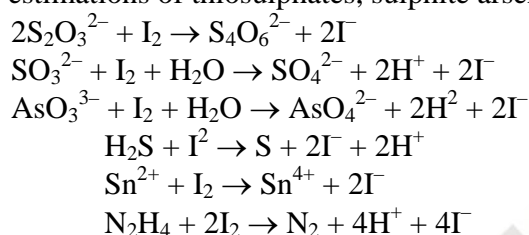
11.3 Iodometry and iodimetry

Iodine acts as mild oxidising agent and its used for titrating several analysis. The titrations are based, upon following half reaction

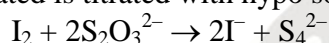


These titrations fall into two categories :

- (a) **Iodimetry** : In these titrations, standard I_2 solution is used to titrate easily oxidisable substances. It includes the estimations of thiosulphates, sulphite, arsenite etc.



- (b) **Iodimetry** : In iodimetric titrations as oxidising agent is allowed to react with excess of KI (or I^-) solution. The I_2 liberated is titrated with hypo solution.



I_2 finds use for selective determination of strong reducing agents. Availability of a sensitive and reversible indicator for makes these titration useful. It includes the estimations of following species

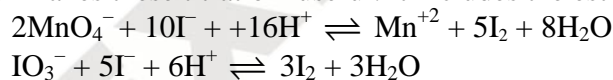
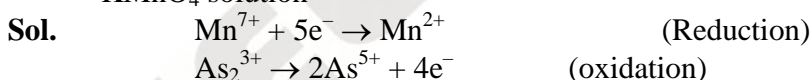


Illustration : 12

KMnO_4 solution is to be standardised by titration against $\text{As}_2\text{O}_3(\text{s})$. A 0.1097 g sample of As_2O_3 requires 26.10 ml of the KMnO_4 solution for its titration. What are the molarity and normality of the KMnO_4 solution



$$\therefore \text{Meq. of } \text{As}_2\text{O}_3 = \text{meq of } \text{KMnO}_4$$

$$\frac{0.1097}{\frac{198}{4}} \times 1000 = 26.10 \times N \quad \left(E_{\text{As}_2\text{O}_3} = M/4 \right)$$

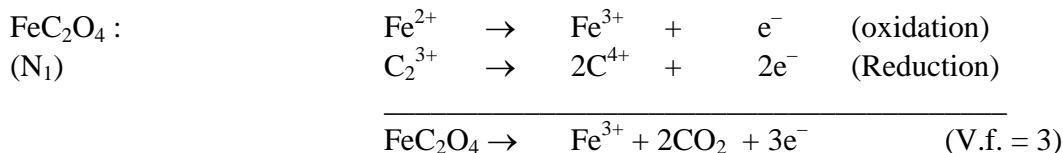
$$\therefore N_{\text{KMnO}_4} = 0.085$$

$$\therefore N_{\text{KMnO}_4} = \frac{0.085}{5} = 0.017$$

Illustration : 13

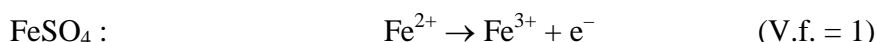
100 ml solution of FeC_2O_4 and FeSO_4 is completely oxidized by 60 ml of 0.02 M KMnO_4 in acid medium. The resulting solution is then reduced by Zn and dil. HCl. The reduced solution is again oxidized completely by 40 ml 0.02 M KMnO_4 . Calculate normality of FeC_2O_4 and FeSO_4 in mixture.

Sol. Consider the redox reaction



$$100 (\text{N}_1 + \text{N}_2) = 60 \times 0.02 \times 5$$

$$(\text{N}_1 + \text{N}_2) = 3 \times 0.02 \quad \dots\dots(1)$$



(N_2)



The resulting solution now contains only Fe^{3+} ions because CO_2 escapes out. The solution is reduced to Fe^{2+} by Zn and dil. HCl. KMnO_4 oxidises these Fe^{2+} again, therefore
 meq. Of Fe^{2+} from FeC_2O_4 + meq. Fe^{2+} from FeSO_4 = meq. Of KMnO_4

$$100 \left(\frac{\text{N}_1}{3} + \text{N}_2 \right) = 40 \times 0.02 \times 5$$

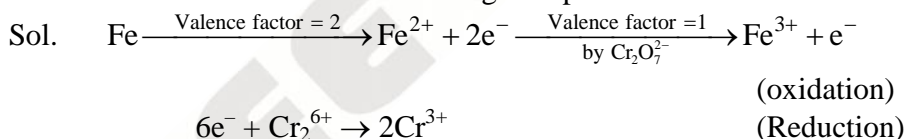
$$\left(\frac{\text{N}_1}{3} + \text{N}_2 \right) = 2 \times 0.02 \quad \dots\dots(2)$$

$$\frac{2\text{N}_1}{3} = 0.02$$

$$\text{N}_1 = 0.03, \text{N}_2 = 0.03$$

Illustration : 14

0.48 g iron are containing X percent of iron was taken in a solution containing all the iron in ferrous state. The solution required X ml of a potassium dichromate solution for oxidation of iron content to ferric state. Calculate the strength of potassium solution.



$$W_{\text{Fe}} = \frac{0.84x}{100} \quad (\text{Given})$$

Meq. of Fe^{2+} in solution (V.f. = 1) meq. of $\text{K}_2\text{Cr}_2\text{O}_7$

$$= \text{X} \cdot \text{N}_{\text{K}_2\text{Cr}_2\text{O}_7} \quad (\text{V.f. } \text{Fe}^{2+} = 1)$$

\therefore meq. of Fe^{2+} in solution (valence factor = 2) $2 \cdot \text{X} \cdot \text{N}$

or Meq. of Fe = $2 \cdot \text{X} \cdot \text{N}$

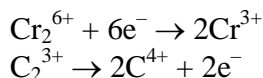
$$\frac{0.84\text{X}}{100 \times 56/2} \times 1000 = 2 \cdot \text{X} \cdot \text{N} \Rightarrow \text{N} = 0.15$$

$$S_{K_2Cr_2O_7} = N \times E = 0.15 \times 49$$

$$(E = \frac{249}{6} = 49) \text{ (E = Equivalent mass)}$$

Illustration : 15

What mass of $K_2Cr_2O_7$ is required to produce 5.0 litre CO_2 at $75^\circ C$ and 1.07 atm pressure from excess of oxalic acid. Also report the volume of 0.1 N NaOH required to neutral the CO_2 evolved.

Sol.

Meq. of $K_2Cr_2O_7$ = meq. of CO_2 formed

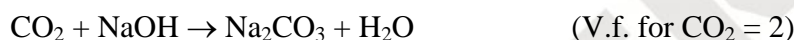
$$= \text{mole of } CO_2 \times 1000 \times 1 \text{ (V.f for } CO_2 = 1)$$

$$= \frac{PV}{RT} \times 1 \times 1000 = \frac{1.07 \times 5 \times 1000}{0.0821 \times 348} = 187.3$$

$$\therefore \frac{W_{K_2Cr_2O_7}}{M/6} \times 1000 = 187.3$$

$$\text{or } W_{K_2Cr_2O_7} = \frac{187.3 \times M}{6 \times 1000} = \frac{187.3 \times 294}{6 \times 1000};$$

$$W = 9.18 \text{ g} \quad (M_{K_2Cr_2O_7} = 294)$$

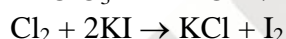
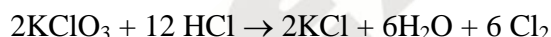


Also meq. Of NaOH = meq. of CO_2 of valence factor 2

$$0.1 \times V = 187.3 \times 2 = 3.746 \text{ L}$$

Illustration : 16

2.480 g of $KClO_3$ are dissolved in conc. HCl and the solution was boiled. Chlorine gas evolved in the reactions was then passed through a solution of KI and liberated iodine was titrated with 100 ml of hypo. 12.3 ml of same hypo solution required 24.6 ml of 0.5 N iodine for complete neutralization. Calculate % purity of $KClO_3$ sample.

Sol :

Also meq. of I_2 = meq. Of hypo = 100×1

$$[\therefore N_{Hypo} \times 12.3 = 24.6 \times 0.5, \therefore N_{Hypo} = 1]$$

$$\text{Also mM of } Cl_2 = \text{mM of } I_2 = \text{mM of } I_2 = \frac{100}{2} = 50$$

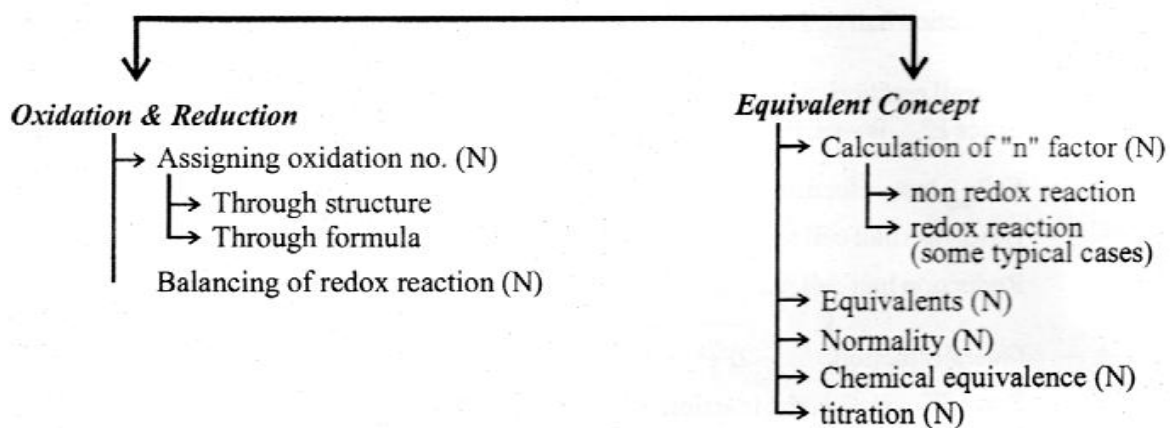
$$\text{Also mM of } KClO_3 = \frac{2 \times \text{mM of } Cl_2}{6} = \frac{2 \times 50}{6} = \frac{50}{3}$$

$$\therefore \frac{W_{KClO_3}}{122.5} \times 1000 = \frac{50}{3} \Rightarrow W_{KClO_3} = 2.042 \text{ [milli-mole (mM) = (mass} \times 1000) \text{ (mol. mass)]}$$

$$\therefore \% KClO_3 = \frac{2.042}{2.48} \times 100 = 82.34 \%$$

The Atlas

Redox Reaction



- (G) represents topic of graphical importance
(T) represents topic of theoretical importance
(N) represents topic of numerical importance

Exercise -1 [Subjective Question]

Balancing of Redox Reaction

- Balancing the following equation
 - $\text{BaCl}_2 + \text{Al}_2(\text{SO}_4)_3 \rightarrow \text{AlCl}_3 + \text{BaSO}_4$.
 - $\text{KCN} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{HCN}$.
 - $\text{BCl}_3 + \text{P}_4 + \text{H}_2 \rightarrow \text{BP} + \text{HCl}$.
 - $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + \text{Cr}_2\text{O}_3 + \text{H}_2\text{O}$.
 - $\text{KMnO}_4 + \text{HCl} \rightarrow \text{MnCl}_2 + \text{H}_2\text{O} + \text{Cl}_2 + \text{KCl}$
 - $\text{Ca}(\text{OCl})_2 + \text{KI} + \text{HCl} \rightarrow \text{I}_2 + \text{CaCl}_2 + \text{H}_2\text{O} + \text{KCl}$.
 - $\text{H}_3\text{AsO}_4 + \text{KI} + \text{HCl} \rightarrow \text{H}_3\text{AsO}_3 + \text{KCl} + \text{I}_2 + \text{H}_2\text{O}$.
 - $\text{NaClO}_3 + \text{KI} + \text{HCl} \rightarrow \text{NaCl} + \text{I}_2 + \text{KCl} + \text{H}_2\text{O}$.
- Predict the product and balance the reaction
 - $\text{Ag}^+ + \text{AsH}_3 \rightarrow \text{H}_3\text{AsO}_3 + \text{H}^+ + \underline{\hspace{2cm}}$
 - $\text{H}_2\text{S} + \text{K}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{S} + \underline{\hspace{2cm}} + \underline{\hspace{2cm}} + \text{H}_2\text{O}$.
 - $\text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{H}_2\text{O} + \underline{\hspace{2cm}}$.
 - $\text{H}_2\text{S} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \rightarrow \text{Cr}_2\text{O}_3 + \underline{\hspace{2cm}} + \text{H}_2\text{O}$

Eq. Mass calculations

- Find then n factor of underlined compound in following interaction
 - $\text{Pb}(\underline{\text{NO}_3})_2 + \underline{\text{Cr}_2(\text{SO}_4)_3} \rightarrow \underline{\text{PbSO}_4} + \underline{\text{Cr}(\text{NO}_3)_3}$
 - $\underline{\text{KMnO}_4} + \underline{\text{MnSO}_4} \rightarrow \underline{\text{MnO}_2}$
 - $\underline{\text{P}_4} \rightarrow \underline{\text{H}_2\text{PO}_2^-} + \underline{\text{PH}_3}$
- Calculate normality of a salt solution [of a metal sulphate] having concentration 21.6% w/v if its superoxide has 16% by mass of oxygen.
- What is the equivalent weight of H_2SO_4 in the reaction ?

$$\text{H}_2\text{SO}_4 + \text{NaI} \rightarrow \text{Na}_2\text{SO}_4 + \text{I}_2 + \text{H}_2\text{S} + \text{H}_2\text{O}$$

Acid Base Titration

- Calculate volume of 1N H_3PO_4 required to react with 20 ml 2N $\text{Ca}(\text{OH})_2$ solution
- Calculate volume of 1N H_2SO_4 required to react with 20 ml 1M $\text{Al}(\text{OH})_3$ solution.
- Calculate volume of 0.4 M NaOH required to react with following mixture
 HCl (1 mol) + H_2SO_4 (2 mol)
- Calculate volume of 0.2 M H_2SO_4 required to react with following mixture
 NaOH (1 mol) + $\text{Ca}(\text{OH})_2$ (2 mol)

[CHEMISTRY]**[REDOX & EQUIVALENT CONCEPTS]**

10. A solution containing 4.2 g of KOH and Ca(OH)_2 is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample
11. How many ml of 0.1 N HCl are required to react completely with 19 gm mixture of Na_2CO_3 and NaHCO_3 containing equimolar amounts of two ?
12. H_3PO_4 is a tri basic acid and one of its salt is NaH_2PO_4 . What volume of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4 ?

Redox Titration

13. It requires 40 ml of 1 M Ce^{4+} to titrate 20 ml of 1M Sn^{+2} to Sn^{+4} . What is the oxidation state of the cerium in the product.
14. a volume of 10.0 ml of 1M SeO_2 reacted with exactly 20 ml of 2 M CrSO_4 . In the reaction, Cr^{2+} was oxidized to Cr^{3+} . To what oxidation state was selenium converted by the reaction.
15. Potassium acid oxalate $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ can be oxidized by MnO_4^- in acid medium. Calculate the volume of 0.1 M KMnO_4 reacting in acid solution with 5.08 gm of the acid oxalate.
16. A 1 g sample of H_2O_2 solution containing x% H_2O_2 by mass requires x cm^3 of KMnO_4 solution of complete oxidation under acidic conditions. Calculate the normality of KMnO_4 solution .
17. Metallic tin in the presence of HCl is oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ to stannic chloride, SnCl_4 . What volume of deci-normal dichromate solution would be reduced by 11.9 gm of tin. [Sn = 119]
18. Calculate the number of millimoles of $\text{K}_2\text{Cr}_2\text{O}_7$ which will completely reacts with 40 ml 0.1 M KI solution.
19. Calculate volume of 0.4 M KMnO_4 required to react with following in acidic medium.
 KHC_2O_4 (1 mol) + $\text{H}_2\text{C}_2\text{O}_4$ (2 mol)
20. Calculate volume of 0.4 M NaOH required to react with following mixture.
 KHC_2O_4 (1 mol) + $\text{H}_2\text{C}_2\text{O}_4$ (2 mol)
21. Calculate volume of 0.2 M KMnO_4 required to react with following mixture in acidic medium.
 KHC_2O_4 (128 gm) + $\text{H}_2\text{C}_2\text{O}_4$ (180 gm)
22. 520 gm mixture of Fe_2O_3 & FeO reacts completely with 158 gm KMnO_4 in acidic medium . Calculate the mole % of Fe_2O_3 in mixture.
23. Calculate the millimoles of Br_2 produced when 10 ml of 0.1 M BrO_3^- reacts with excess of Br^- .
24. 5g sample of brass was dissolved in one litre dil. H_2SO_4 . 20 ml of this solution were mixed with KI, liberating I_2 and Cu^+ and the I_2 required 20 ml of 0.03 N hypo solution for complete titration. Calculate the percentage of Cu in the alloy.

[CHEMISTRY]**[REDOX & EQUIVALENT CONCEPTS]**

25. A 0.96 g sample of Fe_2O_3 solid of 50% purity is dissolved in acid and completely reduced by heating the solution with zinc dust. The resultant solution is called and made upto 100.0 mL. An aliquot 25.0 mL of this solution requires 30 mL of 0.01 M solution of an oxidising agent for titration. Calculate the number of moles of electrons taken up by 1 mol of oxidising agent in the reaction of the above titration.
26. 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the content to ferric state. Calculate the normality of dichromatic solution.
27. 5g of pyrolusite (impure MnO_2) were heated with conc. HCl and Cl_2 evolved was passed through excess of KI solution. The iodine liberated required 40 mL of N/10 hypo solution. Find the % of MnO_2 in the pyrolusite.
28. A 5.0 cm^3 solution of H_2O_2 liberates 0.508 g of iodine for an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at S.T.P
29. An aqueous solution containing 0.10 g KIO_3 (formula wt. = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 ml of thiosulphate solution to decolourise the blue starch – iodine complex. Calculate the molarity of the sodium thiosulphate solution.
30. How many millilitre of 0.5 M H_2SO_4 are needed to dissolved 0.5 gm of copper II carbonate ?
31. 50 gm of a sample of $\text{Ca}(\text{OH})_2$ is dissolved in 50 ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.3 N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of $\text{Ca}(\text{OH})_2$.
32. One gm of impure sodium carbonate is dissolved in water and the solution is made up to 250 ml. To 50 ml of this made up solution. 50 ml of 0.1 N – HCl is added and the mix after shaking well required 10 ml of 0.16 N – NaOH solution for complete titration. Calculate the % purity of the sample.
33. 10 g CaCO_3 were dissolved in 250 ml of 1 M HCl. What volume of 2 M KOH would be required to neutralise excess HCl

Hardness of Water

34. Calculate the weight of CaO required to remove hardness of 10^6 L of water containing 1.62 gram $\text{Ca}(\text{HCO}_3)_2$ per litre.
35. Hardness of water is 180 ppm of MgSO_4 . Express it in terms of ppm of CaCO_3 .
36. 0.00012% MgSO_4 and 0.000111% CaCl_2 is present in water. What is the measured hardness of water & millimoles of washing soda required to purify 1000 L .water.

Exercise -2 [Objective Question]

(I). Fill in the blanks with appropriate items :

1. The balancing of chemical equation is based upon _____.
2. The atomic mass of iron is 56. The equivalent mass of the metal in FeCl_2 is _____ and that in FeCl_3 is _____.
3. The equivalent weight of Na_2HPO_4 when it reacts with excess of HCl is _____.
4. A metallic oxide contains 60% metal. The equivalent weight of the metal is _____.
5. The number of gm of anhydrous Na_2CO_3 present in 250 ml of 0.25 N solution is _____.
6. _____ ml of 0.1 M H_2SO_4 is required to neutralize 50 ml of 0.2 M NaOH solution.
7. Value of n factor on H_2CO_3 _____ in presence of NaOH if product is NaHCO_3 .

(II) True or False Statements :

1. The equivalent mass of KMnO_4 in alkaline medium is molar mass divided by five.
2. The equivalent mass of $\text{Na}_2\text{S}_2\text{O}_3$ in its reaction with I_2 is molar mass divided by two.
3. In a reaction, H_2MoO_4 is changed to MoO_2^{+} . In this case, H_2MoO_4 acts as an oxidising agent.
4. KBrO_3 acts as a strong oxidising agent. It accepts 6 electrons to give KBr .
5. 0.1 M sulphuric acid has normality of 0.05 N.
6. The reaction, $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ is not an example of a redox reaction.
7. The disproportionation reaction

$$2\text{Mn}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + \text{Mn}^{+2} + 4\text{H}^{+}$$
 Is an example of a redox reaction.
8. The oxidation number of hydrogen is always taken as + 1 in its all compounds.
9. The increase in oxidation number of an element that the element has undergone reduction.
10. The oxidation state of oxygen atom in potassium super oxide is $-1/2$.

(III) OBJECTIVE TYPE :**Single Correct**

- The number of moles of KMnO_4 that will be needed to react completely with one mole of ferrous oxalate in acid solution is
(A) $3/5$ (B) $2/5$ (C) $4/5$ (D) 1
- The number of moles of KMnO_4 that will be needed to react with one mole of sulphite ions in acidic solution is
(A) $2/5$ (B) $3/5$ (C) $4/5$ (D) 1
- The normality of 0.3 phosphorus acid (H_3PO_3) is
(A) 0.1 (B) 0.9 (C) 0.3 (D) 0.6
- An aqueous solution of 6.3 gm of oxalic acid dihydrate is made upto 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is
(A) 40 ml (B) 20 ml (C) 10 ml (D) 4 ml
- In the standardization of $\text{Na}_2\text{S}_2\text{O}_3$ using $\text{K}_2\text{Cr}_2\text{O}_7$ by iodometry the equivalent mass of $\text{K}_2\text{Cr}_2\text{O}_7$ is
(A) $\frac{\text{M.mass}}{2}$ (B) $\frac{\text{M.mass}}{6}$ (C) $\frac{\text{M.mass}}{3}$ (D) Same as M. Mass
- MnO_4^- is good oxidising agent in different medium changing to -
 $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$
 $\rightarrow \text{MnO}_4^{2-}$
 $\rightarrow \text{MnO}_2$
 $\rightarrow \text{Mn}_2\text{O}_3$
 Changes in oxidation number respectively are-
 (A) 1, 3, 4, 5 (B) 5, 4, 3, 2 (C) 5, 1, 3, 4 (D) 2, 6, 4, 3
- Oxidation number of Cl in CaOCl_2 (bleaching powder) is -
 (A) Zero, since it contains Cl_2 (B) -1, since it contains Cl^-
 (C) +1, since it contains ClO^- (D) +1 and -1 since it contains ClO^- and Cl^-
- Which of the following is a redox-reaction-
 (A) $2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \rightarrow \text{Na}[\text{Zn}(\text{CN})_4] + 2\text{Ag}$
 (B) $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
 (C) $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$
 (D) $\text{AgNO}_3 + \text{KI} \rightarrow \text{AgI} + \text{KNO}_3$
- In the coordination compound, $\text{K}_4[\text{Ni}(\text{CN})_4]$, the oxidation state of nickel is -
 (A) +1 (B) +2 (C) -1 (D) 0
- What would happen when a solution of potassium chromate is treated with an dilute nitric acid ?
 (A) CrO_4^{2-} is reduced to +3 state of Cr (B) CrO_4^{2-} is oxidized to state of Cr
 (C) Cr^{+3} and $\text{Cr}_2\text{O}_7^{2-}$ are formed (D) $\text{Cr}_2\text{O}_7^{2-}$ and H_2O are formed

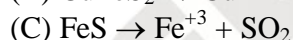
[CHEMISTRY]**[REDOX & EQUIVALENT CONCEPTS]**

11. If m_A gram of a metal A displaces m_B gram of another metal B from its salt solution and if the equivalent weights are E_A and E_B respectively then equivalent weight of A can be expressed as
 (A) $E_A = \frac{m_A}{m_B} \times E_B$ (B) $E_A = \frac{m_A \times m_B}{E_B}$ (C) $E_A = \frac{m_B}{m_A} \times E_B$ (D) $E_A = \sqrt{\frac{m_A}{m_B} \times E_B}$
12. When BrO_3^- ion reacts with Br^- in acid medium, Br_2 is liberated. The equivalent weight of Br_2 in this reactions is
 (A) $\frac{5M}{8}$ (B) $\frac{5M}{3}$ (C) $\frac{3M}{5}$ (D) $\frac{4M}{6}$
13. Calculate the mass of anhydrous oxalic acid, which can be oxidised to $\text{CO}_2(\text{g})$ by 100 ml of an MnO_4^- solution, 10 ml of which is capable of oxidising 50 ml of 1 N I^- to I_2 .
 (A) 45 gm (B) 22.5 gm (C) 30 gm (D) 12.25 gm
14. 1 gram of a sample of CaCO_3 was strongly heated and the CO_2 liberated was absorbed in 100 mL of 0.5 M NaOH. Assuming 90% purity for the sample. How much mL of 0.5 M HCl would be required to react with the solution of the alkali to reach the phenolphthalein end point ?
 (A) 73 mL (B) 41 mL (C) 82 mL (D) 87 mL
15. An equimolar mixture of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$ required V_1 litre of 0.1 M KMnO_4 in acidic medium for complete oxidation. The same amount of the mixture required V_2 litre of 0.2 M NaOH for neutralization. The ratio of V_1 to V_2 (V_1/V_2) is :
 (A) 2 : 5 (B) 1 : 2 (C) 4 : 5 (D) None of these
16. 2 gm of an impure mixture of MgCO_3 was dissolved in 50 ml of 0.8 M HCl. The excess of acid required 20 ml of 0.2 M NaOH for complete neutralization. The percentage of MgCO_3 in the sample will be
 (A) 7.56% (B) 37.8% (C) 75.6% (D) None of these

Match the column

17. To find molarity of 2 separate solutions of KMnO_4 and O_2 ($\text{O}_2 \rightarrow \text{O}^{2-}$), a student titrated 20 ml of KMnO_4 (in neutral medium) and 10 ml of O_2 separately using 3 reagents A, B, & C, performing 3 different experiments for KMnO_4 and O_2 each. He found molarity of KMnO_4 and O_2 as $1/20$ M and $1/10$ M respectively.

A, B & C are FeCr_2O_4 , CuFeS_2 , FeS respectively and their reactions are :



Column-I represents solution of A, B, C used for titration

Column -II represents milli moles of A, B, C consumed with KMnO_4 or with O_2 .

Column-I	Column-II
(A) FeCr_2O_4	(P) $\frac{3}{11}$
(B) CuFeS_2	(Q) $\frac{3}{7}$
(C) FeS	(R) $\frac{4}{7}$
	(S) $\frac{4}{11}$

Exercise -3 [Sections -A]

[JEE Advanced Previous Year's Question]

1. 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 ADV. 2017]
 (A) 3 (B) 4 (C) 5 (D) 6
2. Match the reactions in Column -I with nature of the reactions/ type of the products in Column -II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the OMR. [For Class 11th students, attempt only "A" and "C" part] [JEE ADV. 2007]
- | Column I | Column II |
|--|---|
| (A) $\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^{2-}$ | (P) Redox reaction |
| (B) $\text{CrO}_4^{2-} + \text{H}^+ \rightarrow$ | (Q) one of the products has trigonal planar structure |
| (C) $\text{MnO}_4^- + \text{H}_2\text{SO}_4 + \text{H}^+ \rightarrow$ | (R) dimeric bridged tetrahedral metal ion |
| (D) $\text{NO}_3^- \rightarrow \text{H}_2\text{SO}_2 + \text{Fe}^{2+} \rightarrow$ | (S) disproportionation |
3. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a [JEE ADV. 2008]
 [Given : $\text{P} + \text{NaOH} \rightarrow \text{PH}_3 + \text{NaH}_2\text{PO}_2$]
 (A) dimerization reaction (B) disproportionation reaction
 (C) condensation reaction (D) precipitation reaction
4. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is [JEE ADV. 2011]
5. Reduction of the metal centre in aqueous permanganate ion involves [JEE ADV. 2011]
 (A) 3 electrons in neutral medium (B) 5 electrons in neutral medium
 (C) 3 electrons in alkaline medium (D) 5 electrons in acidic medium
6. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen ? [JEE ADV. 2012]
 (A) HNO_3 , NO, NH_4Cl , N_2 (B) HNO_3 , NO, N_2 , NH_4Cl
 (C) HNO_3 , NH_4Cl , NO, N_2 (D) NO, HNO_3 , NH_4Cl , N_2
7. Bleaching power and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry. 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 $\text{Na}_2\text{S}_2\text{O}_3$ was used to reach the end point. The molarity of the household bleach solution as : [JEE ADV. 2012]
 (A) 0.48 M (B) 0.96 M (C) 0.24 M (D) 0.024 M

8. For the reaction : [JEE ADV. 2014]

$$\text{I}^- + \text{ClO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{Cl}^- + \text{HSO}_4^- + \text{I}_2$$

 The correct statement(s) in the balanced equation is/are
 (A) Stoichiometric coefficient of HSO_4^- is 6.
 (B) Iodide is oxidized.
 (C) Sulphur is reduced.
 (D) H_2O is one of the products.
9. IN dilute aqueous H_2SO_4 , the complex diaquodixalato ferrate (II)ferrate (II) is oxidized by MnO_4^- . For this reaction, the ratio of the rate of change of $[\text{H}^+]$ to the rate of change of $[\text{MnO}_4^-]$ [JEE ADV. 2015]
10. In neutral or faintly alkaline solution, 8 moles of permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. The magnitude of X is [JEE ADV. 2016]

[Sections -B]

[JEE Main Previous Year's Question]

1. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the volume of 0.1 M aqueous KOH solution required is [AIEEE 2004]
 (A) 10 mL (B) 20 mL (C) 40 mL (D) 60 mL
2. The oxidation state of Cr in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ is - [AIEEE 2005]
 (A) +2 (B) +3 (C) 0 (D) +1
3. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is - [AIEEE 2005]
 (A) +6 (B) +4 (C) +3 (D) +2
4. Which of the following chemical reactions depicts the oxidizing behavior of H_2SO_4 ? [AIEEE 2006]
 (A) $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$
 (B) $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$
 (C) $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \rightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$
 (D) $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
5. Amount of oxalic acid present in a solution can be determined by its titration with KMnO_4 solution in the presence of H_2SO_4 . The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl : [AIEEE 2008]
 (A) gets oxidised by oxalic acid to chlorine
 (B) furnishes H^+ ions in addition to those from oxalic acid
 (C) reduces permanganate to Mn^{2+}
 (D) oxidises oxalic acid to carbon dioxide and water

6. Three reactions involving H_2PO_4^- are given below : [AIEEE 2010]
(i) $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$
(ii) $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$
(iii) $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_3\text{PO}_4 + \text{O}^{2-}$
In which of the above does H_2PO_4^- act as an acid ?
(A) (i) only (B) (ii) only (C) (i) and (ii) (D) (iii) only
7. The mass of potassium dichromate crystals required to oxidise 750 cm^3 of 0.6 M Mohr's salt solution is : [JEE Main 2011]
(Given molar mass : potassium dichromate = 294, Mohr's salt = 392)
(A) 22.05g (B) 2.2g (C) 0.49 g (D) 0.45 g
8. Consider the following reactions :
$$x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + z\text{H}^+ \rightarrow x\text{Mn}^{2+} + 2y\text{CO}_2 + z/2 \text{H}_2\text{O}$$

The value of x, y and z in the reaction are, respectively. [JEE Main 2013]
(A) 2, 5 and 8 (B) 2, 5 and 16 (C) 5, 2 and 8 (D) 5, 2 and 16
9. In which of the following reactions H_2O_2 acts as a reducing agent ? [JEE Main 2014]
(i) $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$
(ii) $\text{H}_2\text{O}_2 - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}^+$
(iii) $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$
(iv) $\text{H}_2\text{O}_2 + 2\text{OH}^- - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$
(A) (iii), (iv) (B) (i), (iii) (C) (ii), (iv) (D) (i), (ii)

Exercise -4

Single Correct

1. FeC_2O_4 solution of same concentration is titrated with KMnO_4 in presence of HCl and in presence of H_2SO_4 separately. If V_{HCl} & $V_{\text{H}_2\text{SO}_4}$ represent volume of oxidising agent consumed in the two cases respectively, then which of the options is correct.

(A) $V_{\text{HCl}} = V_{\text{H}_2\text{SO}_4}$ (B) $V_{\text{HCl}} > V_{\text{H}_2\text{SO}_4}$

(C) $V_{\text{HCl}} < V_{\text{H}_2\text{SO}_4}$ but $V_{\text{HCl}} \neq \frac{1}{2} V_{\text{H}_2\text{SO}_4}$ (D) $V_{\text{HCl}} = \frac{1}{2} V_{\text{H}_2\text{SO}_4}$
2. For a redox reaction, $\text{FeS}_2 + \text{KMnO}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{S}_8 + \text{Mn}^{+2}$ if 1 mole of S_8 is produced then calculate moles of KMnO_4 consumed

(A) 1 mole (B) 8/5 mole (C) 16/5 mole (D) 12/5 mole
3. H_2O_2 acts as both oxidising as well as reducing agent. As oxidising agent, its product is H_2O , but as reducing agent, its product is O_2 . Volume strength has great significance for chemical reactions.

The strength of '10V' means 1 volume (or litre) of H_2O_2 on decomposition ($\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$) gives 10 volumes (or litre) of oxygen at NTP.

15 gm $\text{Ba}(\text{MnO}_4)_2$ sample containing inert impurity is completely reacting with 100 ml of '11.2V' H_2O_2 in acidic medium then what will be the % purity of $\text{Ba}(\text{MnO}_4)_2$ in the sample ?

(Atomic mass Ba = 137, Mn = 55)

(A) 5% (B) 10% (C) 50% (D) none
4. To a 10 ml 1 M aqueous solution of Br_2 , excess of NaOH is added so that all Br_2 is disproportionated to Br^- and BrO_3^- . The resulting solution is freed from Br^- , by extraction and excess of OH^- neutralised by acidifying the solution. The resulting solution is sufficient to react with 1.5 gm of impure CaC_2O_4 ($M = 128 \text{ gm/mol}$) sample. The % purity of Oxalate sample is

The relevant reactions are

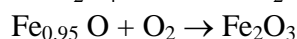
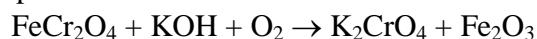
$$\text{Br}_2(\text{aq.}) + \text{OH}^- \rightarrow \text{Br}^-(\text{aq.}) + \text{BrO}_3^-$$

$$\text{BrP}_3^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Br}^- + \text{CO}_2$$

(A) 85.3% (B) 12.5% (C) 90% (D) 50%

Comprehension**Question No. 5 to 8 (4 questions)**

Chromium exists as FeCr_2O_4 in the nature and it contains $\text{Fe}_{0.95} \text{O}$ & other impurity. To obtain pure chromium from FeCr_2O_4 , the ore is fused with KOH and oxygen is passed through the mixture when K_2CrO_4 and Fe_2O_3 are produced

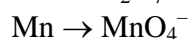
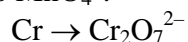


2 g of ore required 270 mL of O_2 at 273 K and 1 atm for complete oxidation of ore. K_2CrO_4 is precipitated as BaCr_2O_4 , when Barium salt is added. To remaining solution 10 mL of 1 M $\text{K}_4\text{Fe}(\text{CN})_6$ is added when Fe^{3+} ions react with it to form $\text{KFe}[\text{Fe}(\text{CN})_6]$, often called 'Prussian Blue'. To determine excess of $\text{K}_4\text{Fe}(\text{CN})_6$ in solution 7 mL of 0.2 N of Fe^{2+} is added when all the $\text{K}_4\text{Fe}(\text{CN})_6$ is precipitated as $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$.

5. Weight of BaCrO_4 precipitated
(A) 1.64 (B) 6.29 (C) 0.82 (D) 3.29
6. % by mass of $\text{Fe}_{0.95}\text{O}$ in the ore
(A) 9.6% (B) 10.1% (C) 8.55% (D) 20.2%
7. n factor for $\text{Fe}_{0.95}$
(A) 0.9 (B) 0.85 (C) $\frac{2}{0.95}$ (D) 1.8
8. Weight of impurities present in the ore
(A) 0.421 (B) 0.123 (C) 0.341 (D) 0.206

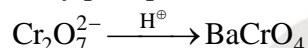
Question NO. 9 to 11 (3 questions)

A steel sample is to be analysed for Cr and Mn simultaneously. By suitable treatment Cr is oxidized as $\text{Cr}_2\text{O}_7^{2-}$ and the Mn to MnO_4^- .



A 10 gm sample of steel is used to produce 250.0 mL of a solution containing $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- .

A 10 mL portion of this solution is added to a BaCl_2 solution and by proper adjustment of the acidity, the chromium is completely precipitated as BaCrO_4 , weighing 0.0549 g.



A second 10 mL portion of this solution requires exactly 15.95 mL of 0.0750 M standard Fe^{2+} solution for its titration (in acid solution)

9. % of chromium in the steel sample
(A) 1.496 (B) 2.82 (C) 1.96 (D) 5
10. Equivalent of Fe^{2+} required for reduction of MnO_4^- is
(A) 5.44×10^{-4} (B) 0.544×10^{-2} (C) 1.196×10^{-3} (D) 11.96×10^{-4}
11. Amount of BaCl_2 required for conversion of $\text{Cr}_2\text{O}_7^{2-}$ to BaCrO_4 in steel sample
(A) 0.045 (B) 0.0549 (C) 1.125 (D) 2.82

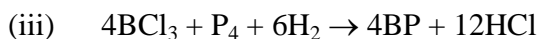
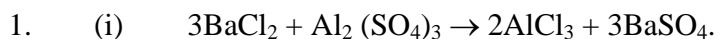
Subjective

12. A mixture of FeO and Fe_2O_3 is reacted with acidified KMnO_4 solution having a concentration of $\frac{2}{5}$ M, 100 ml of which was used. The solution was then titrated with Zn dust which converted Fe^{3+} of the solution of Fe^{2+} . The Fe^{2+} required 1000 ml of $\frac{2}{15}$ M $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Find the % by mol of FeO & Fe_2O_3 .
13. A substance of crude copper is boiled in H_2SO_4 till all the copper has reacted. The impurities are inert to the acid. The SO_2 liberated in the reaction is passed into 100 mL of 0.4 M acidified KMnO_4 ($\text{SO}_2 \rightarrow \text{SO}_4^{2-}$). The solution of KMnO_4 after passage of SO_2 is allowed to react with oxalic acid and requires 25 mL of 1 M oxalic acid. IF the purity of copper is 95.25%, what was the weight of the sample.

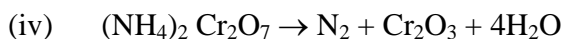
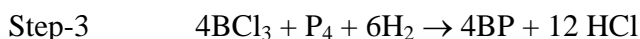
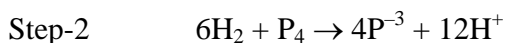
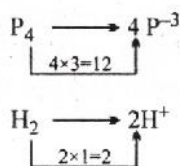
[CHEMISTRY]**[REDOX & EQUIVALENT CONCEPTS]**

14. 24 mL of a solution containing HCl was treated with excess of 0.004M KIO_3 and KI solution of unknown concentration where I_2 liberated is titrated against a standard solution of 0.02 M $\text{Na}_2\text{S}_2\text{O}_3$ solution whose 24 mL were used up. Find the molarity of HCl and volume of KIO_3 solution consumed.
15. A mixture containing equal mole of CuS and Cu_2S was treated with 100 mL of 1.5 M $\text{K}_2\text{Cr}_2\text{O}_7$. The products obtained were Cr^{3+} , Cu^{2+} and SO_2 . The excess oxidant was reacted with 50 mL of Fe^{2+} solution. 25 ml of the same Fe^{2+} solution required 0.3 M acidic KMnO_4 the volume of which used was 20 mL. Calculate moles of each substance in original mixture.
16. H_2O_2 is reduced rapidly by Sn^{2+} , the products being Sn^{4+} & water. H_2O_2 decomposes slowly at room temperature to yield O_2 & water. Calculate the volume of O_2 produced at 273 K & 1.00 atm when 200 g of 10.0% by mass H_2O_2 in water is treated with 88.2 ml of 1 M Sn^{2+} & then the mixture is allowed to stand until no further reaction occurs.
17. 80 gm of a sample of Anhydrous CuSO_4 was dissolved in water and made to 250 ml. 25 ml of this solution after taking usual precautions was treated with a little excess of KI solution. A white ppt. of Cu_2I_2 and iodine was evolved. The iodine so evolved required 40 ml of 1 M of hypo solution. What is the approximate purity of CuSO_4 solution. [Mol. wt. of $\text{CuSO}_4 = 160$]
18. A 458 g sample containing Mn_3O_4 was dissolved and all manganese was converted to Mn^{2+} . In the presence of fluoride ion, Mn^{2+} is titrated with 3 lit of KMnO_4 solution (which was 1.25 N against oxalate in acidic medium), both reactants being converted to a complex of Mn(III). What was the % of Mn_3O_4 in the sample ?
19. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution requires 30 ml of 0.4 N NaOH for complete neutralization. Find the % of free SO_3 in the sample of oleum.

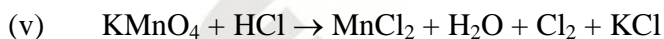
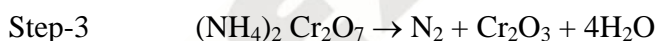
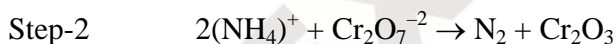
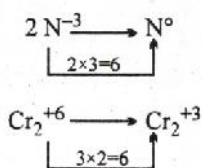
ANSWER KEY

EXERCISE-1

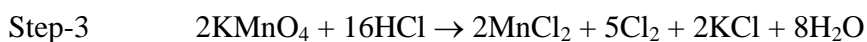
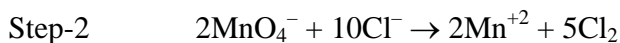
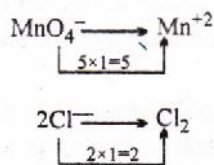
Step-1



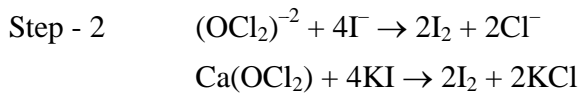
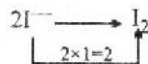
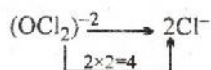
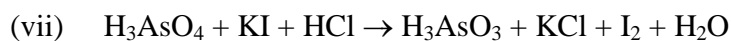
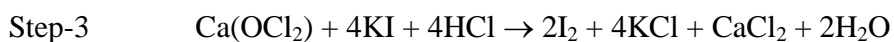
Step-1



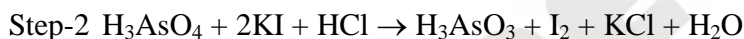
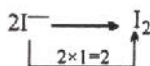
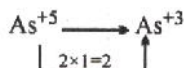
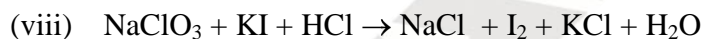
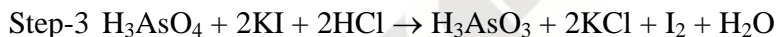
Step-1



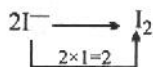
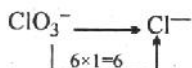
Step -1

**Balancing of other elements.**

Step-1

**Balancing of other elements.**

Step-1



2. (i) $6\text{Ag}^+ + \text{AsH}_3 + 3\text{H}_2\text{O} \rightarrow 6\text{Ag} + 6\text{H}^+ + \text{H}_3\text{AsO}_3$
 (ii) $3\text{H}_2\text{S} + 2\text{K}_2\text{CrO}_4 + 5\text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + 2\text{K}_2\text{SO}_4 + 8\text{H}_2\text{O} + 3\text{S}$
 (iii) $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}_2 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$
 (iv) $24\text{H}_2\text{S} + 8\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^+ \rightarrow 8\text{Cr}_2\text{O}_3 + 3\text{S}_8 + 32\text{H}_2\text{O}$

[CHEMISTRY]**[REDOX & EQUIVALENT CONCEPTS]**

3. (i) 2, 6, 2, 3 (ii) 3,2,6/5 (iii) $n_f = 3$, $n_f = 1$, $n_f = 3$,
4. 1 5. 61.25 6. 40 ml 7. 60 ml 8. 12.5 l
9. 12.5 l 10. KOH = 35%, Ca(OH)₂ = 65% 11. V = 3 lit. 12. 200 mL
13. +3 14. Zero 15. V = 160 ml 16. 0.588 N 17. 4 lit.
18. 2/3 19. 3l 20. 12.5 l 21. 6 l 22. 16.66%
23. 3 24. 38% 25. 5 26. 0.15 N
27. 0.174 g; 3.48% 28. 4.48% 29. 0.0623 M 30. 8.097 ml
31. 1.406% 32. 90.1% 33. V = 25 mL 34. 560 kg 35. 150 ppm
36. 2 ppm, 20 m mole.

EXERCISE-2**(I).**

1. Law of conservation of mass 2. 56/2, 56/3 3. $\frac{\text{Molecular weight}}{2}$
4. 12 5. 3.3125 g 6. 50 7. 1

(II)

1. False 2. False 3. True 4. True 5. False
6. False 7. True 8. False 9. False 10. True

(III)

1. A 2. A 3. D 4. A 5. B
6. C 7. D 8. A 9. D 10. D
11. A 12. C 13. B 14. C 15. C
16. C 17. (A) → q, r; (B) → p, s; (C) → q, r;

EXERCISE-3**Section - A**

1. D 2. (A) → p, s; (B) → r; (C) → p, q; (D) → p; 3. B
4. 5 5. ACD 6. B 7. C 8. ABD
9. 8 10. 6

Section - A

- | | | | | |
|------|------|------|------|------|
| 1. C | 2. B | 3. C | 4. D | 5. C |
| 6. B | 7. B | 8. B | 9. C | |

EXERCISE-4

- | | | | | |
|--|---|----------|---------|-------|
| 1. B | 2. D | 3. C | 4. A | 5. D |
| 6. B | 7. B | 8. C | 9. B | 10. A |
| 11. C | 12. $\text{FeO} = 40\%; \text{Fe}_2\text{O}_3 = 60\%$ | 13. 5g | | |
| 14. $V_{\text{KIO}_3} = 20\text{ mL}, [\text{HCl}] = 0.02$ | 15. 0.06 | 16. 5.6L | 17. 80% | |
| 18. 50% | 19. 78.22% | | | |