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.

OXIDATION AND REDUCTION

Classical Concept :

(A) Oxidation

(i) Oxidation is a chemical reaction in which oxygen is added

$2HNO_2 + O_2 \longrightarrow 2HNO_3$; $2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$

(ii) Hydrogen is removed i.e. hydrogen becomes less

$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$; $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(iii) Electronegative element is added

$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$; $2Sb + 3Cl_2 \longrightarrow 2SbCl_3$

(iv) Electropositive element is removed

$2NaI + H_2O_2 \longrightarrow 2NaOH + I_2$;

(B) Reduction

(i) Addition of Hydrogen.

$H_2 + Cl_2 \longrightarrow 2HCl$, $N_2 + 3H_2 \longrightarrow 2NH_3$

(ii) Loss of Oxygen.

$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3$ $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

(iii) Addition of electropositive element.

$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$ $CuCl_2 + Cu \longrightarrow Cu_2Cl_2$

(iv) Losss of electronegative element.

$2FeCl_3 + H_2 \longrightarrow 2FeCl_2 + 2HCl$ $PbS + H_2 \longrightarrow Pb + H_2S$

(v) Valency of electropositive element decreases.

$$\underset{(Cu^{+2})}{CuSO_4} + Fe \longrightarrow FeSO_4 + \underset{(Cu^{0})}{Cu}$$

$$\underset{(Fe^{+3})}{FeCl_3} + H_2S \longrightarrow \underset{(Fe^{+2})}{FeCl_2} + 2HCl + S \Big]$$

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.

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

$$Na \longrightarrow Na^{+1} + e^-$$
$$Al \longrightarrow Al^{+3} + 3e^-$$

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

$$Sn^{+2} \longrightarrow Sn^{+4} + 2e^-$$
$$Hg^{+1} \longrightarrow Hg^{+2} + e^-$$

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

$$2O^{-2} \longrightarrow O_2 + 4e^-$$
$$2N^{-3} \longrightarrow N_2 + 6e^-$$

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

$$[Fe(CN)_6]^{-4} \longrightarrow [Fe(CN)_6]^{-3} + e^-$$

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

$$H_2O_2 \longrightarrow 2H^{+1} + O_2 + 2e^-$$

Note : *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 a 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.

$$N + 3e^- \longrightarrow N^{-3} \qquad S + 2e^- \longrightarrow S^{-2}$$

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

$$Mg^{+2} + 2e^- \longrightarrow Mg^{o} \qquad Al^{+3} + 3e^- \longrightarrow Al^{o}$$

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

$$Cu^{+2} + e^- \longrightarrow Cu^{+1} \qquad Fe^{+3} + e^- \longrightarrow Fe^{+2}$$

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

$$MnO_4^{-1} + e^- \longrightarrow MnO_4^{-2}$$
$$[Fe(CN)_6]^{-3} + e^- \longrightarrow [Fe(CN)_6]^{-4}$$

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

$$O_2 + 4e^- \longrightarrow 2O^{-2} \qquad I_2 + 2e^- \longrightarrow 2I^{-1}$$

Note : *In reduction reactions– Positive charge decreases and negative charge increases.*

BASIC TERMS

(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.

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Example : $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

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

(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. Example,

$$MnO_2 + 4H^+ + 4Cl^- \rightarrow Mn^{2+} + 2Cl^- + 2H_2O + Cl_2$$

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

(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.

$$Zn + 2H^+ + 2Cl^- \longrightarrow Zn^{+2} + 2Cl^- + H_2$$

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

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

(5) **Reducing agent :** The substance that loses electrons and is thereby oxidised to a higher valency state is called a reducing agent.

TYPES OF REDOX REACTIONS

(1) **Direct and Indirect redox reactions :**

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

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

(2) **Inter molecular redox reactions**

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

$$Zn\,(s) + CuSO_4\,(aq) \longrightarrow ZnSO_4\,(aq) + Cu(s)$$

Oxidation $\quad Zn\,(s) \rightarrow Zn^{+2}\,(aq) + 2e^-$

Reduction $\quad Cu^{+2}\,(aq) + 2e^- \longrightarrow Cu(s)$

(3) **Intra-molecular redox reactions**

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

eg. $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

Oxidation $2N^{3-} \longrightarrow (N^o)_2 + 6e^-$

Reduction $(Cr^{+6})_2 + 6e^- \longrightarrow (Cr^{+3})_2$

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(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 it 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,

(1) $H_2\overset{-1}{O_2} + H_2\overset{-1}{O_2} = H_2\overset{-2}{O} + \overset{0}{O_2}$ (increase: $-1 \rightarrow 0$; decrease: $-1 \rightarrow -2$)

(2) $4K\overset{+5}{Cl}O_3 \rightarrow 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$ (decrease: $+5 \rightarrow -1$; increase: $+5 \rightarrow +7$)

(3) $4\overset{0}{P} + 3NaOH + 3H_2O \rightarrow 3NaH_2\overset{+1}{P}O_2 + \overset{-3}{P}H_3$ (decrease: $0 \rightarrow -3$; increase: $0 \rightarrow +1$)

(4) $3\overset{0}{Cl_2} + 6NaOH \longrightarrow 5\,Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3\,H_2O$ (decrease: $0 \rightarrow -1$; increase: $0 \rightarrow +5$)

(5) Comproportionation reaction

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

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.

OXIDISERS AND REDUCERS

Oxidizers

Substances that have the ability to oxidize other substances are said to be oxidative oroxidizing 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.

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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; i.e., 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 complexeswith 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) Hydracids : 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_2, 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.

Example : 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.

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Illustration

1. 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

Ans. B

Sol. 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.

Exercise

1. State which of the following reactions is neither oxidation nor reduction –

(A) $Na \rightarrow NaOH$ (B) $Cl_2 \rightarrow Cl^- + ClO^-_3$

(C) $P_2O_5 \rightarrow H_4P_2O_7$ (D) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

Ans. C

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 extent 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 compounds, however, in covalent compounds it represents for imaginary charge.

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.

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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 × Oxidation Number of K + Oxidation Number of Mn + 4 (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.$C_2O_4^{2-}$. 2 × Oxidation Number of C + 4 (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, +1) 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)

Exceptions

(i) Oxidation Number of Cl in Cl_2O is +1, because Cl acts as an electropositive element in this.
(ii) Oxidation Number of Cl in ClF_3 = +3
(iii) Oxidation Number of Cl in $KClO_3$ = +5
(iv) Oxidation Number of I in IF_7 = +7
(v) Oxidation Number of I in IF_5 = +5
(vi) Oxidation Number of Cl in Cl_2O_7 = +7
(vii) Oxidation Number of Cl in HClO = +1
(viii) Oxidation Number of Cl in $HClO_2$ = +5
(ix) Oxidation Number of Cl in $HClO_3$ = +5
(x) Oxidation Number of Cl in $HClO_4$ = +7

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Oxidation Number of Radicals

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

(i) 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}),sulphide (S^{-2}) is equal to charge (–2) present on each of them.

(ii) Oxidation Number of each of the anions, Cl^-, Br^-, I^-, NO_3^-, CN^-, OH^-,SCN^-,CH_3COO^- and HCO_3^- is –1.

(iii) Oxidation Number of each of the anions. PO_4^{-3}, BO_3^{-3}, AsO_4^{-3}. (Arsenate) and AsO_3^{-3} (Arsenite) is –3.

(iv) Oxidation Number of each of the cations, CH_3^+, NH_4^+, Na^+, K^+ is +1.

(v) Oxidation Number of each of the cations, Ca^{+2}, Mg^{+2}, Sr^{+2} and Fe^{+2} is +2.

(vi) Oxidation Number of Al in $[Al(H_2O)_6]^{+3}$ is +3.

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	$2(-1) + x + 3(-2) = 0$	$+2 + x - 6 = 0$	$x = +4$

Oxidation no. of P element

1. Oxidation number of P in P_4 = 0
2. P in PO_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 $Mg_2P_2O_7$: $2(2) + 2x + 7(-2) = 0 + 4 + 2x - 14 = 0$, $2x = 10$, $x = +5$

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 $Cr_2O_7^{-2}$	: $2x - 14 = -2$,	$2x = 12$	$x = +6$
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)

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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 $Mn(C_2O_4)_2.2H_2O$	: $x - 4 = 0$,	$x = +4$

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.

Iin 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_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Oxidation number of carbon	– 4	– 2	0	+ 2	+ 4

OXIDATION AND REDUCTION IN TERMS OF OXIDATION NUMBER

(1) **Oxidation :** Chemical process involving increase in oxidation number.

(2) **Reduction :** Chemical process involving decrease in oxidation number.

(3) **Oxidising agent :** substance which undergoes decrease in oxidation number of one or more of its element.

(4) **Reducing agent :** Substance which undergoes increase in oxidation number of one or more of its elements.

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(5) List of some 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_2O_2	$H_2O_2 \rightarrow H_2O$	O	$-1 \rightarrow -2$
$KMnO_4 / H_2SO_4$	$MnO_4^{-1} \rightarrow MnO_4^{-2}$	Mn	$+7 \rightarrow +2$
$KMnO_4 / KOH$	$MnO_4^- \rightarrow MnO_4^{-2}$	Mn	$+7 \rightarrow +6$
$KMnO_4 / H_2O$	$MnO_4^- \rightarrow MnO_2$	Mn	$+7 \rightarrow +4$
Conc. HNO_3	$HNO_3 \rightarrow NO_2$	N	$+5 \rightarrow +4$
$K_2Cr_2O_7 / H_2SO_4$	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	Cr	$+6 \rightarrow +3$
KIO_3 / HCl	IO_3^-	I	$+5 \rightarrow -1$

(6) List of some common reducing agents:

Reagent	Chemical Change	Element changin g 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	$0 \rightarrow +4$
$S_2O_3^{2-}$	$S_2O_3^{2-} \rightarrow S_4CO_6^{2-}$	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
chloric (I) acid	$ClO^- \rightarrow Cl^-$	2
KIO_3 in dilute acid	$IO_3^- \rightarrow I$	5
KIO_3 in concentrated acid	$IO_3^- \rightarrow I^-$	4

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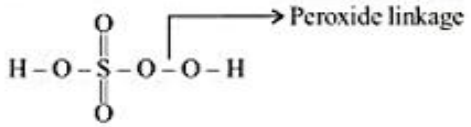
Reducing agent	Effective Change	Increase in O.N.
iron(II) salts (acid)	$Fe^{2+} \rightarrow Fe^{3+}$	1
tin (II) salts (acid)	$Sn^{2+} \rightarrow Sn^{4+}$	2
sulphites (acid)	$SO_3^{2-} \rightarrow SO_4^{2-}$	2
hydrogen sulphide	$S^{2-} \rightarrow S$	2
iodidies (dilute acid)	$I^- \rightarrow I$	1
iodides (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.

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

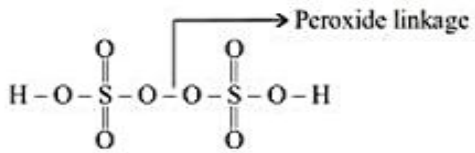
(i) Oxidation number of S in H_2SO_5
(Permonosulphuric acid or Caro's acid)
By usual method; H_2SO_5
$2 \times 1 + x + 5 \times (-2) = 0$ or $x = +8$
But this cannot be true as maximum oxidation number for S cannot exceed + 6. Since S has only 6 electrons in its valence shell. This exceptional value 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,
$2 \times (+1) + x + 3 \times (-2) + 2 \times (-1)$
(for H) (for S) (for O) (for O-O)
or $2 + x - 6 - 2 = 0$ or $x = +6$.

(ii) Oxidation number of S in $H_2S_2O_8$
(Peroxidisulphuric acid or Marshall's acid)
By usual method ; $H_2S_2O_8$
$1 \times 2 + 2x + 8(-2) = 0$
$2x = +16 - 2 = 14$ or $x = +7$

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



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

$2 \times (+1) + 2 \times (x) + 6 \times (-2) + 2 \times (-1) = 0$

(for H) (for S) (for O) (for O-O)

or $2 + 2x - 12 - 2 = 0$ or $x = +6$.

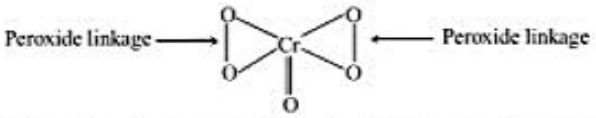
(iii) Oxidation number of Cr in CrO_5

(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

$x + 1 \times (-2) + 4 (-1) = 0$

(for Cr) (for O) (for O-O)

or $x - 2 - 4 = 0$ or $x = +6$.

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 element 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 $HC \equiv N$ and $HN \rightleftarrows C$

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

In such cases, evaluation of oxidation number should be made using indirect concept or by the original concepts of chemical bonding.

(i) Oxidation number of carbon in $H - N \rightleftarrows C$

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

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

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

(for H) (for N) (for C)

or $1 + x - 3 = 0$ or $x = +2$.

(ii) Oxidation number of carbon in $HC \equiv N$

In $HC \equiv N$, 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

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

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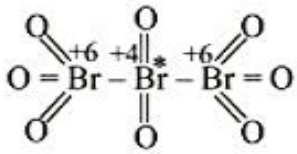
(b) Oxidation number of carbon in C_3O_2

$$O = \overset{+2}{C} = \overset{0}{C^*} = \overset{+2}{C} = O$$

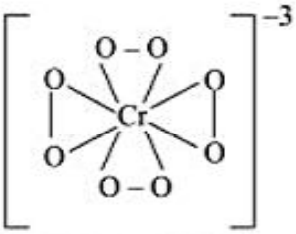
Structure of C_3O_2
(Carbon suboxide)

(c) Oxidation number of Br in Br_3O_8



Structure of Br_3O_8 (tribromooctaoxide)

(d) Oxidation number of Cr in $K_3[CrO_8]$



$K_3[CrO_8]$
$[CrO_8]^{-3}$
$x - 8 = -3$
$x = 5$

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 $Na_2S_2O_3$

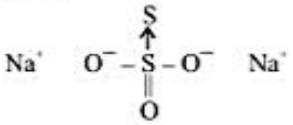
By usual method

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

But this is unacceptable as the two sulphur atoms in $Na_2S_2O_3$ 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.

$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + S + H_2O$$

In this case, the oxidation number of sulphur is evaluated from concepts of chemical bonding. The chemical structure of $Na_2S_2O_3$ 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 coordinated S)
or $+2 - 6 + x - 2 = 0$ or $x = +6$

Thus two sulphur atoms in $Na_2S_2O_3$ have oxidation number of - 2 and +6.

(ii) Oxidation number of chlorine in $CaOCl_2$
(bleaching powder)

In bleaching powder, Ca(OCl)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.

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(iii) Oxidation number of N in NH_4NO_3

By usual method $N_2H_4O_3$; $2x + 4 \times (+1) + 3 \times (-1) = 0$

$2x + 4 - 3 = 0$ 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^-

NH_4^+ $x + 4 \times (+1) = +1$ or $x = -3$

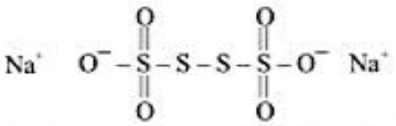
NO_3^- $x + 3\ (-2) = -1$ or $x = +5$.

(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 ($Na_2S_4O_6$)

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.

$2 \times x + 2 \times 0 + 6 \times (-2) = -2$

(for S) (for S-S) (for O)

$x = +5$.

Illustration

1. Determine Oxidation number of the element underlined in each of the following :

(a) $\underline{Fe}SO_4\ (NH_4)_2SO_4 \cdot 6H_2O$:

Sol. Put sum of Oxidation Numbers of $SO_4 = -2$

Sum of Oxidation Numbers in $(NH_4)_2SO_4 = 0$ [$(NH_4)_2SO_4$ is a complete molecule]

Sum of Oxidation Numbers in $H_2O = 0$ [H_2O is complete molecule]

$x + (-2) + 0 + 0 = 0$; $\therefore$ $x = +2$

(b) $\underline{Fe}_{0.94}O$:

Sol. $x \times 0.94 + (-2) = 0$; $x = 200/94$

(c) $Na_2[\underline{Fe}(CN)_5NO]$:

Sol. NO in iron complexes has NO^+ nature.

Thus $2 \times 1 + x + 5 \times (-1) + 1 = 0$

(for Na) (for Fe) (for CN) (for NO); $\therefore$ $x = +2$

(d) $\underline{Fe}NO(H_2O)_5SO_4$:

Sol. $x + 1 + 5 \times 0 + (-2) = 0$; $\therefore$ $x = +1$

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Exercise

1. Oxidation number of Fe in $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, $[Fe(SCN)]^{+2}$ and $[Fe(H_2O)_6]^{+3}$ respectively would be–

(A) +3, +2, +3 and +3(B) +3, +3, +3 and +3(C) +3, +2, +2 and +2(D) +2, +2, +2 and +2

Ans. A

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

(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-I : $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

(Skeleton equation)

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

$$\overset{0}{Cu} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \rightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

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

$$\overset{0}{Cu} \rightarrow \overset{+2}{Cu}(NO_3)_2 \quad .....(i)$$

$$H\overset{+5}{N}O_3 \rightarrow \overset{+4}{N}O_2 \quad .....(ii)$$

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Increase in oxidation number of copper = 2 units per molecule Cu
Decrease in oxidation number of nitrogen = 1 unit per molecule HNO_3

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

$$Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

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

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

This is the balanced equation.

(2) Ion-electron method (half reaction method)

Jette and LaMev developed the method for balancing redox-reactions by ion electron method in 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 done in acidic or neutral solutions.
(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 charge 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,

$$Cr_2O_7^{2-} + C_2O_4^{2-} \xrightarrow{H^+} Cr^{3+} + CO_2$$

(b) Write both the half reactions.

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$ (Reduction half reaction)

$C_2O_4^{2-} \rightarrow CO_2$ (Oxidation half reaction)

(c) Atoms other than H and O are balanced

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

$C_2O_4^{2-} \rightarrow 2CO_2$

(d) Balance O–atoms by the addition of H_2O to another side

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

$C_2O_4^{2-} \rightarrow 2CO_2$

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(e) Balance H–atoms by the addition of H^+ ions to another side

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

$C_2O_4^{2-} \rightarrow 2CO_2$

(f) Now, balance the charge by the addition of electrons (e^-).

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

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

(g) Multiply equations by a constant to get number of electrons same in both side. In the above case second equation is multiplied by 3 and then added to first equation.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$3C_2O_4^{2-} \rightarrow 6CO_2 + 6e^-$$
$$\overline{Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O}$$

In alkaline medium

(a) Consider the reaction

$$Cr(OH)_3 + IO_3^- \xrightarrow{OH^-} I^- + CrO_4^{2-}$$

(b) Separate the two half reactions.

$Cr(OH)_3 \rightarrow CrO_4^{2-}$ (Oxidation half reaction)

$IO_3^- \rightarrow I^-$ (Reduction half reaction)

(c) Balance O– atoms by adding H_2O.

$H_2O + Cr(OH)_3 \rightarrow CrO_4^{2-}$

$IO_3^- \rightarrow I^- + 3H_2O$

(d) Balance H–atoms by adding H_2O to side having deficiency and OH^- to side having deficiency of H–atoms.

$5OH^- + H_2O + Cr(OH)_3 \rightarrow CrO_4^{2-} + 5H_2O$

$5OH^- + Cr(OH)_3 \rightarrow CrO_4^{2-} + 4H_2O$

$IO_3^- + 6H_2O \rightarrow I^- + 3H_2O + 6OH^-$

or $IO_3^- + 3H_2O \rightarrow I^- + 6OH^-$

(e) Balance the charges by electrons

$5OH^- + Cr(OH)_3 \rightarrow CrO_4^{2-} + 4H_2O + 3e^-$

$IO_3^- + 6H_2O + 6e^- \rightarrow I^- + 3H_2O + 6OH^-$

(f) Multiply first equation by 2 and add to second to give

$10OH^- + 2Cr(OH)_3 \rightarrow 2CrO_4^{2-} + 8H_2O + 6e^-$

$IO_3^- + 6H_2O + 6e^- \rightarrow I^- + 3H_2O + 6OH^-$

$$\overline{4OH^- + 2Cr(OH)_3 + IO_3^- \rightarrow 5H_2O + 2CrO_4^{2-} + I^-}$$

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Illustration

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

$H_2C_2O_4 + xH_2O_2 \rightarrow yCO_2 + zH_2O$

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

Ans. B

Sol. (i) The half reaction for oxidation is, $H_2C_2O_4 \rightarrow CO_2$

Balancing carbon atoms on both sides, $H_2C_2O_4 \rightarrow 2CO_2$

Balancing hydrogen atoms on both sides,

$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+$$

Balancing the charge on both sides,

$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$ (balanced)

(ii) The half reaction for reduction is –

$$H_2O_2 \rightarrow H_2O$$

Balancing oxygen atoms on both sides,

$$H_2O_2 \rightarrow 2H_2O$$

Balancing hydrogen atoms,

$$H_2O_2 + 2H^+ \rightarrow 2H_2O$$

Balancing the charge,

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (balanced)

Now, adding both equation,

$$H_2C_2O_4 + H_2O_2 \rightarrow 2CO_2 + 2H_2O$$

This is balanced equation.

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

$xI_2 + yOH^- \rightarrow IO_3^- + zI^- + 3H_2O$

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

Ans. C

Sol.

$\overset{0}{I_2} \rightarrow \overset{+5}{IO_3}$ ..... (i) Oxidation

$\overset{0}{I} \rightarrow \overset{-1}{I^-}$ ..... (ii) Reduction

Balancing atoms of Iodine on two sides,

$I_2 \rightarrow 2IO_3^-$

or, $I_2 + 12OH \rightarrow 2IO_3^- + 6H_2O$

Balancing change,

$I_2 + 12OH^- \rightarrow 2IO_3^- + 6H_2O + 10e^-$

$I_2 \rightarrow 2I^-$

and $(I_2 + 2e^- \rightarrow 2I^-) \times 5$

Adding, $6I_2 + 12OH^- \rightarrow 2IO_3 + 10I^- + 6H_2O$

or, $\mathbf{3I_2 + 6OH^- \rightarrow IO_3^- + 5I^- + 3H_2O}$

It is balanced equation.

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Exercise

1. What will be the value of a, b, c, d, e and f in the following equation –

$aMnO_4^- + bC_2O_4^{--} + cH^+ \rightarrow dMn^{++} + eCO_2 + f\,H_2O$

(A) 2, 2, 10, 8, 5, 16 (B) 2, 5, 16, 2, 10, 8 (C) 2, 5, 10, 2, 8,16 (D) 2, 8, 16, 2, 5, 10

Ans. B

2. Balance the following equations using basic medium:

(i) $AsO_3^{3-} + MnO_4^- \rightarrow AsO_4^{3-} + MnO_2 + OH^-$

(ii) $HNO_3 + As_2S_5 \rightarrow H_2SO_4 + H_3AsO_4 + NO_2$

(iii) $N_2H_4 + Cu(OH)_2 \rightarrow N_2 + Cu$

(iv) $S + OH^- \rightarrow S^{2-} + S_2O_3^{2-}$

(v) $S_2O_4^{2-} + Ag_2O \rightarrow Ag + SO_3^{2-}$

Ans. (i) $3AsO_3^{3-} + 2MnO_4^- + H_2O \rightarrow 3AsO_4^{3-} + 2MnO_2 + 2OH^-$

(ii) $40HNO_3 + As_2S_5 \rightarrow 5H_2SO_4 + 2H_3AsO_4 + 40NO_2 + 12H_2O$

(iii) $N_2H_4 + 2Cu(OH)_2 \rightarrow N_2 + 2Cu + 4H_2O$

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

(v) $S_2O_4^{2-} + Ag_2O + 2OH^- \rightarrow 2Ag + 2SO_3^{2-} + H_2O$

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 that 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

$$Mg + Cl_2 \longrightarrow MgCl_2$$

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.

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

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

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

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

(A) 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.

$$H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$$

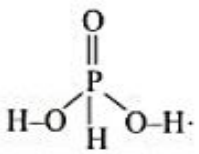
Although one mole of H_2SO_4 has 2 replaceable H atoms but in this reaction H_2SO_4 has given only one H^+ ions, so its n-factor would be 1.

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

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

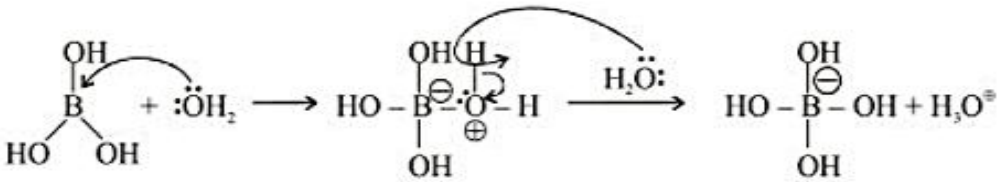
Similarly, n-factor of H_2SO_4	=	1 or 2
n-factor of H_2CO_3	=	1 or 2
n-factor of H_3PO_4	=	1 or 2 or 3
n-factor of H_3PO_3	=	1 or 2 because one of the H is not replaceable in H_3PO_3.

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



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The net reaction is $H_3BO_3 + 2H_2O \rightarrow [B(OH_4]^- + H_3O^+$.

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

(B) 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 moles of replaceable OH^- ions present in 1 mole of base.

For example,
n-factor of NaOH = 1
n-factor of $Zn(OH)_2$ = 1 or 2
n-factor of $Ca(OH)_2$ = 1 or 2
n-factor of $Al(OH)_3$ = 1 or 2 or 3
n-factor of $NH_4(OH)$ = 1

(C) Salts

(i) When no atom undergoes change in oxidation state

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

$$2\ Na_3PO_4 + 3\ BaCl_2 \rightarrow 6\ NaCl + Ba_3(PO_4)_2$$

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 $Ba_3(PO_4)_2$ 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.

$$KMn^{+7}O_4 \xrightarrow{H^+} Mn^{+2}$$

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

$$\therefore \text{ n-factor of } KMnO_4 = |1 \times (+7) - 1 \times (+2)| = 5$$

Similarly

(a) $KMn^{+7}O_4 \xrightarrow{H_2O} Mn^{+4}$
n-factor of $KMnO_4 = |1 \times (+7) - 1 \times (+4)| = 3$

(b) $KMn^{+7}O_4 \xrightarrow{OH^-} Mn^{+6}$
n–factor of $KMnO_4 = |1 \times (+7) - 1 \times (+6)| = 1$

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.

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(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 $K_2Cr_2O_7$ for the given chemical change.

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

In this reaction, state of Cr changes from +6 to +3 in both products.
$\therefore$ n-factor of $K_2Cr_2O_7 = |2 \times (+6) - 2 \times (+3)| = 6$

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

Consider a chemical change, $2Mn^{7+} \rightarrow Mn^{4+} + Mn^{2+}$
Out of the two moles of Mn^{7+}, one mole M^{7+} changes to Mn^{+4} by gaining 3 moles 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

$$3Mn^{7+} \rightarrow 2Mn^{2+} + Mn^{4+}$$

Out of 3 moles of Mn^{7+}, two moles 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 electrons. 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 exchanged but it is the number of moles of electrons exchanged which can be a fraction.

Now, if the reaction would have been $3Mn^{7+} \rightarrow Mn^{2+} + 2Mn^{4+}$. Thus, each mole of Mn^{2+}. 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 different 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
$2Mn^{7+} \rightarrow Mn^{7+} + M^{2+}$ (the compounds containing Mn in + 7 state in reactant and product are different)

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.

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(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.

For example, for following reaction $Cu_2^{1+}S^{2-} \rightarrow Cu^{2+} + S^{4+}O_2$

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

$\therefore$ n-factor of $Cu_2S = (1 \times 2) + (1 \times 6) = 8$

(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

$$KCl^{5+}O_3^{2-} \rightarrow KCl^{1-} + \overset{0}{O_2}$$

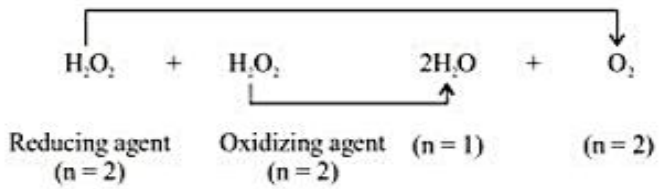
In this reaction, O^{2-} is getting oxidised to O_2 and Cl^{5+} is getting reduced to Cl^{1-}. In each case, 6 mole of electrons are exchanged whether we consider oxidation or reduction
n–factor of $KClO_3$ considering oxidation $= |3(-2) - 3(0)| = 6$
or n-factor of $KClO_3$ considering reducing $= |1 \times (+5) - 1 \times (-1)| = 6$

(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. The 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, $2H_2O_2 \rightarrow 2H_2O + O_2$
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 would be $O_2^{2-} \rightarrow O_2^0 + 2e^-$

and when 1 mole of H_2O_2 gets reduced to H_2O, the half-reaction would be $O_2^{2-} + 2e^- \rightarrow 2O^{2-}$
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,



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Or when the reaction is written as

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

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 $\frac{2}{2} = 1$

$$\underset{(n=1)}{2H_2O_2} \longrightarrow \underset{(n=1)}{2H_2O} + \underset{(n=2)}{O_2}$$

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

$$6Br_2 + 12\,OH^- \longrightarrow 10\,Br^- + 2BrO_3^- + 6H_2O$$

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 of the moles of Br_2. Of the 6 moles of Br_2 used, one mole is getting oxidized, loosing 10 electrons (as reducing agent) and 5 moles of Br_2 are getting reduced and accepts 10 moles of electron (as oxidizing agent)

$$Br_2 \longrightarrow 2Br^{+5} + 10\,e^-$$
$$5Br_2 + 10e^- \longrightarrow 10Br^-$$

$$\underset{\text{Reducing agent}\ (n=10)}{Br_2} + \underset{\text{Oxidizing agent}\ (n=2)}{5Br_2} \longrightarrow \underset{(n=1)}{10\,Br^-} + \underset{(n=5)}{2\,Br^{+5}}$$

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

$$6Br_2 \longrightarrow 10Br^- + 2Br^{5+}$$

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 of 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.

$$\underset{(N=5/3)}{6Br_2} \rightarrow \underset{(N=1)}{10\,Br^-} + \underset{(N=5)}{2\,Br^{5+}}$$

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Illustration

1. 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

Ans. A

Sol. N_A no of electron will be removed by

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

= 42.83 gm of metal M

∴ equivalent wt. of metal is 42.83

2. The equiv. wt. of the salt

$KHC_2O_4, H_2C_2O_4, 4H_2O$ (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) $\frac{\text{Mol. wt}}{4}$

Ans. D

Sol. Per mole of this salt contains 2 moles of $C_2O_4^{2-}$

∴ no of electrons transferred per moles of this salt is

$2C_2O_4^{2-} \longrightarrow 2 \times 2e = 2CO_2 \times 2$

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

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

3. What weight of HNO_3 is needed to convert 62 gm of P_4 in H_3PO_4 in the reaction ?

$P_4 + HNO_3 \longrightarrow H_3PO_4 + NO_2 + H_2O$

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

Ans. B

Sol. The equiv. wt. of $P_4 = \frac{31 \times 4}{5 \times 4} = \frac{31}{5}$

∴ 62 gm $P_4 = \frac{62 \times 5}{31}$ equiv. of P_4

= 10 equiv. of P_4

The equiv. wt. of $HNO_3 = \frac{\text{Mol. wt}}{1} = \frac{63}{1}$

∴ the wt. of HNO_3 required

$= 10 \times 63 = 630$ gm

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

(a) $K_2Cr_2O_7 \xrightarrow{H^+} Cr^{3+}$ (b) $C_2O_4^{2-} \longrightarrow CO_2$

(c) $S_2O_3^{2-} \xrightarrow{\text{alkaline}} SO_4^{2-}$ (d) $I^- \longrightarrow ICl$

Sol. (a) $K_2\overset{+6}{Cr_2}O_7 \xrightarrow{H^+} Cr^{3+}$

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

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

(b) $\overset{+3}{C_2}O_4^{2-} \rightarrow \overset{+4}{C}O_2$

Carbon get oxidized from +3 to +4

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

(c) $\overset{+2}{S_2}O_3^{2-} \xrightarrow{\text{alkaline}} \overset{+6}{S}O_4^{2-}$

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

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

(d) $I^- \longrightarrow \overset{+1}{I}Cl$

I^- get oxidized to I^+

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

5. $H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O$

As per the above mentioned equation what is the equivalent weight of H_3PO_4 ?

Sol. In the mentioned reaction 3 replacable H atoms present in H_3PO_4 are replaced by Na

$\therefore$ the n = 3

$\therefore$ equiv. wt of H_3PO_4 $= \dfrac{\text{Mol. wt. of } H_3PO_4}{3} = \dfrac{98}{3}$ **Ans.**

6. On heating 5×10^{-3} equiv. of $CaCl_2.xH_2O$, 0.18 gm. of water is obtained, what is the value of x?

Sol. Equiv. wt of $CaCl_2$, xH_2O

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

$\therefore$ 5×10^{-3} equiv of $CaCl_2$, xH_2O

$= 5 \times 10^{-3} (55.5 + 9x)$ gm

of $CaCl_2$, xH_2O.

$\therefore$ amount of water obtained

$= \dfrac{18x}{111+18x} \times 5 \times 10^{-3} (55 + 9x)$

$= 9x \times 5 \times 10^{-3}$

$\therefore$ $9x \times 5 \times 10^{-3} = 0.18$

or $x = \dfrac{0.18}{9 \times 5} \times 10^3 = 4$

$\therefore$ x = 4 **Ans.**

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Exercise

1. In the reaction

$Br_2 + Na_2CO_3 \longrightarrow NaBr + NaBrO_3 + CO_2$

The equivalent wt. of $NaBrO_3$ is

(A) $\frac{\text{Mol. wt}}{1}$ (B) $\frac{\text{Mol. wt}}{10}$ (C) $\frac{\text{Mol. wt}}{5}$ (D) $\frac{\text{Mol. wt}}{4}$

Ans. C

2. The equivalent wt. of hypo in the reaction

$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow$

$Na_2SO_4 + H_2SO_4 + HCl$

is –

(A) $\frac{\text{Mol. wt}}{2}$ (B) $\frac{\text{Mol. wt}}{4}$ (C) $\frac{\text{Mol. wt}}{1}$ (D) $\frac{\text{Mol. wt}}{8}$

Ans. D

LAW OF EQUIVALENCE

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

(i) $aA + bB \rightarrow mM + nN$

m.eq of A = m. eq. of B = m.eq of M = m.eq. of N

(ii) In a compound M_xN_y

m.eq of M_xN_y = m.eq of M = m.eq of N

Illustration

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

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

Ans. (A)

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

x (mole) × 2 = 1 × 5

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

Exercise

1. What volume of 6 M HCl and 2 M HCl should be mixed to get litre of 3M HCl ?

Ans. 1.5 L

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Drawbacks of Equivalent concept :

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

$$\text{eg. } 5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 2H_2O$$

$$\therefore \quad \text{Eq. wt of } MnO_4^- = \frac{MnO_4^-(\text{Mol.wt.})}{5}$$

$$\text{eg. } MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4\,OH^-$$

$$\therefore \quad \text{Eq. wt. } MnO_4^- = \frac{MnO_4^-}{3}$$

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

2 Normality of any solution depends on reaction while molarity does not.
For example
Consider 0.1 mol $KMnO_4$ 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 × 5 = 0.5 N. This same sample of $KMnO_4$, if employed in a reaction giving MnO_2 as product (Mn in + 4 state) will have normality 0.1 × 3 = 0.3 N.

ELECTROCHEMICAL CELL

An electrochemical cell is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.
A voltaic or galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

A voltaic cell consists of two half-cells that are electrically connected. Each half cell is the portion of an electrochemical cell in which a half-reaction take place.

A simple half-cell can be made from a metal strip that dips into a solution of its metal ion. An example is the zinc-zinc ion half-cell (often called simply a zinc electrode), which consists of a zinc metal strip dipping into a solution of a zinc salt. Another simple half-cell consists of a copper metal strip dipping into a solution of a copper salt (copper electrode).

In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to another through an external circuit, and ions flow from one half-cell to another through an internal cell connection. Figure given below illustrates an atomic view of a voltaic cell consisting of a zinc electrode and a copper electrode. As long as there is an external circuit, electrons can flow through it from one electrode to another. Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions to produce copper metal, and an electric current flows through the external circuit.

The two half-cells must be connected internally to allow ions to flow between them. As zinc ions continue to be produced, the zinc ion solution begins to build up a positive charge. Similarly, as copper ions plate out as copper, the solution builds up a negative charge. The half cell reactions

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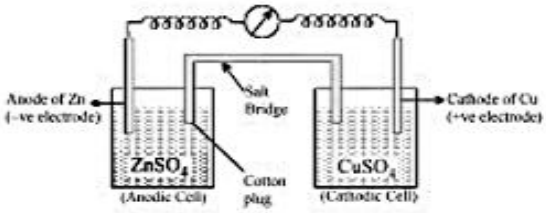
will stop unless positive ions can move from the zinc half-cell to the copper half cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flow occur without mixing of the zinc ion and copper ion solutions. If copper ion come in contact with the zinc metal, for example, direct reaction would occur without an electric current being generated . The voltage would drop, and the battery would run down quickly.



The two half-cells of a voltaic cell are connected by a salt bridge. A salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell; the salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants. The half-cells are connected externally so that an electric current flows.
The two half-cell reactions, as noted earlier, are

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^- \qquad \text{(oxidation half-reaction)}$$

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad \text{(reduction half-reaction)}$$

The first half-reaction, in which a species loses electrons, is the oxidation half-reaction. The electrode at which oxidation occurs is called the anode. The second half-reaction which a species gains electrons, is the reduction half-reaction. The electrode at which reduction occurs is called the cathode. These definitions of anode and cathode hold for all electrochemical cells, including electrolytic cells.
Sum of the two half-reaction

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

The net reaction that occurs in the voltaic cell, it is called the cell reaction.

Electrons are given up by the anode (from the oxidation half-reaction) and thus flow from it, whereas electrons are used up by the cathode (by the reduction half-reaction) and so flow into this electrode. The anode in a voltaic cell has a negative sign, because electrons flow from it. The cathode in a voltaic cell has a positive sign.

Note : **1.** Salt-bridge contains solution of strong ionic salts like NaCl, $NaNO_3$, KNO_3, KCl etc., which is soaked in a colloidal solution of agar-agar gel which permits the movement of ions of salts only.

2. Salt-bridge maintains the electrical neutrality of the solutions in the two half-cells. In the absence of salt bridge, a reverse potential difference is set up in the two half-cells which results in breaking the continuous supply of voltage.

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EMF (ELECTRO MOTIVE FORCE)

The efficiency of a cell depends on the tendency of anode to lose electrons to cathode and the ability of cathode to receive electrons. Cell efficiency is measured in terms of emf (electromotive force), which is the difference in potentials of two electrodes due to which electrons flow from anode to cathode. EMF value of a cell is constant for given concentration of electrolyte, temperature and the pressure (in case of gases). Therefore, it depends on concentration, temperature and pressure.

EMF of a cell is measured in terms of the difference in electric potential (electrical pressure) between anode and cathode. Its unit is V(volt). The potential of half-cell is known as electrode potential, which is the tendency of an electrode to get oxidized or reduced. Thus, tendency to get oxidized is called oxidation potential and the tendency to get reduced is called reduction potential.

It is not possible to measure the potential of a single electrode; only emf's of cells can be measured. By convention, the reference chosen for comparing electrode potentials is the standard hydrogen electrode.

Normal or Standard hydrogen electrode (NHE or SHE)

The inert electrode is present in contact with the gas at 1 atm pressure (unless specified) and its ions in the solution The nature of inert electrode should be such that, when the external voltage is changed even by small amount from the equilibrium value, the reaction will proceed one way or the other. Most suitable electrode is platinum with fine coat of platinum powder or platinum black. It is denoted as :

$H^+ \mid H_2$ (1 atm) $\mid$ Pt

When reduction occurs at NHE

$$2H^+_{(aq)} + e^- \longrightarrow H_{2(g)}$$

When oxidation occurs at NHE

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$$

CELL NOTATION

A cell can be represented as :

LHE (Anode) ‖ RHE (Cathode)

The anode or oxidation half-cell is always written on the left and the cathode or reduction half-cell is written on the right. The two electrodes are electrically connected by means of a salt bridge shown by two vertical bars.

$$\underset{\text{anode}}{Zn_{(s)}} \mid \underset{\text{salt bridge}}{Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)}} \mid \underset{\text{Cathode}}{Cu_{(s)}}$$

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The half-cell which has higher reduction potential, acts as cathode and the electrode with lower reduction potential or higher oxidation potential acts as anode.

The cell terminals are at the extreme ends in this cell notation, and a single vertical bar indicates a phase boundary - say between a solid terminal and the electrode solution. For the anode of the same cell, you have

$$\underset{\text{anode terminal}}{Zn_{(s)}} \quad \underset{\text{phase boundary}}{|} \quad \underset{\text{anode electrolyte}}{Zn^{2+}_{(aq)}}$$

When the half-reaction involves a gas, an inert material such as platinum serves as a terminal and as an electrode surface on which the half-reaction occurs. The platinum catalyzes the half-reaction but otherwise is not involved in it. Hydrogen bubbles over a platinum plate that is immersed in an acidic solution. The cathode half-reaction is

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

The notation for the hydrogen electrode, written as a cathode, is

$$H^+_{(aq)} \,|\, H_{2(g)} \,|\, Pt \quad \text{or} \quad H^+_{(aq)} \,|\, H_{2(g)}, Pt \quad \text{or} \quad H^+_{(aq)} \,|\, Pt\ H_2$$

when this electrode acts as an anode

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$$

$$Pt \,|\, H_{2(g)} \,|\, H^+_{(g)}$$

Additional examples of electrodes. A comma separates ions present in the same solution.

Cathode	Cathode Reaction
$Cl_{2(g)} \,|\, Cl^-_{(aq)} \,|\, Pt$	$Cl_{2(aq)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$
$Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \,|\, Pt$	$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$
$Cd^{+2}_{(aq)} \,|\, Cd_{(s)}$	$Cd^{2+}_{(aq)} + 2e^- \longrightarrow Cd_{(s)}$

ELECTRO CHEMICAL SERIES

The emf of a voltaic cell depends on the concentrations of substances and the temperature of the cell. For purposes of tabulating electrochemical data, it is usual to choose thermodynamic standard-state conditions for voltaic cells. The standard emf, E^0_{cell}, is the emf of a voltaic cell operating under standard-state conditions (solute concentrations are each 1 M, gas pressures are each 1 atm, and the temperature has a specified value – usually 25°C). Note the superscript degree sign (0), which signifies standard-state conditions.

In this series all species are arranged in decreasing order of their standard reduction potential.

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ELECTRO CHEMICAL SERIES

S.NO.	Reduction half cell reaction	E° in volts at 25°C
1.	$F_2 + 2e^- \longrightarrow 2F^-$	+2.65
2.	$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+2.01
3.	$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.82
4.	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+1.65
5.	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.52
6.	$Au^{3+} + 3e^- \longrightarrow Au$	+1.50
7.	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36
8.	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
9.	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
10.	$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.07
11.	$NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O$	+0.96
12.	$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92
13.	$Cu^{2+} + I^- + e^- \longrightarrow CuI$	+0.86
14.	$Ag^+ + e^- \longrightarrow Ag$	+0.799
15.	$Hg_2^{2+} + 2e^- \longrightarrow 2\,Hg$	+0.79
16.	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
17.	$I_2 + 2e^- \longrightarrow 2I^-$	+0.535
18.	$Cu^+ + e^- \longrightarrow Cu$	+0.53
19.	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
20.	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.27
21.	$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.222
22.	$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.15
23.	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.13
24.	$2H^+ + 2e^- \longrightarrow H_2$	0.00
25.	$Fe^{3+} + 3e^- \longrightarrow Fe$	−0.036
26.	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.126
27.	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
28.	$AgI + e^- \longrightarrow Ag + I^-$	−0.151
29.	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.25
30.	$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
31.	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.403
32.	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.41
33.	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
34.	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.74
35.	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.762
36.	$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	−0.828
37.	$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.18
38.	$Al^{3+} + 3e^- \longrightarrow Al$	−1.66
39.	$H_2 + 2e^- \longrightarrow 2H^-$	−2.25
40.	$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.37
41.	$Na^+ + e^- \longrightarrow Na$	−2.71
42.	$Ca^{2+} + e^- \longrightarrow Ca$	−2.87
43.	$Ba^{2+} + 2e^- \longrightarrow Ba$	−2.90
44.	$Cs^+ + e^- \longrightarrow Cs$	−2.92
45.	$K^+ + e^- \longrightarrow K$	−2.93
46.	$Li^+ + e^- \longrightarrow Li$	−3.03

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Applications of Electrochemical Series :

The important applications of electrochemical series are:

(a) Strength of Oxidising and Reducing Agents :

Standard electrode potentials are useful in determining the strengths of oxidizing and reducing agents under standard-state conditions.

$$\text{Strength of reducing agent} \propto \frac{1}{\text{Standard reduction potential}}$$

Strength of oxdising agent $\propto$ standard reduction potential

Li is strongest reducing agent and F_2 is strongest oxidising agent.

(b) **Standard EMF of a cell (E^0_{Cell}) :**

E^0 = difference in potentials of two half-cells

E^0 = {standard oxidation potential of anode – standard oxidation potential of cathode}

$$E^0_{cell} = (E^0_{oxidation})_{anode} - (E^0_{oxidation})_{cathode}$$

OR

E^0 = {standard reduction potential of a cathode – standard reduction potential of anode}

$$E^0_{cell} = (E^0_{reduction})_{cathode} - (E^0_{reduction})_{anode}$$

(c) **Predicting feasibility of a redox reaction :** In general, a redox reaction is feasible only if the species which has higher reduction potential is reduced i.e., accepts the electrons and the species which has lower reduction potential is oxidised i.e. loses the electrons. Otherwise, a redox reaction is not feasible. In other words, the species to release electrons must have lesser reduction potential as compared to the species which is to accept electrons.

(d) **To predict whether a metal can liberate hydrogen from acid or not :** only those metals which have negative reduction potentials, can liberate hydrogen from the acids.

Illustration

1. Writing the cell Reaction from the Cell Notation

(a) Write the cell reaction for the voltaic cell

$$Tl_{(s)} \mid Tl^+_{(aq)} \parallel Sn^{+2}_{(aq)} \mid Sn_{(s)}$$

(b) Write the cell reaction for the voltaic cell

$$Zn_{(z)} \mid Zn^{2+}_{(aq)} \parallel Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \mid Pt$$

Sol.

(a) The half-cell reactions are

$$Tl_{(s)} \longrightarrow Tl^+_{(aq)} + e^-, \; Sn^{2+}_{(aa)} + 2e^- \longrightarrow Sn_{(s)}$$

Multiplying the anode reaction by 2 and then summing the half-cell reactions gives

$$2Tl_{(s)} + Sn^{2+}_{(aq)} \longrightarrow 2Tl^+_{(aq)} + Sn(s)$$

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(b) The half cell reactions are

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$. $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ and the cell reaction is :

$Zn_{(s)} + 2Fe^{3+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$

The nature of inert electrode should be such that, when the external voltage is changed even by small amount from the equilibrium value, the reaction will proceed one way or the other. Most suitable electrode is platinum with fine coat of platinum powder or platinum black. **fully specify the voltaic cell, it is necessary to give the concentrations of solutions or ions and the pressure of gases. In the cell notation, these are written within parentheses for each species.**

For example : $Zn_{(s)} \mid Zn^{2+}$ **(1.0 M)** $\parallel H^+$ **(1.0 M)** $\mid H_2$ **(1.0 atm)** $\mid Pt$

2. Write cell electrode for the following reactions :

(a) $2MnO_4^- + 6H^+ + 5H_2C_2O_4 \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_{2(g)}$

(b) $Cu(OH)_{2(s)} \longrightarrow Cu^{2+} + 2OH^-$

Sol. (a) Half-cell reactions are

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

$2CO_2 + 2H^+ + 2e^- \longrightarrow H_2CO_4$

$MnO_4^-, Mn^{2+}, H^+ \mid Pt$ and $Pt \mid CO_2 \mid H^+$

(b) Half-cell reactions are

$Cu(OH)_{2(s)} + 2e^- \longrightarrow Cu + 2OH^-$

$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$ and electrodes are

$Cu^{2+} \mid Cu$ and $Pt \mid Cu(OH)_2 \mid OH^-$

3. Using the standard electrode potentials predict the reaction, if any, that occurs between the following:

(a) $Fe^{3+}_{(aq)}$ and $I^-_{(aq)}$ (b) $Ag^+_{(aq)}$ and $Cu_{(s)}$

(c) $Fe^{3+}_{(aq)}$ and $Br^-_{(aq)}$ (d) $Ag_{(s)}$ and $Fe^{3+}_{(aq)}$

(e) $Br_{2(aq)}$ and $Fe^{2+}_{(aq)}$

Given : $E^0_{Fe^{3+}/Fe^{2+}} = +0.77V$, $E_{I_2/I^-} = +0.54V$ $E^0_{Ag^+/Ag} = +0.80V$, $E^0_{Cu^{2+}/Cu} = +0.34V$

$E^0_{Br_2/Br^-} = +1.08V$

Sol. **(a)** $I^-_{(aq)}$ loses electrons and $Fe^{3+}_{(aq)}$ gains electrons. Thus

Oxidation half cell reaction $2I^- \longrightarrow I_2 + 2e^-$, $E^0 = -0.54V$

Reduction half cell reaction $[Fe^{3+} + e^- \longrightarrow Fe^{2+}] \times E^0 = +0.77V$

Overall reaction $2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$, $E^0_{cell} = 0.23V$

Since E^0_{cell} is +ve, the reaction is spontaneous i.e., the reaction does take place.

(b) $Cu_{(s)}$ loses electrons and $Ag^+_{(aq)}$ gains electrons. Thus

Oxidation half cell reaction: $Cu \longrightarrow Cu^{2+} + 2e^-$, $E^0 = -0.34V$

Reduction half cell reaction $[Ag^+ + e^- \longrightarrow Ag] \times 2$, $E^0 = +0.80V$

Overall reaction $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$, $E^0_{cell} = 0.46V$

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Since E^0_{cell} is +ve, the reaction is spontaneous

(c) $Br^-_{(aq)}$ loses electrons and $Fe^{3+}_{(aq)}$ gains electrons. Thus

Oxidation half cell reaction $2Br^- \longrightarrow Br_2 + 2e^-$, $E^0 = -1.08V$

Reduction half cell reaction $2Fe^{3+} + 2e^- \longrightarrow Br_2 + 2Fe^{2+}$, $E^0 = +0.77V$

Overall reaction $2Br^- + 2Fe^{3+} \rightarrow Br_2 + 2Fe^{2+}$, $E^0_{cell} = 0.31V$

Since E^0_{cell} is –ve, the reaction is non-spontaneous, i.e., reaction does not take place.

(d) Ag loses electrons and $Fe^{3+}_{(aq)}$ gains electrons. Thus

Oxidation half cell reaction $Ag \longrightarrow Ag^+ + e^-$, $E^0 = -0.80V$

Reduction half cell reaction $Fe^{3+} + e^- \longrightarrow Fe^{2+}$, $E^0 = +0.77V$

Overall reaction $Ag + Fe^{3+} \longrightarrow Ag^+ + Fe^{2+}$, $E^0_{cell} = -0.03V$

Since E^0_{cell} is –ve, the reaction is non-spontaneous, i.e., reaction does not take place.

(e) $Fe^{2+}_{(aq)}$ loses electrons and $Br_{2(aq)}$ gains electrons. Thus

Oxidation half cell reaction $2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^-$, $E^0 = -0.77$

Reduction half cell reaction $Br_2 + 2e^- \longrightarrow 2Br^-$, $E^0 = +1.08V$

Overall reaction $2Fe^{2+} + Br_2 \rightarrow 2Fe^{3+} + 2Br^-$, $E^0_{cell} = +0.31V$

Since E^0_{cell} is +ve, the reaction is spontaneous.

Exercise

1. Calculate the values for cell

$Zn_{(s)} | Zn^{+2}_{(aq)}(1M) || Cu^{+2}_{(aq)}(1M) | Cu_{(s)}$ (i) cell reaction and (ii) e.m.f. of cell

Given : $E^0_{Cu^{2+}/Cu} = +0.35V$; $E^0_{Zn^{2+}/Zn} = -0.76V$

Ans. (i) $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ (ii) 1.11 V

2. Electrode potential of the metals in their respective solution are provided. Arrange the metals in their increasing order of reducing power.

$K^+/K = -2.93V$, $Ag^+/Ag = +0.80V$, $Hg^+/Hg = +0.79V$, $Mg^{2+}/Mg = -2.37V$

$Cr^{3+}/Cr = -0.74V$

Ans. Ag < Hg < Cr < Mg < K

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.

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(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, $Cr_2O_7^{2-}$ 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 sought substance is reduced to its lower oxidation state and to ensure that no reducing agent other that the sought material is present 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

$$2Fe^{3+} + Zn \rightarrow 2Fe^{2+} + Zn^{2+}$$

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

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

(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, aresenious acid etc.

Sample of oxidizing agents that are not fairly soluble in water may be analyzed by treating 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

$$MnO_2 + FeSO_4 \rightarrow MnSO_4 + Fe^{3+}$$
$$FeSO_4(\text{excess}) + MnO_4^- \rightarrow MnSO_4 + Fe^{3+}$$

(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 "$Na_2S_2O_3$" (hypo solution), which reacts with iodine as

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

(Applications of Redox Processes)

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Titrations 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.

$$\text{Titrate} + \text{Titrant} \rightarrow \text{Products}$$

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

or $N_1V_1 = N_2V_2$

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

1. Acidified $KMnO_4$
2. Acidified $K_2Cr_2O_7$
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 solutions

Reagent	Usual conditions for use	Half-reaction	Stability of solution
Potassium permanganate ($KMnO_4$)	Strong acid Weakly acid or neutral strongly basic	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + H_2O$ $MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$ $MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	Solution require Occasional standardization
Quadrivalent cerium (Ce^{4+})	H_2SO_4 solution	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	Indefinitely stable
Potassium dichromemate ($K_2Cr_2O_7$)	Acid solution	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	Indefinitely stable
Potassium iodate (KIO_3)	Strong HCl solution	$IO_3^- + 2Cl^- + 6H^+ + 4e^- \rightleftharpoons ICl_2^- + 3H_2O$	Stable
Potassium bromated ($KBrO_3 + KBr$)	Dilute acid solution	$BrO_3^- + 5Br^- + 6H+ \rightleftharpoons 3Br_2 + 3H_2O$ $Br_2 + 2e \rightleftharpoons 2Br^-$	Indefinitely stable
Iodine (I_3^-)	Neutral, dilute acid or base solution	$I_3^- + 2e \rightleftharpoons 3I^-$	Restandardisation necessary

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 :

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

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

In weakly acidic or neutral medium :

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

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

In alkaline medium :

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}$$

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

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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.

$2MnO_4^- + 10Cl^- + 16\ H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8\ H_2O$

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 stoichiometry of a permanganate oxidation. Also permanganate solution have limited stability and need occasional stabilisation.

Some important titrations using $KKnO_4$ are given below :

(a) $KMnO_4$ vs. oxalic acid :

$$\underset{\substack{\text{Titrant}\\\text{oxidising}\\\text{agent}}}{2\ KMnO_4} + \underset{\substack{\text{Titrate}\\\text{reducing}\\\text{agent}}}{5H_2C_2O_4} + 3H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + 10\ CO_2 + 8H_2O$$

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

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) 2 m-mol $KMnO_4$ reacts with 5 m–mol oxalic acid.

(ii) meq. of $KMnO_4$ = meq. of oxalic acid

$$N_{KMnO_4} \times V_{KMnO_4} = N_{oxalic\ acid} \times V_{oxalic\ acid}$$

(iii) $$\frac{1}{2} \times M_{KMnO_4} \times V_{KKnO_4} = \frac{1}{5} \times M_{oxalicacid} \times V_{Oxalic\ acid}$$

(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 :

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

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 MnO_4^- Meq. of Fe^{2+}

or $N_{KMnO_4} \times V_{KMnO_4} = N_{Fe^{2+}} \times V_{Fe^{2+}}$

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or $5 \times M_{KMnO_4} \times V_{KMnO_4} = M_{Fe^{2+}} \times V_{Fe^{2+}}$

$(\because N_{KMnO_4} = 5 \times M_{KMnO_4}, N_{Fe^{2+}} = M_{Fe^{2+}})$

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

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$Fe^{2+} + C_2O_4^{2-} \rightarrow Fe^{3+} + 2CO_2 + 2e^-$$

so $E_{Fe\text{-}oxalate} = \frac{M}{3}$ (E = 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 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 KMnO4 = Meq. of oxalic acid + Meq. of sodium oxalate

2. Titration using acidified $K_2Cr_2O_7$:

In volumetric analysis $Cr_2O_7^{2-}$ 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+}.

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

$$E_{Cr_2O_7^{2-}} = \frac{M_{Cr_2O_7^{2-}}}{6} = \frac{296}{6} = 49$$

These titrations are made in 1–2 N acid solution. In neutral or alkaline medium, it is not used. In alkaline medium orange $Cr_2O_7^{2-}$ changes to yellow CrO_4^{-2}.

3. Iodometry and Iodimetry

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

$$I_3^- + 2e^- \rightleftharpoons 3I^-$$

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These titrations fall into two categories :

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

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$
$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2I^-$$
$$AsO_3^{3-} + I_2 + H_2O \rightarrow AsO_4^{2-} + 2H^+ + 2I^-$$
$$H_2S + I_2 \rightarrow S + 2I^- + 2H^+$$
$$Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$$
$$N_2H_4 + 2I_2 \rightarrow N_2 + 4H^+ + 4I^-$$

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

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4^{2-}$$

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

$$2MnO_4^- + 10\,I^- + 16H^+ \rightleftharpoons Mn^{+2} + 5I_2 + 8H_2O$$
$$IO_3^- + 5\,I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$

Illustration

1. $KMnO_4$ solution is to be standardised by titration against $As_2O_3(s)$. 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 ?

Sol.

$$Mn^{7+} + 5e^- \rightarrow Mn^{2+} \quad \text{(Reduction)}$$
$$As_2^{3+} \rightarrow 2As^{5+} + 4e^- \quad \text{(oxidation)}$$

$\therefore$ Meq. of As_2O_3 = meq of $KMnO_4$

$$\frac{\frac{0.1097}{198}}{4} \times 1000 = 26.10 \times N \qquad \left(E_{As_2O_3} = M/4\right)$$

$\therefore$ $N_{KMnO_4} = 0.085$

$\therefore$ $M_{KMnO_4} = \frac{0.085}{5} = 0.017$

2. 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

FeC_2O_4 : (N_1)

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

(oxidation)
(Reduction)

$$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2 + 3e^- \qquad (V.f. = 3)$$

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$100\,(N_1 + N_2) = 60 \times 0.02 \times 5$

$(N_1 + N_2) = 3 \times 0.02$ .....(1)

$FeSO_4$: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (V.f. = 1)

(N_2)

$KMnO_4$: $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$

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. of Fe^{2+} from $FeSO_4$ = meq. of $KMnO_4$

$$100\left(\frac{N_1}{3} + N_2\right) = 40 \times 0.02 \times 5$$

$$\left(\frac{N_1}{3} + N_2\right) = 2 \times 0.02 \qquad .....(2)$$

$$\frac{2N_1}{3} = 0.02$$

$$N_1 = 0.03,\ N_2 = 0.03$$

3. 0.84 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.

Sol. $Fe \xrightarrow{\text{Valence factor} = 2} Fe^{2+} + 2e^- \xrightarrow[\text{by } Cr_2O_7^{2-}]{\text{Valence factor} = 1} Fe^{3+} + e^-$ (oxidation)

$6e^- + Cr_2^{6+} \longrightarrow 2Cr^{3+}$ (Reduction)

$$W_{Fe} = \frac{0.84X}{100} \qquad \text{(Given)}$$

Meq. of Fe^{2+} in solution (V.f. = 1) = meq. of $K_2Cr_2O_7$

$= = X.N_{K_2Cr_2O_7}$ (V. f Fe^{2+} = 1)

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

or Meq. of Fe = 2.X.N

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

$$S_{K_2Cr_2O_7} = N \times E = 0.15 \times 49 \qquad \left(E = \frac{249}{6} = 49\right)\ (E = \text{Equivalent mass})$$

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4. What was of $K_2Cr_2O_7$ is required to produce 5.0 litre CO_2 at 75°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. $Cr_2^{6+} + 6e^- \rightarrow 2Cr^{3+}$

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

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

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

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

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

$$\text{or } w_{K_2}Cr_2O_7 = \frac{187.3 \times M}{6 \times 1000} = \frac{187.3 \times 294}{6 \times 1000};$$

$w = 9.18$ g $\qquad (M_{K_2Cr_2O_7} = 294)$

$CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad$ (V.f. for CO_2 = 2)

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

$0.1 \times V = 187.3 \times 2 = 3.746$ L

5. 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 of 0.5 iodine for complete neutralization. Calculate % purity of $KClO_3$ sample.

Sol. $2KClO_3 + 12\,HCl \rightarrow 2KCl + 6H_2O + 6\,Cl_2$

$Cl_2 + 2KI \rightarrow 2\,KCl + I_2$

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

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

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

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

$$\therefore \quad \frac{w_{KClO_3}}{122.5} \times 1000 = \frac{50}{3} \quad \Rightarrow \quad w_{KClO_3} = 2.042$$

[milli-mole (mM) = (mass × 1000) (mol. mass)]

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

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Exercise

1. 20 ml of 0.2 M $MnSO_4$ are completely oxidized by 16 ml of $KMnO_4$ of unknown normality, each forming Mn^{4+} oxidation state. Find out the normality and molarity of $KMnO_4$ solution

Ans. 0.5, 0.167

BACK TITRATION

In neutralization methods of analysis, if end point is exceeded by adding extra acid or base than required for neutralization, additional acid or bases left un-neutralized are determined back by titrating the residual solution against a standard acid or alkali.

Consider titration of a 25 ml solution of CH_3COOH against a standard 0.1 M alkali solution. If 20 ml alkali is exactly required to reach the equivalence point, this gives an idea that $20 \times 0.1 = 2$ meq of acid was present in the 25 ml of its solution.

If, by mistake, end point is exceeded in the titration by adding 25 ml of alkali, the original solution will become alkaline due to additional 0.5 meq of base present unneutralized in the solution as shown below :

	CH_3COOH +	$NaOH \longrightarrow$	CH_2COONa +	H_2O
Initial meq.	2.0	2.5	0.0	0.0
Final meq.	0.0	0.5	2.0	

The excess base is determined by titration them back with a known solution of standard acid viz. HCl or H_2SO_4.

Illustration

1. 9.0 g of an ammonia solution is treated with 50 ml 0.5 N H_2SO_4 solution, 20 ml of 0.1 N NaOH is required for back titration. What is the percentage of ammonia in the solution ?

Sol. meq. of acid taken initially $= 50 \times 0.5 = 25$

meq. of NaOH used up in back titration $= 20 \times 0.1 = 2$

meq. of H_2SO_4 reacted with $NH_3 = 25.00 - 2.00 = 23$

$= \text{meq of } NH_3$

$\Rightarrow$ Mass of ammonia $= 23 \times 10^{-3} \times 17 = 0.391$ g

$\Rightarrow$ Mass percentage of ammonia $= \dfrac{0.391}{9} \times 100 = 4.34$

Exercise

1. 1.0 g of a crude ammonium salt is treated with concentrated KOH solution and liberated ammonia is dissolved and collected in 50 ml 0.5 N HCl solution. 1.5 ml 0.5 N NaOH is required for back titration. Calculate percentage of ammonia in the sample

Ans. 41.225%

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IMPORTANT VARIATIONS

(1) Oxidising property $\propto$ Tendency of accepting electron(s)

(2) Oxidising property $\propto$ Electronegativity

(3) Oxidising property $\propto \frac{1}{\text{Ionic or atomic size}}$

(4) Oxidising property $\propto$ Oxidation number

(5) Reducing property $\propto$ Tendency of losing electron(s)

(6) Reducing property $\propto$ Ionic or atomic size

(7) Reducing property $\propto \frac{1}{\text{Electronegativity}}$

(8) Reducing property $\propto \frac{1}{\text{Oxidationnumber}}$

(9) Decreasing order of reducing strength of metals

$Zn > Fe > Pb > Cu > Ag$

(10) Decreasing order of oxidising strength of metal ion

$Ag^{+} > Cu^{+2} > Pb^{+2} > Fe^{+2} > Zn^{+2}$

(11) Order of oxidising efficiency

$F_2 > Cl_2 > Br_2 > I_2$

(12) Order of reducing efficiency

$I^{-1} > Br^{-1} > Cl^{-1} > F^{-1}$

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SOLVED EXAMPLE

Q.1 In the reaction

$C_2O_4^{-2} + MnO^-_4 + H^+ \rightarrow Mn^{+2} + CO_2$

the reductant is –

(A) $C_2O_4^{-2}$ (B) H^+ (C) MnO^-_4 (D) None of the above

Ans. **(A)**

Sol. In the above reaction $C_2O_4^{-2}$ acts as a reductant because it is oxidised to CO_2 as :

$$C_2O_4^{-2} \rightarrow 2CO_2 + 2e^-(\text{oxidation})$$

$C_2O_4^{-2}$ reduces MnO_4^- to Mn^{+2} ion in solution.

Q.2 Oxidation number of cobalt in $[Co(NH_3)_6]Cl_2Br$ is –

(A) + 6 (B) Zero (C) + 3 (D) + 2

Ans. **(C)**

Sol. Let the O.N.of Co be x

O.N. of NH_3 is zero

O.N. of Cl is –1

O.N. of Br is –1

Hence, x + 6 (0) – 1 x 2 –1 = 0

$\therefore$ x = + 3

so, the oxidation number of cobalt in the given complex compound is +3.

Q.3 Arrange the following in order of

a) Increasing oxidation number : $MnCl_2$, MnO_2, $Mn(OH)_3$, $KMnO_4$

b) Increasing oxidation number : HIO_4, ICl, HI, I_2

c) Decreasing oxidation number : HXO_4, HXO, HXO_3, HXO_2

Sol.

a)	$MnCl_2$	<	$Mn(OH)_3$	<	MnO_2	<	$KMnO_4$
	Ox. no. +2		+3		+ 4		+7
	HI	<	I_2	<	ICl	<	HIO_4
b)	Ox. no. +7		+5		+3		+1
	HXO_4	>	HXO_3	>	HXO_2	>	HXO
c)	Ox. no. -1		0		+1		+7

Q.4 The composition of a sample of wustite is $Fe_{0.93}O$. What percentage of iron is present in the form of Fe(III) ?

Sol. Ox. no. of Fe in wustite $= \frac{200}{93}$

It is an intermediate value in between the oxidation state of Fe(II) and Fe(III). let percentage of Fe(III) in wustite be x then

$$2x(100 - x) + (3 \times x) = \frac{200}{93} \times 100 \qquad \therefore x = 15.05\%$$

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Q.5 One mole of N_2H_4 loses 10 mole electrons to form a new compound Y. Assuming that all the N_2 appears in new compound, what is the oxidation state of Nitrogen in Y ?(There is no change in the oxidation state of H)

Sol. $N_2H_4 \rightarrow (Y) + 10e^-$

($\because$ Y contains all N atoms)

$\therefore N_2^{2-} \rightarrow (2N)^x + 10e^-$

$-4 = 2x - 10$

$x = +3$

$\therefore$ oxidation state of N in Y is $+3$

Q.6 Balance the equation :

$Cr_2O_7^{2-} + C_2O_4^{2-} + H^+ \rightarrow Cr^{+3} + CO_2 + H_2O$

Sol. Reduction : $Cr_2O_7^{2-} \rightarrow Cr^{+3}$ Oxidation : $C_2O_4^{2-} \rightarrow CO_2$

Balacing atoms other than O and H : $Cr_2O_7^{2-} \rightarrow 2Cr^{+3}$

Reaction is taking place in acidic medium

Balancing O

$Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

Balancing H

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

Balancing charges we get reduction half- reaction .

$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$ (1)

Balancing oxidation reaction:

Balancing C $C_2O_4^{2-} \rightarrow 2CO_2$

Balancing O $C_2O_4^{2-} \rightarrow 2CO_2$

Balancing charges, we get oxidation half-reaction

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ (2)

Multiplying (2) by 3 and adding to (1) (To cancel out the electrons)

$C_2O_7^{2-} + 14H^+ + 3C_2O_4^{2-} \rightarrow 2Cr^{+3} + 7H_2O + 6CO_2$

Q.7 Balance the equation

$Cr(OH)_3 + IO^-_3 \rightarrow I^- + CrO_4^{2-}$

Sol. Oxidation : $Cr(OH)_3 \rightarrow CrO_4^{2-}$ Reduction : $IO_3^- \longrightarrow I^-$

Balancing oxidation reaction : Balancing atoms other than H and O

$Cr(OH)_3 \rightarrow CrO_4^{2-}$

Balancing O ; $2OH^- + Cr(OH)_3 \rightarrow CrO_4^{2-} + H_2O$

Balancing H; $3OH^- + 2OH^- + Cr(OH)_3 \rightarrow CrO_4^{2-} + H_2O + 3H_2O$

Balancing charge : $5OH^- + Cr(OH)_3 \rightarrow CrO_4^{2-} + 4H_2O + 3e^-$ (1)

Balancing reduction reaction :

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Balancing O; $IO_3^- + 3H_2O \longrightarrow 6OH^- + I^-$

Balance the charge $6e^- + IO_3^- + 3H_2O \longrightarrow 6OH^- + I^-$ (2)

Multiply (1) by 2 and adding to (2)

$$2Cr(OH)_3 + IO_3^- + 4OH^- \rightarrow 2CrO^{2-}_4 + 5H_2O + I^-$$

Q.8 Find the number of electrons released or absorbed to produce 18.6 gm aniline from nitrobenzene in acidic medium is

(A) 1.2 moles released (B) 1.2 moles absorbed (C) 6 moles released (D) 6 moles absorbed

Ans. **(B)**

Sol. Balanced reaction

$$6e^- + C_6H_5\overset{+3}{N}O_2 + 6H^+ \longrightarrow C_6H_5\overset{-3}{N}H_2 + 2H_2O$$

O. No. O. No.

$\because$ To produce 93 gm (or 1 mole) aniline absorbed number of moles of electron in above reaction = 6

$\therefore$ To produce 18.6 gm (or 1 mole) aniline absorbed number of moles of electron in above reaction

$$= \frac{6}{93} \times 18.6 \Rightarrow 1.2 \qquad \text{Ans.}$$

Q.9 In the redox reaction:

$x\ MnO + y\ PbO_2 + z\ HNO_3 \longrightarrow a\ HMnO_4 + b\ Pb(NO_3)_2 + c\ H_2O$

(A) x = 2, y = 5, z = 10 (B) x = 2, y = 7, z = 8

(C) x = 2, y = 5, z = 8 (D) x = 2, y = 5, z = 5

Ans. **(A)**

Sol. $2MnO + 5PbO_2 + 10\ HNO_3 \rightleftharpoons 2HMnO_4 + 5\ Pb(NO_3)_2 + 4\ H_2O$

Q.10 Calculate the sum of stoichiometric coefficients of products in minimum integral balanced following chemical reaction.

$$a\ CrCl_3 + b\ H_2O_2 + c\ NaOH \longrightarrow x\ Na_2CrO_4 + y\ NaCl + z\ H_2O$$

Ans. 16

Sol.

$$\underbrace{CrCl_3}_{2\times(-3e^-)} + \underbrace{H_2O_2}_{3\times(+2e^-)} \longrightarrow \overset{(+6)}{Na_2CrO_4} + \overset{(-4)}{2H_2O}$$

(balanced skelton) $2CrCl_3 + 3H_2O_2 + 10NaOH \longrightarrow 2Na_2CrO_4 + 6H_2O + 6NaCl + 2H_2O$

$2CrCl_3 + 3H_2O_2 + 10NaOH \longrightarrow 2Na_2CrO_4 + 6NaCl + 8H_2O$

$\Rightarrow$ a = 2 b = 3 and c = 10

Q.11 Number of moles of electrons produced per mole of $FeCr_2O_4$ in the following redox reaction.

$$FeCr_2O_4 + KOH + O_2 \longrightarrow K_2CrO_4 + Fe_2O_3$$

(A) 6 (B) 1 (C) 7 (D) 3

Ans. **(C)**

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

$Cr_2^{6+} \longrightarrow Cr^{+6} + 6e^-$

$FeCr_2O_4 \longrightarrow Fe_2O_3\ K_2CrO_4 + 7e^-$

Q.12 $H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI$

0.01 equivalent of the mentioned acid will neutralize how many grams of NaOH ?

Sol. $H_3\overset{+3}{As}O_3 + I_2 + H_2O = H_3\overset{+5}{As}O_4 + 2HI$

$\therefore$ n = 2

$\therefore$ equiv. wt of H_3AsO_3

$$= \frac{\text{Mol. wt. of } H_3AsO_3}{2} = \frac{126}{2} = 63$$

$\therefore$ 0.01 equiv of H_3AsO_3 = 0.63 gm H_3AsO_3

$H_3AsO_3 + 2NaOH = Na_2HAsO_3 + 2H_2O$

126gm H_3AsO_3 reacts

with 80 gm. of NaOH

0.63 gm. H_3AsO_3 reacts

with $\frac{80}{126} \times 0.63$ gm of NaOH

= 0.4 gm of NaOH Ans.

Q.13 The equivalent weight of a metal is 36. What weight of the metal would give 9.322 gm of its chloride ?

Sol. The equiv. wt. of metal = 36

The equiv. wt. of chlorine = 35.5

Equiv wt of metal chloride = 71.5

71.5 gm. metal chloride contain 36 gm of metal

9.322 gm metal chloride contain

$\frac{36}{71.5} \times 9.322$ gm of metal

= 4.6935 gm of metal

$\therefore$ 4.6935 gm metal give 9.322 gm metal chloride Ans.

Q.14 In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millitre of 0.15 M NaOH should be added for this requirement ?

Sol. Amount of NaOH present in 1000 ml of 0.15 M NaOH = 0.15 × 40 = 6 g

$\therefore$ 1 ml of this solution contain NaOH = $\frac{6}{100} \times 10^{-3}$

$\therefore$ 1.184 g of NaOH will be present in $\frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33$ ml

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Q.15 What weight of Na_2CO_3 of 85% purity would be required to prepare 45.6 ml of 0.235 N H_2SO_4 ?

Sol. Meq. of Na_2CO_3 = Meq. of H_2SO_4

$= 45.6 \times 0.235$

$$\therefore \frac{W_{Na_2CO_3}}{E_{Na_2CO_3}} \times 1000 = 45.6 \times 0.235$$

$$\Rightarrow \frac{W_{Na_2CO_3}}{106/2} \times 1000 = 45.6 \times 0.235$$

$$\therefore \quad W_{Na_2CO_3} = 0.5679 \text{ g}$$

For 85 g of pure Na_2CO_3, weighed sample = 100 g

$$\therefore \quad \text{For 0.5679 g of pure } Na_2CO_3\text{, weighed sample} = \frac{100}{85} \times 0.5679 = 0.6681 \text{ g}$$

Q.16 Two solution of 0.1 M $Cr_2O_7^{2-}$ (aq) and 0.1 M MnO_4^- (aq) are to be titrate Fe^{2+} (aq) separately:
(a) With which solution, $Cr_2O_7^{2-}$ (aq) or MnO_4^- (aq), would the greater volume of titrant (titrating solution) be required for a given solution of Fe^{2+} (aq).
(b) If a given titration required 24.50 ml of 0.1 M $Cr_2O_7^{2-}$ (aq), how many ml of 0.100 M MnO_4^- (aq) would have been required if it had been used instead ?

Sol. Redox changes with MnO_4^- and $Cr_2O_7^{2-}$ are :

(a) $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $\qquad$ $Fe^{2+} \rightarrow Fe^{3+} + e^-$

$Cr_2^{6+}\ 6e^- \rightarrow 2Cr^{3+}$ $\qquad$ $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$

When solution containing same equivalent of Fe^{2+}, are titrated with $Cr_2O_7^{2-}$ and MnO_4^- separately, then

meq. of Fe^{2+} = meq. of $Cr_2O_7^{2-}$ = meq. of MnO_4^-

meq. of $Fe^{2+} = 0.1 \times 6 \times V_1 = 0.1 \times 5 \times V_2$ .....(1)

$$\therefore \quad = \frac{V_2(\text{for } MnO_4^-)}{V_1(\text{for } Cr_2O_7^{2-})} = \frac{6}{5} = 1.20$$

Thus, volume of MnO_4^- required will be 1.2 times of volume of $Cr_2O_7^{2-}$.

(b) To calculate $V_{MnO_4^-}$ needed. Using the given data in eq. (1)

$$24.5 \times 0.1 \times 6 = 0.1 \times 5 \times V_{MnO_4^-}$$

$$\Rightarrow \quad V_{MnO_4^-} = 29.4 \text{ ml}$$

Q.17 A 200 ml sample of a citrus fruit drinks containing ascorbic acid (Vitamin C, mol. wt. 176.13) was acidified with H_2SO_4 and 10 ml of 0.0250 M I_2 was added. Some of the iodine was reduced by the ascorbic acid to I^-. The excess of I_2 required 4.6 ml of 0.01 M $Na_2S_2O_3$ for reduction. What was the vitamin C content of the drink in mg vitamin per mL drink ? The reactions are :

$$C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2HI$$

$$5H_2O + S_2O_3^{2-} + 4I_2 \rightarrow 2SO_4^{2-} + 8I^- + 10\ H^+$$

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Sol. $I_2^{\circ} + 2e^- \rightarrow 2I^-$
$S_2^{2+} \rightarrow 2S^6 + 8e^-$

V.f. for I_2 and $S_2O_3^{2-}$ are 2 and 8 respectively.
Now, meq. of ascorbic acid in 200 mL solution
= meq. of I_2 used by ascorbic acid
= meq. of I_2 added – meq. of I_2 left
$= 0.0250 \times 2 \times 10 - 0.01 \times 8 \times 4.6$
$= 0.5 - 0.368 = 0.132$

$$\therefore \quad w = \frac{0.132 \times \text{Eq.mass}}{1000} = \frac{0.132 \times 176.13}{2 \times 1000}$$

$$\left(\because C_6^{(2/3)+} \rightarrow C_6^{+} + 2e; \therefore E = \frac{M}{2}\right)$$

$\therefore$ = 0.0116 g/200 ml = 0.058 mg/ml

Q.18 The "saponification number" of a fat or oil is defined as the number of milligram of KOH required to saponify 1.0 g of fat or oil To a sample of butter weighing 2.0 g is added a 25 ml 0.5 N KOH solution. After saponification is complete, 8.13 ml of 0.5 N HCl is found to be required to neutralize the excess alkali. What is the "Saponification number" of butter ?

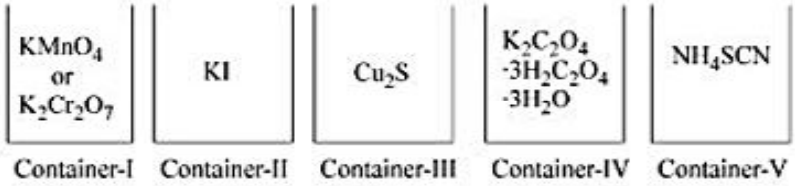
Sol. Meq. of KOH added = 25 × 0.5 = 12.5
Meq of HCl required for back titration = 4.065
Meq of KOH used up for saponification
= 12.5 – 4.065 = 8.435

mg of KOH used for saponification
= 8.435 × 56 = 472.36
mg of KOH used for saponification of 1.0 g butter = 472.36 / 2 = 236.18
Saponification number = 236.18

Q.19 Container–I may contain 1 mol $K_2Cr_2O_7$ or 1 mol $KMnO_4$ in acidic medium. This container–I is mixed with other container–II, III, IV or V, due to which compound present in these containers undergo following half reaction.

$KI \longrightarrow IO_3^-$ $\qquad$ $K_2C_2O_4 \cdot 3H_2C_2O_4 \cdot 2H_2O \longrightarrow CO_2$

$Cu_2S \longrightarrow Cu^{2+} + SO_2$ $\qquad$ $NH_4SCN \longrightarrow SO_4^{2-} + HCN$



Column I represents the two container which are mixed.
Column II represents the number of moles of substance which reacts with 1 mol of substance (may be $KMnO_4$ or $K_2Cr_2O_7$) present in container–I.

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Match the column I with Column–II.

	Column I		Column II
(A)	Container–I + Container–III	(P)	$\frac{3}{4}$
(B)	Container–II + Container–I	(Q)	$\frac{5}{8}$
(C)	Container–I + Container–V	(R)	1
(D)	Container–IV + Container–I	(S)	$\frac{5}{6}$

Ans. (A) P,Q; (B) R,S; (C) R,S; (D) P,Q

Sol. (A) Container–I reacts with container–II

n factor of KI = 6

$KMnO_4$: $1 \times 5 = x \times 6$, $x = \frac{5}{6}$

$K_2Cr_2O_7$: $1 \times 6 = x \times 6$, $x = 1$

(B) n factor of $Cu_2S = 8$

$KMnO_4$: $1 \times 5 = x = 8$, $x = \frac{5}{8}$

$K_2Cr_2O_7$: $1 \times 6 = x \times 8$, $x = \frac{6}{8} = \frac{3}{4}$

(C) n factor of $K_2C_2O_4 \cdot 3H_2C_2O_4 \cdot 3H_2O = 8$

$KMnO_4$: $x = \frac{5}{8}$

$K_2Cr_2O_7$: $x = \frac{3}{4}$

(D) n factor of $NH_4SCN = 6$

$KMnO_4$: $x = \frac{5}{6}$

$K_2Cr_2O_7$: $x = 1$

Q.20 0.1 N $K_2C_2O_4 . 3H_2C_2O_4 . 4H_2O$ solution reacts completely with 20 ml 0.05 M of $KMnO_4$ solution in acidic medium. Another sample of same solution of $K_2C_2O_4 . 3H_2C_2O_4 . 4H_2O$, having same volume is titrated with $\frac{1}{8}$ M NaOH solution, then volume of NaOH solution is

(A) 20 ml (B) 30 ml (C) 50 ml (D) None of these

Ans. **(B)**

Sol. Redox titration

Eq. of $K_2C_2O_4 . 3H_2C_2O_4 . 4H_2O$ = Eq. of $KMnO_4$

$$\frac{0.1 \times V}{1000} = \frac{20 \times 0.05 \times 5}{1000}$$

V = 50 ml

n factor of $K_2C_2O_4 . 3H_2C_2O_4 . 4H_2O$

for redox titration = 8

for acid base titration = 6

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$\therefore$ for acid base titration normality of $K_2C_2O_4.3H_2C_2O_4.4H_2O = \frac{0.1}{8} \times 6\,N$

Eq. of acid = Eq. of base

$$\frac{0.1 \times 50}{8 \times 1000} \times 6 = \frac{1}{8} \times \frac{Vml}{1000}$$

Vml = 30 ml Ans.

Q.21 $(NH_4)_3PO_4$ get converted into NO_3^- and PH_3 on reacting with $KMnO_4$ in acidic medium. If 50 ml of 0.2 M $(NH_4)_3PO_4$ solution reacts with 16 ml of $KMnO_4$ solution, then normality of $KMnO_4$ solution is

(A) 5 (B) 8 (C) 10 (D) 20

Ans. **(C)**

Sol. $(NH_4)_3\,PO_4 \xrightarrow[16\,ml]{KMnO_4} NO_3^- + PH_3$

$-3 \quad +5 \qquad +5 \quad -3$

$+24 - 8 = 16$

50×0.2 M

n–factor of $KMnO_4$ in acidic medium = 5

n-factor of $(NH_4)_3PO_4$ = 16

Eq. of $(NH_4)_3PO_4$ = Eq. of $KMnO_4$

$$\frac{0.2 \times 50}{1000} \times 16 = \frac{N \times 16}{1000}$$

N = 10 Ans.

Q.22 The number of moles of NaOH required to completely react with 20 ml of 0.1 M NaH_2PO_3 solution and 40 ml of 0.1 M $NaHCO_3$.

(A) 8×10^{-3} (B) 2×10^{-3} (C) 4×10^{-3} (D) 6×10^{-3}

Ans. **(D)**

Sol. Eq. of NaH_2PO_3 + Eq. of $NaHCO_3$ = Eq. of NaOH

$$\frac{20 \times 0.1}{1000} \times 1 + \frac{40 \times 0.1}{1000} \times 1 = x$$

$x = 6 \times 10^{-3}$ Ans.]

Q.23 70 ml of a solution containing HCl was treated with excess of $KBrO_3$ and KBr solution of unknown concentration where Br_2 liberated is titrated against a standard solution of 21 ml of 2M $Na_2S_2O_3$ solution. Molarity of HCl solution is

(A) $\frac{2}{10}$ (B) $\frac{36}{100}$ (C) $\frac{6}{10}$ (D) $\frac{86}{100}$

Ans. **(C)**

Sol. $2BrO_3^- + 10\,Br^- + 12\,HCl \longrightarrow 6Br_2 + 6H_2O + 12\,Cl^-$

Mol of $Br_2 = \frac{21 \times 2}{2} = 21$ m mol

No. of eq. of Br_2 produced in 1st Reaction $= 21 \times \frac{5}{3} = 35$ meq.

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$\therefore 70 \times M \times \frac{10}{12} = 35$

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

Q.24 20 ml of $K_4Fe(CN)_6$ solution is divided into 2 equal parts. One part is completely reacted with 10 ml of $FeCl_3$ solution to form $KFe[Fe(CN)_6]$ & KCl. Another part of $K_4Fe(CN)_6$ solution is completely reacted with 20 ml of 0.5 M $FeCl_2$ solution to produce $K_2Fe[Fe(CN)_6]$ & KCl. Molarity of $FeCl_3$ solution is

(A) 1M (B) 2M (C) $\frac{3}{2}$ M (D) 4M

Ans. **(A)**

Sol. $K_4Fe(CN)_6 + FeCl_3 \longrightarrow KFe[Fe(CN)_6] + 3KCl$

n = 3 n = 3

$K_4Fe(CN)_6 + FeCl_2 \longrightarrow K_2Fe[Fe(CN)_6] + 2KCl$

n = 2 n = 2

$(MV)_{K_4Fe(CN)_6} = (MV)_{FeCl_3}$

$10 \times M_1 = M_2 \times 10$

$(MV)_{K_4Fe(CN)_6} = (MV)_{FeCl_2}$

$10 \times M_1 = 0.5 \times 20$

$M_{FeCl_3} = 1$ M Ans.

Q.25 20 ml of $KMnO_4$ solution completely reacts with 10 ml of 1M FeS_2 solution and 20 ml of 1 M CuS solution to produce Cu^{+2}, Fe^{+3}, SO_2. Normality of $KMnO_4$ solution is

(A) 57.5 N (B) 6.5 N (C) 11.5 N (D) 8.5 N

Ans. **(C)**

Sol. $KMnO_4 + FeS_2 + CuS \longrightarrow Cu^{+2} + Fe^{+3} + SO_2$

n = 11 n = 6

Eq. of $KMnO_4$ = Eq. of FeS_2 + Eq. of CuS

$$\frac{N \times V}{1000} = \frac{MV_{FeS_2}}{1000} \times n + \frac{MV_{CuS}}{1000} \times n$$

$$\frac{N \times 20}{1000} = \frac{10 \times 1}{1000} \times 11 + \frac{20 \times 1 \times 6}{1000}$$

$$N = \frac{110 + 120}{20} = \frac{230}{20} = 11.5\,N \text{ Ans.}$$

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