Redox Reaction

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Introduction

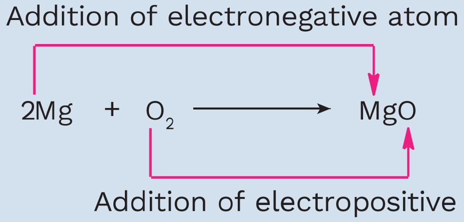
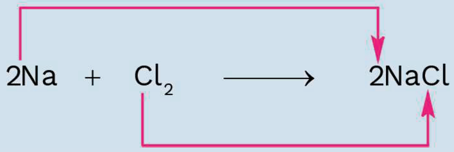
- Chemical reactions in which reduction and oxidation takes place are known as **redox reactions**.
- In order to define oxidation and reduction, there were many concepts which are as following:

Classical concept

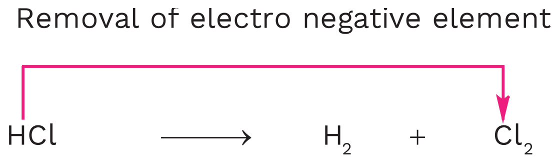
OXIDATION	**REDUCTION**
Addition of oxygen or Removal of hydrogen	Addition of hydrogen or Removal of oxygen
e.g. Addition of O $2\,Mg + O_2 \longrightarrow 2MgO$ Oxidation of Mg	**e.g.** $H_2 + Cl_2 \longrightarrow 2HCl$ Reduction of Cl_2
e.g. $2HCl \longrightarrow H_2 + Cl_2$ Oxidation of HCl	**e.g.** Redox $2H_2O \longrightarrow 2H_2 + O_2$ Oxidation Reduction of H_2O, Oxidation of H_2O

Note: Above definitions failed to define oxidation and reduction in all reactions. Hence, its concept was modified later as following:

OXIDATION	**REDUCTION**
Addition of electronegative element Or Removal of electropositive element	Addition of electropositive element or Removal of electronegative element

OXIDATION	REDUCTION
e.g.  $2Mg + O_2 \longrightarrow MgO$ Oxidation of magnesium and also Reduction of O_2	e.g.  $2Na + Cl_2 \longrightarrow 2NaCl$ Oxidation of Na and Reduction of Cl_2

e.g.



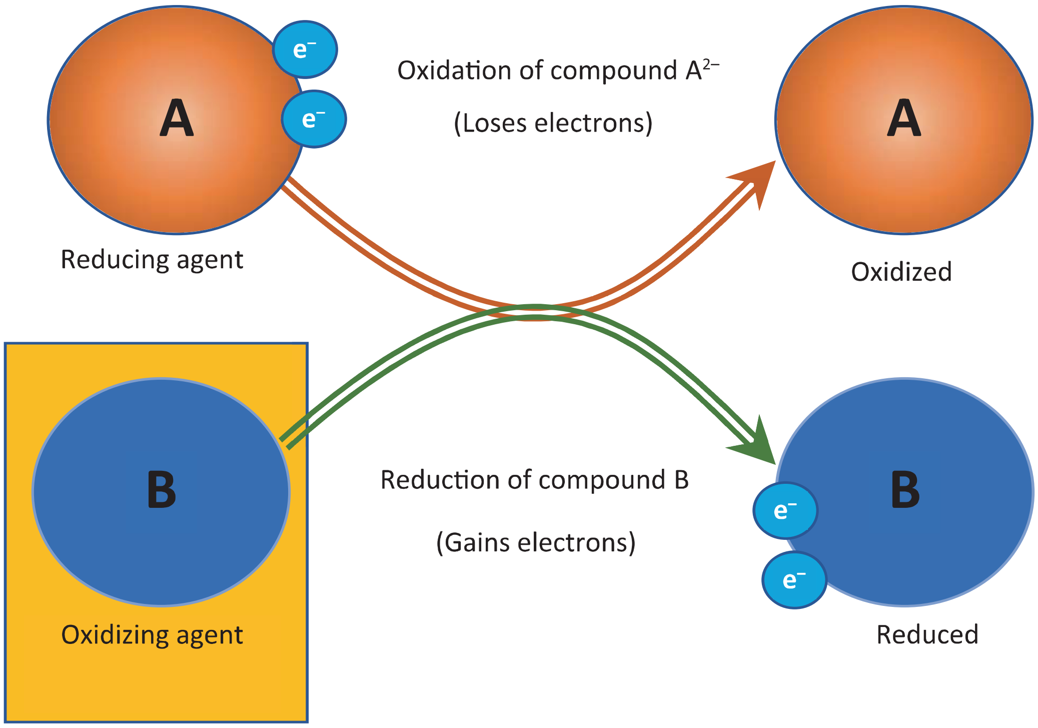
$HCl \longrightarrow H_2 + Cl_2$

Oxidation and reduction of HCl

Modern Concept

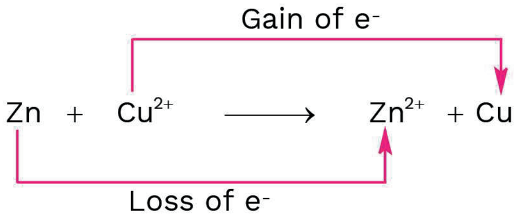
- It is an electronic concept.
- This concept is based upon transfer of electrons.

OXIDATION	REDUCTION
The process in which substance looses some electrons.	The process in which substance gains some electrons.



(i)

e.g.

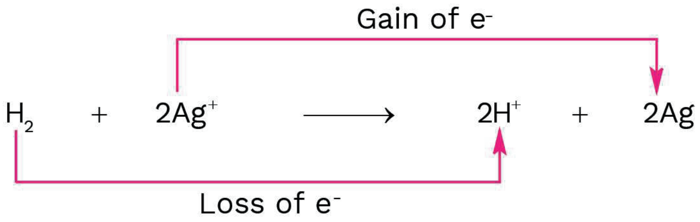


$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

Oxidation of Zn and reduction of Cu^{2+}.

(ii)

e.g.



$$H_2 + 2Ag^{+} \longrightarrow 2H^{+} + 2Ag$$

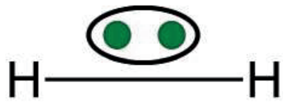
Oxidation of H_2 and reduction of Ag^{+}.

Note: Modern concept can be used to identify oxidation and reduction only in ionic reactions.

Oxidation Number

- The average charge per atom possessed by an element in a specie is called "**oxidation number"** of that element in that species (atom, molecule, ion).
- In a specie, the charge is developed on atoms due to difference in electronegativity between bonded atoms or due to transfer of electrons.

e.g. H_2

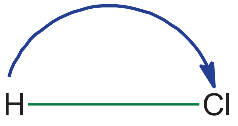


$$(\text{Oxidation number})_H = \frac{\text{Total charge on H atoms}}{\text{Total number of H}-\text{atoms}}$$
$$= \frac{0}{2}$$
$$= 0$$

Oxidation number of hydrogen in H_2 = zero

e.g. **i) HCl**

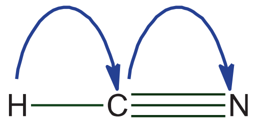
$$(O.N)_H = \frac{(+1)}{1} = +1$$
$$(O.N)_{Cl} = \left(\frac{-1}{1}\right) = -1$$



More electronegative

ii) HCN

$$(O.N)_H = \frac{+1}{1} = +1$$
$$(O.N)_C = \frac{-1+3}{1} = +2$$
$$(O.N)_N = \frac{-3}{1} = -3$$

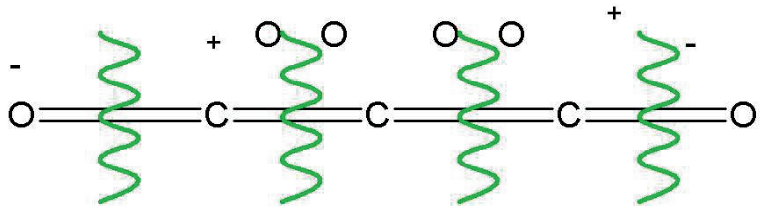


Order of electronegativity
H < C < N

Note: Oxidation number may be positive, negative, integer, fractional or even zero.

e.g.

i) C_3O_2 (carbon suboxide)

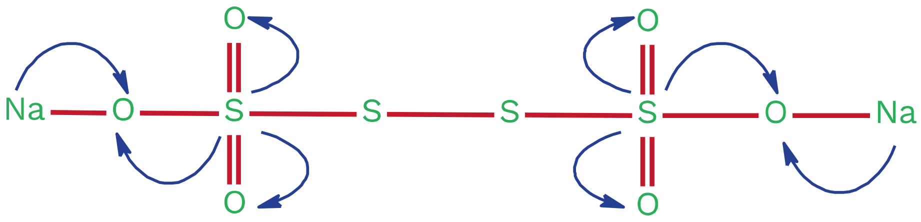


Now,

$$(O.N)_O = \frac{-2-2}{2} = (-2)$$

$$(O.N)_C = \frac{+2+0+2}{3} = \left(\frac{+4}{3}\right)$$

ii) $Na_2S_4O_6$



$$(O.N)_{Na} = \frac{+1+1}{2} = (+1)$$

$$(O.N)_O = \frac{-12}{6} = (-2)$$

$$(O.N)_S = \frac{+5+0+0+5}{4}$$

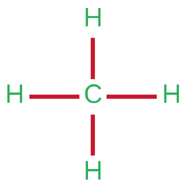
$$= (+2.5)$$

Note: An element can show different oxidation number in different species.

e.g.

i) $\overset{+4}{C}O_2$ and $\overset{-4}{C}H_4$

O = C = O and



$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-H$$

Oxidation number of carbon in CO_2 is +4 and in CH_4 is −4.

ii) $\overset{0}{H_2}$, $\overset{+1}{H}Cl$ and $Na\overset{+1}{OH}$

Oxidation number of hydrogen in H_2, HCl and NaOH is 0, +1 and +1 respectively.

Determination of Oxidation Number

For a specie, the sum of oxidation number of each atom present is equal to the charge possessed by that specie.

Let $A_xB_yC_z$

- $x(p) + y(q) + z(r) = 0$

$(A_xB_yC_z)^{\phi}$

- $x(p) + y(q) + z(r) = \phi$

e.g.

i) H_2O
- $2(+1) + 1(-2) = 0$

ii) CF_4
- $1(+4) + 4(-1) = 0$

iii) CO_2
- $1(+4) + 2(-2) = 0$

Oxidation Number of Some Common Elements

- For elements present in their free state (Natural form at room temperature and pressure), the oxidation number is zero.

e.g.

$$\left.\begin{matrix} H_2, & He, & C, & N_2, & O_2, & F_2 \\ Na, & Mg, & S_8, & P_4, & Cl_2 & \\ Fe, & Zn, & Ag, & \text{etc.} & & \end{matrix}\right\} \text{Oxidation number} = 0$$

- All IA group elements show (+1) oxidation number in their compounds.

i.e.

$$\left.\begin{matrix} \text{Li} \\ \text{Na} \\ \text{K} \\ \text{Rb} \\ \text{Cs} \end{matrix}\right\} \text{In compounds, Oxidation number} = (+1) \text{ always}$$

- All IIA group elements show (+2) oxidation numbers in their compounds

i.e.

$$\left.\begin{matrix} \text{Be} \\ \text{Mg} \\ \text{Ca} \\ \text{Sr} \\ \text{Ba} \end{matrix}\right\} \text{In compounds, Oxidation number} = (+2) \text{ always}$$

Note: Fluorine is most electronegative element hence always show (–1) oxidation number in its compounds.

- **For hydrogen**
  General oxidation number = (+1)
  But , In metal hydrides, $(\text{oxidation number})_H = (-1)$
  $(\text{Electronegativity})_{\text{Metal}} < (\text{Electronegativity})_H$

e.g.

$\text{LiH} \Rightarrow 1(+1) + 1(x) = 0$

$\Rightarrow x = -1$

$CaH_2 \Rightarrow 1(+2) + 2(x) = 0$

$\Rightarrow x = -1$

- **For oxygen**
  General oxidation number = (–2) in oxides.
  But, In peroxides, oxidation number = (–1)
  In superoxides, oxidation number = $\left(-\frac{1}{2}\right)$

Na_2O	Na_2O_2	NaO_2
$2(+1)+1(x)=0$ $x=(-2)$	$2(+1)+2(x)=0$ $x=(-1)$	$1(+1)+2x=0$ $x=\left(-\frac{1}{2}\right)$
Oxide	Peroxide	Superoxide

- **Compounds of oxygen with fluorine**

OF_2	O_2F_2
$1(x)+2(-1)=0$ $x=(+2)$	$2(x)+2(-1)=0$ $x=+1$

- **p–block Elements**
  Generally have a range of oxidation number of following:

$\boxed{(n-8) \text{ to } (+n)}$

Where, ‘n’ is number of valence electrons.

- **For halogens (except F)**

$\boxed{\text{Oxidation Number Range} = (-1) \text{ to } (+7)}$

$$\left[\overset{-1}{Cl^-}, \quad \overset{0}{Cl_2}, \quad \overset{+1}{Cl}O^-, \quad \overset{+3}{Cl}O_2^-, \quad \overset{+5}{Cl}O_3^-, \quad \overset{+7}{Cl}O_4^-\right]$$

- **Oxidation number of Chlorine**

Case – I	Chlorine in chlorides	Cl^- $1(x) = -1$ $x = -1$
Case – II	Chlorine molecule	Cl_2 $2(x) = 0$ $x = 0$
Case – III	Chlorine with more electronegative atom	ClO^{-1} $1(x) + 1(-2) = -1$ $x = +1$

- **For chalcogens except oxygen**
  Oxidation number range = (–2) to (+6)
  e.g. $\overset{-2}{S}{}^{2-}, \overset{-1}{S_2^{2-}}, \overset{0}{S_8}, \overset{+4}{S}O_2, \overset{+6}{S}O_3$
- **For Nitrogen family**
  Oxidation number =(-3) to (+5)
  e.g. $\overset{-3}{N}H_3, \overset{-2}{N_2}H_4, \overset{0}{N_2} \quad \overset{+1}{N_2}O \quad \overset{+2}{N}O \quad \overset{+3}{N_2}O_3 \quad \overset{+4}{N}O_2, \overset{+5}{N_2}O_5$
- **d–block elements** show multiple but fixed oxidation number in their compounds.

e.g.
Fe = (+2), (+3)
Ti = (+2), (+4)
Cu = (+2), (+1)
Mn = (+2), (+4), (+5), (+6), (+7)
Cr = (+6), (+3)
Zn = (+2)
Ag = (+1) etc.

Note: Maximum possible oxidation number of an element in species is $\boxed{+8}$ which is for Osmium and Xenon in their particular compounds.

e.g.

CrO_5

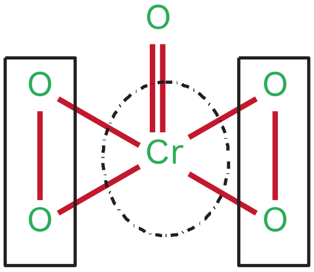
Oxidation of Cr

$1(x) + 5(-2) = 0$

x= (+10)

Not possible

i.e.



i.e. $(O.N)_{Cr} = (+6)$

Note: In calculations , if O.N of p–block elements comes beyond the range then it is incorrect.

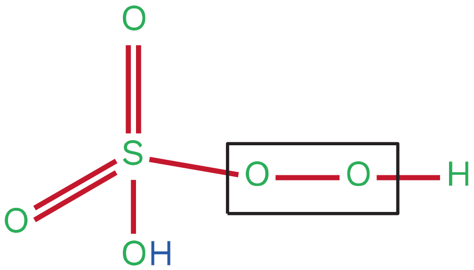
e.g.

$\overset{+1}{H_2}\,\overset{x}{S}\,\overset{-2}{O_5}$

Oxidation no of S

$2(+1) + (x) + 5(-2) = 0$

X = +8



i.e. $(O.N)_S = (+6)$

Practice questions

1. Calculate the oxidation number of underlined elements in the following compounds:

i) $\underline{Fe}_3O_4$

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

$3x = 8$

$x = \frac{8}{3}$

Oxidation number of Fe is +8/3.

ii) $\underline{Fe}O$

$x + (-2) = 0$

$x = +2$

Oxidation number of Fe is +2.

iii) $Na_2S_4O_6$

Oxidation number of S in $Na_2\underline{S}_4O_6$

$\Rightarrow \quad 2(+1) + 4x + 6(-2) = 0$

$2 + 4x - 12 = 0$

$4x = 10$

$x = \frac{10}{4}$

$x = +2.5$

iv) $\underline{C}_2H_5OH$

$2(x) + 5(1) + (-2) + (1) = 0$

$2x + 5 - 2 + 1 = 0$

$2x = -4$

$x = -2$

Oxidation number of C in C_2H_5OH is –2.

v) $\underline{F}eSO_4(\underline{N}H_4)_2SO_4.\ 6H_2O$

$FeSO_4 \Rightarrow x + (-2) = 0 \Rightarrow \boxed{x = +2}$

$NH_4^+ \Rightarrow x + 4(1) = +1 \Rightarrow \boxed{x = -3}$

Oxidation number of Fe in $FeSO_4.(NH_4)_2SO_4.6H_2O = +2$

Oxidation number of N in $FeSO_4.(NH_4)_2SO_4.6H_2O = -3$

vi) $\underline{C}O_2$

$x + 2(-2) = 0$

$x = +4$

Oxidation number of C in CO_2 is + 4.

vii) $Fe\underline{S}_2$

$(+2) + 2(x) = 0$

$2x = -2$

$x = -1$

O.N. of S in FeS_2 is (–1).

viii) PbS

$x + (-2) = 0$

$\boxed{x = +2}$

Oxidation number of Pb in PbS is +2.

ix) $\underline{C}S_2$

$x + 2(-2) = 0$

$x - 4 = 0$

$x = +4$

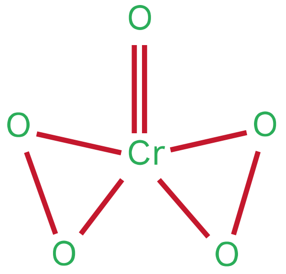
Oxidation number of C in CS_2 is +4.

x) CrO_5

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

$x-2-4 = 0$

O.N. of Cr in CrO_5 is +6



Note: 4 oxygen atoms in peroxide linkages.

xi) $(\underline{N}_2H_5)_2SO_4$

$2(2x + 5(1)) + (-2) = 0$

$4x + 8 = 0$

$4x = -8$

$x = -8/4 = -2$

Oxidation number of N in $(N_2H_5)_2SO_4$ is (–2).

xii) $\underline{N}_2O_5$

$2(x) + 5(-2) = 0$

$2x - 10 = 0$

$\Rightarrow \quad 2x = 10$

$\Rightarrow \quad x = 10/2$

$\Rightarrow \quad x = +5$

Oxidation number of N in N_2O_5 is + 5.

xiii) HCN

Oxidation number of C:

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

$\boxed{x = +2}$

Oxidation number of N:

$1 + (+2) + x = 0$

$\boxed{x = -3}$

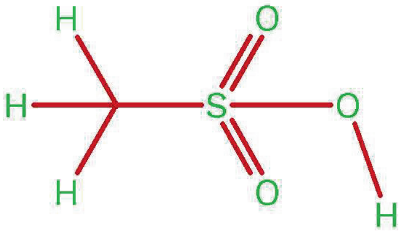
Oxidation number of C in HCN is (+2).
Oxidation number of N in HCN is (–3).

xiv) $Ba[H_2PO_2]_2$
Oxidation number of Ba is +2
Oxidation number of P is:
$(+2)+ 2 [2(+1) + x+2(-2)] = 0$
$2 + 2 (2+x - 4) = 0$
$2 + 4 + 2x-8 = 0$
$2x - 2 = 0$
$2x = 2$
$\boxed{x = +1}$ $\quad\therefore$ O.N of P in $Ba[H_2PO_2]_2$ is (+1)

xv) $\underline{Os}O_4$
$x+4(-2) = 0$
$x = 8$
Oxidation number of Os in OsO_4 is (+8).

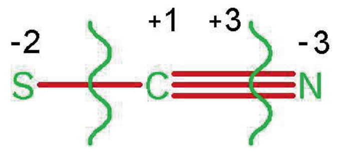
xvi) $H_2\underline{S}_2O_3$
$2(+1) + 2(x) + 3(-2) = 0$
$2 + 2x - 6 = 0$
$2x - 4 = 0$
$2x = 4$
$x = 2$
Oxiation number of S in $H_2S_2O_3$ = (+2)

xvii) $\underline{C}H_3\underline{S}O_3H$
Oxidation number of C is (–2)
Oxidation number of S is (+4)



xix) $Ba_2\underline{Xe}O_6$
Oxidation number of Xe is +8.
$2(+2) + x + 6(-2) = 0$
$x = +8$

xx) $Ba(SCN)_2$
Oxidation number of S is (–2).
Oxidation number of C is (+4).
Oxidation number of N is(–3).



Q1 **Select the compound in which chlorine shows oxidation state +7:**

(A) $HClO_4$

(B) $HClO_3$

(C) $HClO_2$

(D) $HClO$

A1 (A)

a) $HClO_4$

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

$x = +7$

O.N of Cl in $HClO_4$ is (+7).

b) $HClO_3$

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

$\boxed{x=+5}$

O.N of Cl in $HClO_3$ is (+5).

c) $HClO_2$

$(+1) + x + 2(-2) = 0$

$\boxed{x=+3}$

O.N of Cl in $HClO_2$ is (+3).

d) $HClO$

$(+1) + x + (-2) = 0$

$\boxed{x=+1}$

Q2 **The oxidation number of C in CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are respectively.**

(A) +4, +2, 0, −2, −4

(B) +2, +4, 0, −4, −2

(C) −4, −2, 0, +2, +4

(D) −2, −4, 0, +4,+2

A2 **(C)**

Oxidation number of C in:

(i) CH_4

$x + 4(1) = 0$

$\boxed{x = -4}$

(ii) CH_3Cl

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

$x + 3 - 1 = 0$

$x = -2$

(iii) CH_2Cl_2

$x + 2 - 2 = 0$

$\boxed{x = 0}$

(iv) $CHCl_3$

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

$\boxed{x = +2}$

(v) CCl_4

$x + 4(-1) = 0$

$\boxed{x = +4}$

Q1 **The correct order of the increasing oxidation states of nitrogen in NO, N_2O, NO_2 and N_2O_3 is:**

(A) $N_2O < NO < N_2O_3 < NO_2$

(B) $N_2O < N_2O_3 < NO < NO_2$

(C) $NO_2 < NO < N_2O_3 < N_2O$

(D) $NO_2 < N_2O_3 < NO < N_2O$

A1 A

Oxidation states of N in NO, N_2O, NO_2 and N_2O_3 are:

NO

$x + (-2) = 0$

$\boxed{x = +2}$

NO_2

$x + 2(-2) = 0$

$x - 4 = 0$

$\boxed{x = +4}$

N_2O

$2x + (-2) = 0$

$2x = +2$

$\boxed{x = +1}$

N_2O_3

$2x + 3(-2) = 0$

$2x - 6 = 0$

$\boxed{x = +3}$

Q2 **Oxidation number of oxygen in K_2O, K_2O_2 and KO_2, respectively, is:**

(A) +1, +2 and +4

(B) +1, +4 and +2

(C) −2, −1 and $\frac{-1}{2}$

(D) −2, −1 and $\frac{+1}{2}$

A2 (C)

$K_2O \longrightarrow$ Oxide

$K_2O_2 \longrightarrow$ Peroxide

$KO_2 \longrightarrow$ Superoxide

Oxidation:

The process in which oxidation number of element increases is known as **oxidation**.

e.g.

(i) $\overset{0}{Zn} \longrightarrow \overset{+2}{Zn^{2+}}$ (ii) $\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$

(iii) $\overset{-1}{Cl^-} \longrightarrow \overset{0}{Cl_2}$ (iv) $\overset{+4}{Mn}O_2 \longrightarrow \overset{+7}{Mn}O_4^-$

Reduction:

The process in which oxidation number of element decreases is known as **reduction**.

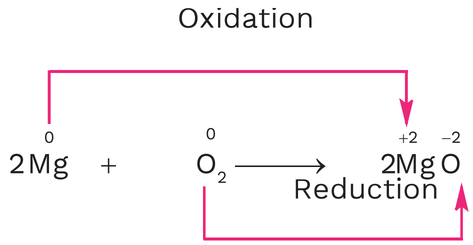
e.g.

(i) $\overset{0}{Br_2} \longrightarrow \overset{-1}{Br^-}$ (ii) $\overset{+5}{Cl}O_3^- \longrightarrow \overset{-1}{Cl^-}$

(iii) $\overset{+2}{Cu^{2+}} \longrightarrow \overset{+1}{Cu^+}$ (iv) $\overset{+6}{Cr_2}O_7^{2-} \longrightarrow \overset{+3}{Cr^{3+}}$

Note: Alone oxidation or alone reduction never takes place means both process are carried out simultaneously and hence the reaction is collectively known as **Redox reaction.**

e.g. (i)

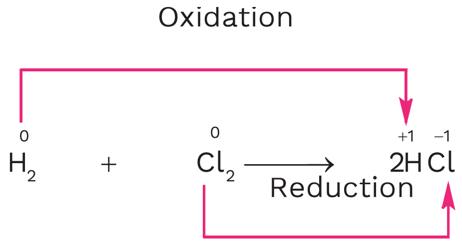


$2\overset{0}{Mg} + \overset{0}{O_2} \longrightarrow 2\overset{+2}{Mg}\overset{-2}{O}$

Mg is oxidized.

O_2 is reduced.

(ii)

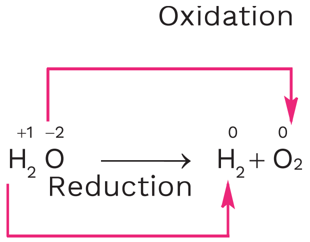


$\overset{0}{H_2} + \overset{0}{Cl_2} \longrightarrow 2\overset{+1}{H}\overset{-1}{Cl}$

H_2 is oxidized.

Cl_2 is reduced.

(iii)



$\overset{+1}{H_2}\overset{-2}{O} \longrightarrow \overset{0}{H_2} + \overset{0}{O_2}$

O is oxidised.

H is reduced.

(iv) Oxidation

$$\overset{0}{Zn} + Cu^{+2} \longrightarrow Zn^{+2} + \overset{0}{Cu}$$

Reduction

Zn is oxidized.
Cu^{+2} is reduced.

(v) Oxidation

$$\overset{+7}{Mn}O_4^- + \overset{+3}{C_2}O_4^{2-} \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+4}{C}O_2$$

Reduction

MnO_4^- is reduced.
$C_2O_4^{-2}$ is oxidized.

(vi)

$$\overset{+1}{H}\overset{-1}{Cl} + \overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} \longrightarrow \overset{+1}{Na}\overset{-1}{Cl} + \overset{+1}{H_2}\overset{-2}{O}$$

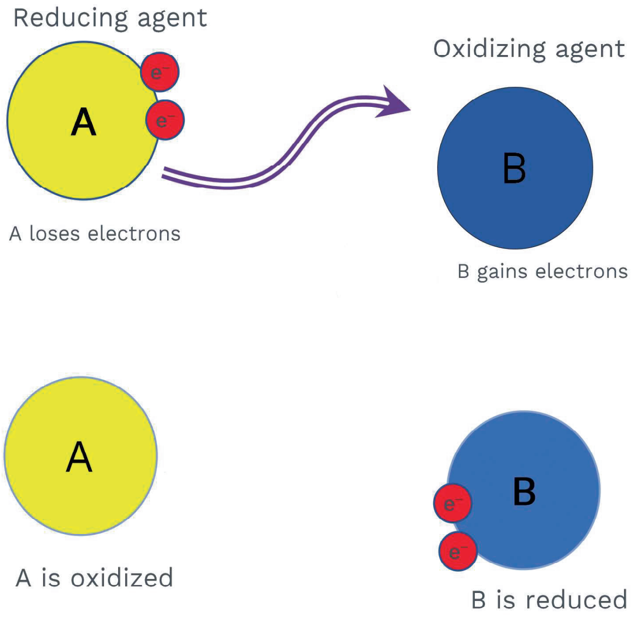
∵ No change in oxidation No.
⇒Non – redox reaction

(vi)

$$\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O_3} \longrightarrow \overset{+2}{Ca}\overset{-2}{O} + \overset{+4}{C}\overset{-2}{O_2}$$

∵ No change in oxidation No.
⇒Non – redox reaction

Oxidizing agent / Oxidant
Substance which oxidizes other substance by getting reduced itself.



Reducing agent / Reductant

Substance which reduces other substances by getting oxidized itself.

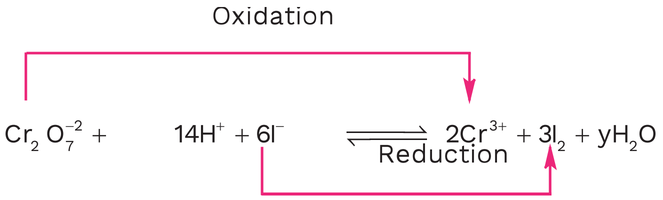
e.g.

(i) $\overset{0}{\mathrm{Fe}} + \overset{+1}{\mathrm{H}^{+}} \longrightarrow \overset{+2}{\mathrm{Fe}^{2+}} + \overset{0}{\mathrm{H}_2}$

i.e. Fe = R.A (Reducing agent)

H^+ = O.A (Oxidizing agent)

(ii)



$$Cr_2O_7^{-2} + 14H^+ + 6I^- \rightleftharpoons 2Cr^{3+} + 3I_2 + yH_2O$$

$Cr_2O_7^{2-}$ is reducing agent.

I^- is oxidizing agent.

Illustration:

Q1 **Which of the following is not a redox change?**

(A) $2H_2S + SO_2 \rightarrow 2H_2O + 3S$
(B) $2BaO + O_2 \rightarrow 2BaO_2$
(C) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$
(D) $2KClO_3 \rightarrow 2KCl + 3O_2$

A1 **(C)**

Non redox reaction means no change in oxidation number.

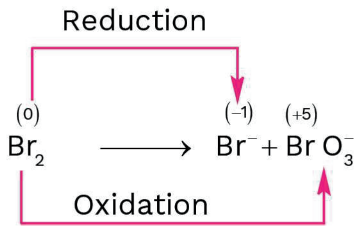
Q2 **In the following reaction**

$$3Br_2 + 6CO_3^{2-} + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

(A) Bromine is oxidized, carbonate is reduced
(B) Bromine is reduced, carbonate is oxidized
(C) Bromine is neither reduced nor oxidizes
(D) Bromine is reduced as well as oxidized

A2 **(D)**

$$3\overset{0}{Br_2} + 6\overset{+4}{C}\overset{-2}{O_3^{2-}} + 3H_2O \longrightarrow 5\overset{-1}{Br^-} + \overset{+5}{Br}\overset{-2}{O_3^-} + 6H\overset{+4}{C}\overset{-2}{O_3^-}$$



Q3 **In the reaction**

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

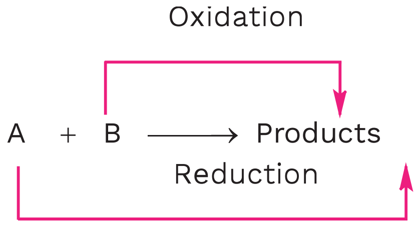
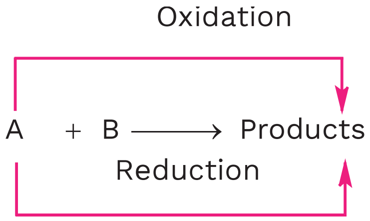
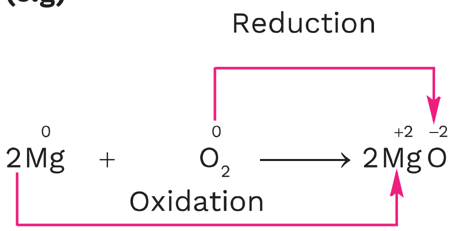
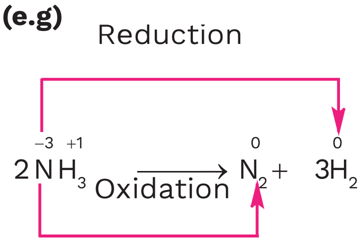
I_2 act as:

(A) Reducing agent
(B) Oxidizing agent
(C) Oxidizing as well as reducing agent
(D) None of above

A3 **(B)**

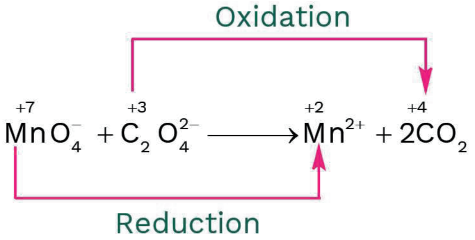
I_2 get reduced from (0) oxidation state in I_2 to –1 oxidation state in NaI.

Classification of redox reactions

1. Intermolecular reactions	**2. Intramolecular reactions**
 $A + B \longrightarrow \text{Products}$ Reaction in which two different elements in different molecules undergo oxidation & reduction.	 $A + B \longrightarrow \text{Products}$ Reaction in which two different elements in same molecule undergo oxidation & reduction.
(e.g)  $2\overset{0}{Mg} + \overset{0}{O_2} \longrightarrow 2\overset{+2}{Mg}\overset{-2}{O}$	**(e.g)**  $2\overset{-3}{N}\overset{+1}{H_3} \longrightarrow \overset{0}{N_2} + 3\overset{0}{H_2}$

e.g.

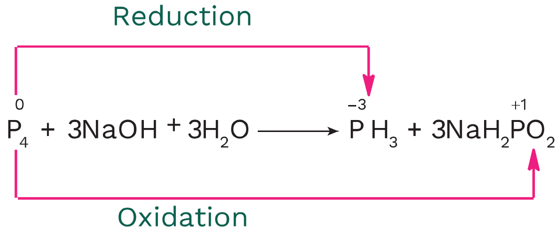
(i)



$\overset{+7}{Mn}O_4^- + \overset{+3}{C_2}O_4^{2-} \longrightarrow \overset{+2}{Mn^{2+}} + 2\overset{+4}{C}O_2$

Inter molecular reaction

(ii)



$\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow \overset{-3}{P}H_3 + 3NaH_2\overset{+1}{P}O_2$

Intramolecular reaction

(3)	**Combination reactions**	(4)	**Decomposition reactions**
(i)	At reactant side, atleast one element in free state is present but no element in free state at product side. $\underset{\text{in free state)}}{\underset{\text{(Atleast one element}}{\text{Reactants}}} \rightarrow \underset{\text{in free state)}}{\underset{\text{(No element}}{\text{Products}}}$	(i)	At reactant side, no element in free state but in product side, there is atleast one element in free state i.e. $\begin{pmatrix}\text{No element}\\ \text{in free state}\\ \text{at reactant side}\end{pmatrix} \rightarrow \begin{pmatrix}\text{At least}\\ \text{one element}\\ \text{in state}\end{pmatrix}$

E.g.

(i) $\overset{-4}{C}H_4 + \underset{\text{Element in free state}}{2\overset{0}{O}_2} \rightarrow \underbrace{\overset{+4}{C}\overset{-2}{O}_2 + 2H_2O}_{\text{No element in free state}}$ Combination Reaction (Intermolecular)

(ii) $\overset{0}{P}_4 + 3NaOH \longrightarrow 3NaH_2\overset{+1}{P}O_2 + \overset{+3}{P}H_3$ Combination Reaction (Intramolecular)

(iii) $\underbrace{4NH_4NO_2}_{\text{No element in free state}} \longrightarrow \underbrace{4N_2}_{\text{Element in free state}} + 3O_2 + 2H_2O$ Decomposition Reaction (Intramolecular)

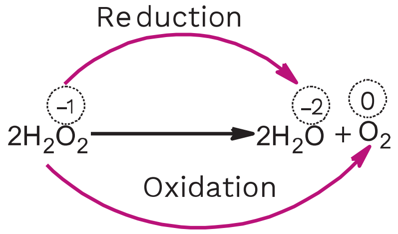
(5)	**Metal Displacement reactions**	(6)	**Non – metal displacement reactions**
(i)	A metal ion present in a compound is displaced by a more electropositive metal present in free state. e.g. $\overset{0}{Zn} + \overset{+2}{Cu}SO_4 \rightarrow \overset{+2}{Zn}SO_4 + \overset{0}{Cu}$ i.e. Cu is displaced by Zn	(i)	A non-metal present in a compound is displaced by a more electronegative non-metal present in free state. e.g. $2H\overset{-1}{Br} + \overset{0}{Cl}_2 \rightarrow 2H\overset{-1}{Cl} + \overset{0}{Br}_2$ i.e. Br is displaced by Cl

7. Disproportion Reaction

- Redox reactions in which an element present in one single oxidation number at reactant side converts into two different oxidation number at product side showing both oxidation and reduction.
- Means only one element is involved in redox reaction.

(e.g)

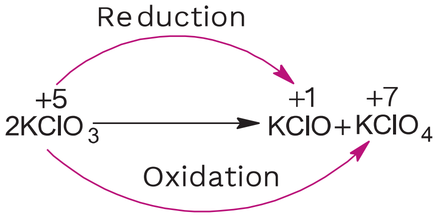
(i) Self decomposition of H_2O_2



$$2H_2\overset{-1}{O}_2 \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O}_2$$

i.e. disproportion reaction

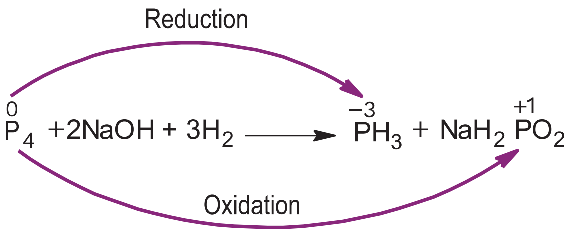
(ii) Disproportion of $KClO_3$



$$2K\overset{+5}{Cl}O_3 \rightarrow K\overset{+1}{Cl}O + K\overset{+7}{Cl}O_4$$

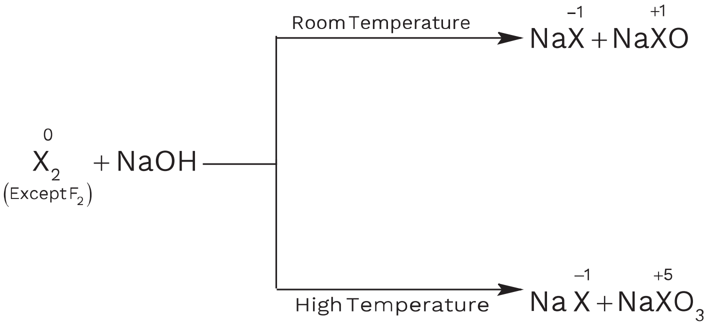
Note: Whenever a non metal present in free state reacts with base, the reaction is always disproportion reaction.

(iii) Disproportion of P_4



$$\overset{0}{P_4} + 2NaOH + 3H_2 \rightarrow \overset{-3}{P}H_3 + NaH_2\overset{+1}{P}O_2$$

(iv) Disproportion of Halogens



$$\overset{0}{X_2} \text{ (Except } F_2) + NaOH \xrightarrow{\text{Room Temperature}} Na\overset{-1}{X} + Na\overset{+1}{X}O$$

$$\overset{0}{X_2} \text{ (Except } F_2) + NaOH \xrightarrow{\text{High Temperature}} Na\overset{-1}{X} + Na\overset{+5}{X}O_3$$

Note: Reverse of disproportionation reaction is known as comproportionation reaction.

(i) $2H_2\overset{-2}{S} + \overset{+4}{S}O_2 \rightarrow 3\overset{0}{S} + 2H_2O$

(ii) $\overset{-3}{N}H_4\overset{+3}{N}O_2 \rightarrow \overset{0}{N_2} + 2H_2O$

Illustration:

Q1 White phosphorus reacts with NaOH as:

$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ is an example of:

(A) Dimerization reaction
(B) Disproportionation reaction
(C) Condensation reaction
(D) Precipitation reaction

A1 B

$$\overset{0}{P}_4 + 3NaOH + 3H_2O \rightarrow \overset{-3}{P}H_3 + 3NaH_2\overset{+1}{S}O_2$$

Q2 Which of the following chemical reactions does not depicts the oxidizing behaviour of H_2SO_4 ?

(A) $Ca(OH)_2 + H_2SO_4 \rightarrow Ca\overset{+6}{S}O_4 + 2\overset{+1}{H}_2O$

(B) $NaCl + H_2SO_4 \rightarrow \overset{+1}{Na}H\overset{+4}{S}O_3 + HCl$

(C) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + \overset{+6}{S}\overset{-2}{O}_2\overset{-1}{Cl}_2$

(D) $2HI + H_2\overset{+6}{S}O_4 \rightarrow I_2 + \overset{+4}{S}O_2 + 2H_2O$

Q2 A and C

Oxidising behaviour of H_2SO_4 means tendency to oxidise or reduction of self.

Example: $2HI + H_2\overset{+6}{S}O_4 \rightarrow I_2 + \overset{+4}{S}O_2 + 2H_2O$

In 1st half : $2HI \longrightarrow I_2$
Oxidation number of I is increases by one thus, oxidation reaction.

In 2nd half : $H_2\overset{+6}{S}O_4 \longrightarrow \overset{+4}{S}O_2$

O.N of S decreases by 2, thus reduction reaction & H_2SO_4 act as oxidising agent.

Balancing of Redox Reactions

Balancing of Redox Reactions:
There are two methods discussed as follows

1. Ion electron method:
This method is applicable for ionic reactions only means it is based upon modern concept.
Step–I: Split the given redox reaction into two half reactions as oxidation and reduction.
Step–II: In both reactions, balance elements other than H and O by hit and trial.
Step–III: Balance O by adding suitable number of H_2O.
Step– IV: To balance hydrogen and oxygen.

In acidic medium → by adding H^+
To balance O $\longrightarrow$ add H_2O to side deficit of O and double number of H^+ ions on the opposite side. The number of H_2O molecules is equal to the number of O atoms deficit.
In basic medium → by adding OH^-
To balance O $\longrightarrow$ add H_2O to side excess of O and same number of OH^- ions on the opposite side. The number of H_2O molecules is equal to the number of O atoms deficit.
To balance H $\longrightarrow$ add H_2O to side deficit of H and same number of OH^- ions on the opposite side. The number of H_2O molecules is equal to the number of O atoms deficit.

Step–V: Balance charge by adding suitable number of electrons at suitable side.
Step–VI: Multiply both reactions by suitable number separately to make same number of electrons in both.
Step–VII: Add both half reactions due to which electrons will be cancelled out and balanced redox reaction is obtained.

Examples:
i) $MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$

Step–I:
$MnO_4^- \rightarrow Mn^{2+}$
$C_2O_4^{2-} \rightarrow CO_2$

Step – II
$MnO_4^- \rightarrow Mn^{2+}$
$C_2O_4^{2-} \rightarrow 2CO_2$

Step–III
$MnO_4^- \rightarrow Mn^+ + 4H_2O$
$C_2O_4^{2-} \rightarrow 2CO_2$

Step–IV

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

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

Step – V

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

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

Step–VI

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

$(C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-) \times 5$

Step – VII

After adding above two reactions we get:

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

ii) $NO_3^- + Br^- \xrightarrow{H^+} NO + Br_2$

$3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O)\times 2$

$2Br^- \rightarrow Br_2 + 2e^-)\times 3$

After adding above two reactions we get

$2NO_3^- + 6Br^- + 8H^+ \rightarrow 2NO + 3Br_2 + 4H_2O$

iii) $Zn + NO_3^- \xrightarrow{OH^-} ZnO_2^{2-} + NH_3$

$1\times(4OH^- + 2H_2O + Zn \rightarrow ZnO_2^{2-} + 4H_2O + 2e^-$

$8e^- + 9H_2O + NO_3^- \rightarrow NH_3 + 3H_2O + 9OH^-$

After adding above two reactions we get

$4Zn + NO_3^- + 7OH^- \rightarrow 4ZnO_2^{2-} + NH_3 + 2H_2O$

iv) $AsO_3^{3-} + NO_3^- \xrightarrow{OH^-} AsO_4^{3-} + NO_2$

$2OH^- + H_2O + AsO_3^{3-} \rightarrow AsO_4^{3-} + 2H_2O + 2e^-$

$2\times(e^- + 2H_2O + NO_3^- \rightarrow NO_2 + H_2O + 2OH^-$

After adding above two reactions we get

$AsO_3^{3-} + 2NO_3^- + H_2O \rightarrow AsO_4^{3-} + 2NO_2 + 2OH^-$

v) $BrO_4^- + Br^- \xrightarrow{H^+} BrO_3^-$

$3x\ (2e^- + 2H^+ + BrO_4^- \rightarrow BrO_3^- + H_2O$

$1\ x\ (3H_2O + Br^- \rightarrow BrO_3^- + 6H^+ + 6e^-$

After adding above two reactions we get

$3BrO_4^- + Br^- \rightarrow 4BrO_3^-$

(vi) $Cl_2 \xrightarrow{OH^-} Cl^- + ClO_3^-$

$2e^- + Cl_2 \rightarrow 2Cl^-$

$12OH^- + 6H_2O + Cl_2 \longrightarrow 2ClO_3^- + 12H_2O + 10e^-$

After adding above two reactions we get

$$6Cl_2 + 12OH^- \longrightarrow 10Cl^- + 2ClO_3^- + 6H_2O$$

Note: If reaction is not given in ionic form then convert it (if possible) by removing all spectator ions.

$$\begin{array}{llll} KCl & = K^+ & + & Cl^- \\ H_2SO_4 & = 2H^+ & + & \multirow{2}{*}{$\left.\begin{array}{l} SO_4^- \\ HSO_4^- \end{array}\right\}$} \\ & = H^+ & + & \\ KMnO_4 & = K^+ & + & MnO_4^- \end{array}$$

Example:

i) $KMnO_4 + KI + HCl \longrightarrow MnCl_2 + I_2 + KCl + H_2O$

If all spectator ions are removed, we get

$$MnO_4^- + I^- \xrightarrow{H^+} Mn^{2+} + I_2$$

Balancing the equation

$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

Final equation:

$$\boxed{2KMnO_4 + 10KI + 16HCl \longrightarrow 2MnCl_2 + 5I_2 + 8H_2O + 12KCl}$$

ii) $K_2Cr_2O_7 + K_2C_2O_4 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + CO_2 + K_2SO_4$

If all spectator ions are removed, we get

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

Balancing,

$$2Cr_2O_7^{2-} + 6C_2O_4^{2-} + 28H^+ \longrightarrow 4Cr^{3+} + 12CO_2 + 14H_2O$$

Final equation:

$$2K_2Cr_2O_7 + 6K_2C_2O_4 + 14H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 12CO_2 + 14H_2O + 8K_2SO_4$$

2. Oxidation number method:

This method is applicable for every redox reaction.

i) Select two species showing oxidation and reduction at reactant side by observing change in oxidation number.
ii) Calculate "Net increase or decrease in oxidation number for these two species".
iii) Make Total increase = Total decrease by multiplying species with suitable numbers.
iv) Now balance others by hit and trial.
v) Balance remaining O by H_2O.
vi) Balance remaining H by H^+ or OH^- and H_2O (discussed in ion electron method).

Examples:

i) $$\overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} + \overset{+4}{S}\overset{-2}{O_2} \longrightarrow \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{H_4}$$

Step: $$H\overset{+5}{N}O_3 + \overset{+4}{S}O_2 \longrightarrow \overset{+4}{N}O_2 + H_2\overset{+6}{S}O_4$$

There is 1 decrease in N and 2 increase in S.

$$\boxed{\mathbf{2HNO_3 + 1SO_2 \longrightarrow 2NO_2 + 1H_2SO_4}}$$

ii) $$\overset{+2}{NO} + \overset{0}{Br_2} \longrightarrow H\overset{+5}{N}O_3 + H\overset{-1}{Br}$$

There is 3 increase in N and 2 decrease in Br_2.

So,

$$\boxed{\mathbf{2NO + 3Br_2 + 4H_2O \longrightarrow 2HNO_3 + 6HBr}}$$

iii) $$Na_2\overset{+2}{S_2}O_3 + \overset{0}{I_2} \longrightarrow Na_2\overset{+2.5}{S_4}O_6 + Na$$

$$\boxed{2Na_2S_2O_3 + 1I_2 \longrightarrow 1Na_2S_4O_6 + 2NaI}$$

iv) $$\overset{+6}{Cr_2}O_7^{2-} + \overset{+3}{C_2}O_4^{2-} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{+4}{C}O_2$$

There is 6 decrease in Cr and 2 increase in C.

$$\boxed{\mathbf{1Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O}}$$

Practice questions

v) $\overset{+6}{Cr}O_4^{2-} + \overset{-1}{I^-} \xrightarrow{H^+} \overset{+3}{Cr^{3+}} + \overset{0}{I_2}$

$1CrO_4^{2-} + 3I^- + 8H^+ \longrightarrow 1Cr^{3+} + 3/2\ I_2 + 4H_2O$

vi) $\overset{+3}{As}O_3^{3-} + \overset{+5}{N}O_3^- \xrightarrow{OH^-} \overset{+5}{As}O_4^{3-} + \overset{+4}{N}O_2$

$1AsO_3^{3-} + 2NO_3^- + H_2O \longrightarrow 1AsO_4^{3-} + 2NO_2 + 2OH^-$

vii) $\overset{+2}{Fe}\overset{-1}{S_2} + \overset{0}{O_2} \longrightarrow \overset{+3}{Fe_2}\overset{-2}{O_3} + \overset{+4}{S}\overset{-2}{O_2}$

$2FeS_2 + 11/2\ O_2 \longrightarrow Fe_2O_3 + 4SO_2$

viii) $\overset{+3}{As_2}\overset{-2}{S_3} + H\overset{+5}{N}O_3 \longrightarrow H_3\overset{+5}{As}O_4 + H_2\overset{+6}{S}O_4 + \overset{+2}{N}O$

$3As_2S_3 + 28HNO_3 + 4H_2O \longrightarrow 6H_3AsO_4 + 9H_2SO_4 + 28NO$

ix) $\overset{0}{Cl_2} \xrightarrow{OH^-} \overset{(-1)}{Cl^-} + \overset{+5}{Cl}O_3^-$

$3Cl_2 + 6OH^- \longrightarrow 5Cl^- + ClO_3^- + 3H_2O$

x) $K\overset{+7}{Mn}O_4 + H_2\overset{+3}{C_2}O_4 + H_2SO_4 \longrightarrow \overset{+2}{Mn}SO_4 + \overset{+4}{C}O2 + K_2SO_4$

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

xi) $K_2\overset{+6}{Cr}O_7 + \overset{+2}{Fe}(NO_3)_2 + HNO_3 \longrightarrow \overset{+3}{Cr}(NO_3)_3 + \overset{+3}{Fe}(NO_3)_3 + KNO_3 + H_2O$

$1K_2Cr_2O_7 + 6Fe(NO_3)_2 + 14HNO_3 \longrightarrow 2Cr(NO_3)_3 + 6Fe(NO_3)_3 + 2KNO_3 + 7H_2O$

xii) $KMnO_4 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2 + KCl$ oxidation no. is not
All HCl is not converting into Cl_2.
$KMnO_4 + 8HCl \longrightarrow 1MnCl_2 + 5/2\ Cl_2 + KCl + 4H_2O$

xiii) $\overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}O_3)_2 + \overset{+4}{N}O_2 + H_2O$

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

Q1 **Consider the following reactionxMnO_4^- + y$C_2O_4^{2-}$ + z H^+ → xMnO^{2+} + 2yCO_2 + $\frac{z}{2}H_2O$**

The value of x, y and z in the reaction are, respectively

(A) 2,5 and 8 **(B) 2,5 and 16**

(C) 5,2 and 8 **(D) 5, 2 and 16**

A1 (B)

Balanced chemical reaction:

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

The values of x, y and z are 2,5 and 16 respectively.

Q2 For the reaction:

$$\mathbf{I^- + ClO_3^- + H_2SO_4 \longrightarrow Cl^- + HSO_4^- + I_2}$$

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

(A) Stoichiometric coefficient of HSO_4^- is 6

(B) Iodide is oxidized

(C) Sulphur is reduced

(D) H_2O is one of the products

A2 (A), (B) & (D)

The balanced equation is:

$$ClO_3^- + 6I^- + 6H_2SO_4 \longrightarrow 3I_2 + Cl^- + 6HSO_4^- + 3H_2O$$

So, stoichiometric coefficient of HSO_4^- is 6.

Equivalent Concept (Gram equivalent concept)

Gram equivalent mass

It is the mass of one gram – equivalent of the substance in grams.

For a substance

$$\textbf{Equivalent mass} = \frac{\textbf{Molar mass}}{\textbf{n - factor}}$$

Number of gm – equivalent

- Equivalents is similar property as moles but its value of not fixed.
  i.e. 1 mole = N_A particles

$$\text{But, 1 equivalent} = \left\{\begin{matrix} N_A \text{ particles} \\ 2N_A \text{ particle} \\ \text{or} \\ N_A / 3 \text{ particles etc.} \end{matrix}\right\} \text{All are possible}$$

- For a substance, equivalent mass and in grams is equal to the mass of one equivalent.
  So for a substance:

$$\text{Number of equivalent} = \frac{\text{Mass of substance(g)}}{\text{Equivalent mass}} = \frac{\text{Mass}}{\text{Molar Mass}} \times \text{n} - \text{Factor}$$

$$= \text{Moles} \times \text{n–factor}$$

Normality(N)

- It is a concentration terms means is defined for solutions
- It is defined as the number of equivalent of solute present in 1 litre of solution.

$$\text{Normality} = \frac{\text{Equivalent of solute}}{\text{Volume of solution(L)}}$$

Unit $\longrightarrow$ equivalent/L or Normal

$$N = \left(\frac{\text{Moles of solute}}{V_{\text{sol.}}}\right) \times \text{n} - \text{Factor}$$

$$\left.\begin{matrix} \boxed{\text{Normality} = \text{Molarity} \times \text{n} - \text{factor}} \\ \boxed{N \times V = (\text{Equivalent})_{\text{Solute}}} \end{matrix}\right\} \text{Aslo}$$

Calculation of n–factor

- n–factor is the property of a substance which have a positive value only.

$$\boxed{\begin{aligned}&\mathrm{n-Factor} \neq 0\\ &\qquad\qquad \neq \mathrm{negative}\end{aligned}}$$

Case –I: When no reaction is provided

i) For atom

$$\boxed{\mathrm{n-factor} \;=\; \mathrm{General\ valency}}$$

e.g.

Atom	n–factor
Na	1
Al	3
Fe	2
B	3
C	4

etc.

- **For ions:**

  [n–factor = |magnitude of charge on ion]

  e.g. $H^+ = 1$
  $Ba^{2+} = 2$
  $OH^- = 1$
  $CO_3^{2-} = 2$
  $PO_4^{3-} = 3$ etc.

- **For acids:**

  $$\boxed{\mathrm{n-factor} = \mathrm{Maximum\ basicity}}$$

  Basicity = number of replacable H^+ per molecule of acid.

  $$\text{e.g.}\ \left.\begin{array}{l}\mathrm{HCl,\ HBr,\ HI,\ HNO_3,\ HCN,}\\ \mathrm{HCOOH,\ CH_3COOH, H_3PO_2,}\\ \mathrm{H_3BO_3\ \ etc.}\end{array}\right\}\ \mathrm{n-factor} = 1$$

  H_2SO_4, $H_2C_2O_4$, H_2CO_3, H_3PO_3 etc. } n–factor = 2

  H_3PO_4, H_3AsO_4 etc.} n–factor = 3

- **For bases:**

  $$\boxed{\mathrm{n-factor} = \mathrm{Maximum\ acidity}}$$

$$\text{Acidity} = \left.\begin{array}{l}\text{No. of replacable OH}^{-}\\ \text{No. of acceptable H}^{+}\end{array}\right\}\text{per molecule of base}$$

e.g. NaOH, KOH, RbOH, CsOH, NH_3, RNH_2 etc.} = 1

$Ba(OH)_2$, $Zn(OH)_2$= $NH_2–CH_2–CH_2–NH_2$ etc.} = 2

- **For salt:**

$$\boxed{\text{n – factor} = \text{Total charge on cation or Total charge on anions}}$$

Salt	Ions	n-factor
NaCl	1 Na^+ and 1 Cl^-	1
K_2SO_4	2 K^+ and 1 SO_4^{2-}	2
$MgBr_2$	1 Mg^{2+} and 2 Br^-	2
$Ba_3(PO_4)_2$	3 Ba^{2+} and 2 PO_4^{3-}	6

Illustration:

Q1 **Determine n–factor of $K_2SO_4.Al_2(SO_4)_3.24H_2O$**

A1 From cation : $2K^+ + 2Al^{+3}$

n – factor = $2 \times 1 + 2 \times 3 = 8$

From anion : $1SO_4^{2-} + 3SO_4^{2-}$

n – factor = $4 \times 2 = 8$

Q2 **Calculate no. of gram equivalents in following:**

i) 54 gm Al^{3+} **ii) 98 gm H_3PO_4**
iii) 2 mole CO_3^{2-} **iv) 1.5 g molecule $Ba(OH)_2$**
v) 12.04×10^{22} ions of SO_4^{2-}

A2 **Using No. of equivalent =** $\frac{\text{Mass}}{\text{Molar mass}} \times \text{n} - \text{facto}$

i) 54 gm Al

$$\text{Equivalent} = \frac{54}{27} \times 3 = 6$$

ii) 98 mg H_3PO_4 $\frac{98}{98} \times 3 = 3$

iii) 2 mole CO_3^{2-} = 2×2 = 4

iv) 1.5 g molecule $Ba(OH)_2$ = 1.5×2 = 3

v) 12.04×10^{22} ions of SO_4^{2-} $= \left(\frac{12.04 \times 10^{22}}{N_A}\right) \times 2 = 0.4$

$$\text{Normality} = \frac{\text{Equivalent of solute}}{\text{Volume of soution(L)}} = \frac{0.5}{500 / 1000} = 1\text{ N}$$

Q3 **Calculate normality of solution prepared by mixing 24.5 gm H_2SO_4 in its 500 ml solution.**

A3 Given 24.5 gm of H_2SO_4

$$\text{Molarity, M} = \frac{\frac{24.5}{98}}{\frac{500}{1000}} = 0.5$$

Normality = Molarity × n–factor = 0.5 × 2 = 1 N

$$\text{or, No. of equivalents} = \frac{\text{Mass}}{\text{Molar mass}} \times \text{n} - \text{factor} = \frac{24.5}{98} \times 2 = 0.5$$

n-factor (Valency Factor)

n–factor in non–redox reaction

$$\boxed{\text{n – factor} = |\text{Charge}|\ \text{Exchanged per molecule}}$$

Or

It is the magnitude of charge per molecule

$$\begin{array}{lccccccc} & \overset{+}{\text{Ag}}\wr\overset{-}{\text{NO}_3} & + & \overset{+}{\text{Na}}\wr\overset{-}{\text{Cl}} & \longrightarrow & \overset{+}{\text{Ag}}\wr\overset{-}{\text{Cl}^-} & + & \overset{+}{\text{Na}}\wr\overset{-}{\text{NO}_3} \\ \text{n-factor} & (1) & & (1) & & (1) & & (2) \end{array}$$

$$\begin{array}{lccccccc} & \text{Ag}\wr\text{NO}_3 & + & \overset{2+}{\text{Ba}}\wr\overset{-}{\text{Cl}_2} & \longrightarrow & \text{Ag}\wr\text{Cl} & + & \text{Ba(NO}_3)_2 \\ \text{n-factor} & (1) & & (2) & & (1) & & (2) \end{array}$$

$$\begin{array}{lccccccc} & \text{Na}_2\text{CO}_3 & + & \text{HCl} & \longrightarrow & \text{H}_2\text{CO}_3 & + & \text{NaCl} \\ \text{n-factor} & (2) & & (1) & & (2) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & \text{Na}_2\text{CO}_3 & + & \text{HCl} & \longrightarrow & \text{NaHCO}_3 & + & \text{NaCl} \\ \text{n-factor} & (1) & & (1) & & (1) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & \overset{+}{\text{H}}\wr\overset{-}{\text{Cl}} & + & \overset{+}{\text{Na}}\wr\overset{-}{\text{OH}} & \longrightarrow & \overset{+}{\text{Na}}\wr\overset{-}{\text{Cl}} & + & \text{H}_2\text{O} \\ \text{n-factor} & (1) & & (1) & & (1) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & \text{H}_2\text{SO}_4 & + & \text{NaOH} & \longrightarrow & \text{Na}_2\text{SO}_4 & + & \text{H}_2\text{O} \\ \text{n-factor} & (2) & & (1) & & (2) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & \text{H}_2\text{SO}_4 & + & \text{NaOH} & \longrightarrow & \text{NaHSO}_4 & + & \text{H}_2\text{O} \\ \text{n-factor} & (1) & & (1) & & (1) & & (1) \end{array}$$

Note:

$$\begin{array}{lccccccc} & \text{Acid} & + & \text{Base} & \longrightarrow & \text{Salt} & + & \text{H}_2\text{O} \\ & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ \text{n-factor} & \text{Basicity} & & \text{Acidity} & & |\text{Charge}| & & (1) \end{array}$$

$$\begin{array}{lccccccc} & \text{H}_3\text{PO}_4 & + & \text{NaOH} & \longrightarrow & \text{Na}_3\text{PO}_4 & + & \text{H}_2\text{O} \\ \text{n-factor} & (3) & & (1) & & (3) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & H_3PO_4 & + & NaOH & \longrightarrow & Na_2HPO_4 & + & H_2O \\ \text{n-factor} & (2) & & (1) & & (2) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & H_3PO_4 & + & NaOH & \longrightarrow & NaH_2PO_4 & + & H_2O \\ \text{n-factor} & (1) & & (1) & & (2) & & (1) \end{array}$$

n–factor in redox reaction

For a substance present in a redox reaction, the "net increase or decrease in oxidation number per molecule" is known as n–factor of that substance in that reaction.

So, in a balanced redox reaction:

$$\boxed{(\text{n - factor})_{\text{Substance}} = \frac{\textbf{Total increase or decrease in the reaction}}{\textbf{Stoichiometric coefficient of substance}}}$$

Example:

$$\begin{array}{lccccccc} & \overset{+5}{HNO_3} & + & \overset{+4}{SO_2} & \longrightarrow & \overset{+4}{NO_2} & + & \overset{+6}{H_2SO_4} \\ \text{n-factor} & (1) & & (2) & & (1) & & (2) \end{array}$$

$$\begin{array}{lccccccc} & \overset{+2}{NO} & + & \overset{0}{Br_2} & \longrightarrow & \overset{+5}{HIO_3} & + & \overset{-1}{HBr} \\ \text{n-factor} & (3) & & (2) & & (3) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & \overset{+2}{Na_2S_2O_3} & + & \overset{0}{I_2} & \longrightarrow & \overset{+2.5}{Na_2S_4O_6} & + & \overset{-1}{NaI} \\ \text{n-factor} & (1) & & (2) & & (2) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & \overset{+6}{Cr_2}O_7^{2-} & + & \overset{+3}{C_2}O_4^{2-} & \longrightarrow & \overset{+3}{Cr^{3+}} & + & \overset{+4}{CO_2} \\ \text{n-factor} & (6) & & (2) & & (3) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & \overset{+6}{Cr}O_4^{2-} & + & \overset{-1}{I^-} & \longrightarrow & \overset{+3}{Cr^{3+}} & + & \overset{0}{I_2} \\ \text{n-factor} & (3) & & (1) & & (3) & & (2) \end{array}$$

$$\begin{array}{lccccccc} & \overset{+3}{As}O_3^{3-} & + & \overset{+5}{N}O_3^- & \longrightarrow & \overset{+5}{As}O_4^{3-} & + & \overset{+4}{N}O_2 \\ \text{n-factor} & (2) & & (1) & & (2) & & (1) \end{array}$$

$$\begin{array}{lccccccc} & 2KMnO_4 & +5H_2C_2O_4 & +3H_2SO_4 \longrightarrow & 2MnSO_4 & +10CO_2 & +K_2SO_4 & +8H_2O \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{n-factor} & \left(\frac{10}{2}\right) & \left(\frac{10}{5}\right) & \left(\frac{10}{3}\right) & \left(\frac{10}{2}\right) & \left(\frac{10}{10}\right) & \left(\frac{10}{1}\right) & \left(\frac{10}{8}\right) \end{array}$$

$$\begin{array}{lccccccc} & 1H_3\overset{5}{As}O_4 & +\ 2K\overset{1}{I} & +2HCl \longrightarrow & 1H_3\overset{+3}{As}O_3 & +\overset{0}{I_2} & +2KCl & +H_2O \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{n-factor} & \left(\frac{2}{1}\right) & \left(\frac{2}{2}\right) & \left(\frac{2}{2}\right) & \left(\frac{2}{1}\right) & \left(\frac{2}{1}\right) & \left(\frac{2}{2}\right) & \left(\frac{2}{1}\right) \end{array}$$

$$\begin{array}{lcccccc} & KMnO_4 & +8HCl \longrightarrow & MnCl_2 & +\frac{5}{2}H_2O & +Cl_2 & +4KCl \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{n-factor} & \left(\frac{5}{1}\right) & \left(\frac{5}{8}\right) & \left(\frac{5}{1}\right) & \left(\frac{5}{5/2}\right) & \left(\frac{5}{1}\right) & \left(\frac{5}{4}\right) \end{array}$$

$$\begin{array}{lccccc} & Cu & +4HNO_3 \longrightarrow & Cu(NO_3)_2 & +2NO_2 & +2H_2O \\ & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{n-factor} & \left(\frac{2}{1}\right) & \left(\frac{2}{4}\right) & \left(\frac{2}{1}\right) & \left(\frac{2}{2}\right) & \left(\frac{2}{2}\right) \end{array}$$

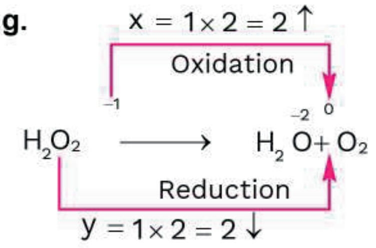
n–factor for disproportionation

$$\boxed{(\text{n - factor})_{\text{disproportion}} = \frac{xy}{x+y}}$$

where x ⟶ n–factor for alone oxidation

y ⟶ n–factor for alone reduction

e.g.



$$(\text{n}-\text{factor})_{H_2O_2} = \frac{2\times 2}{2+2} = 1$$

$$Cl_2 \longrightarrow Cl^- + ClO_3^-$$

$$(\text{n}-\text{factor})_{Cl_2} = \frac{2\times 10}{2+10} = \frac{5}{3}$$

$$\underset{\text{Reduction}}{KMnO_4} + \underset{\text{Oxidation}}{MnSO_4} \longrightarrow \underset{\text{Disproportion}}{MnO_2}$$

$$(n - \text{factor})_{M_nO_2} = \frac{3 \times 2}{3 + 2} = \frac{6}{5}$$

Note: $A_xB_y \rightarrow$ Product
n–Factor $\neq 0$
$\neq (-ve)$

e.g. $NH_3 \longrightarrow N_2 + H_2$

$$(n - \text{Factor})_{NH_3} \neq 0$$
$$= 3$$

$$\therefore \underset{\left(\frac{6}{2}\right)}{2NH_3} \longrightarrow \underset{\left(\frac{6}{1}\right)}{N_2} + \underset{\left(\frac{6}{3}\right)}{3H_2}$$

$$\underset{(2)}{H_2} + \underset{(4)}{O_2} \longrightarrow \underset{(2)}{H_2O}$$

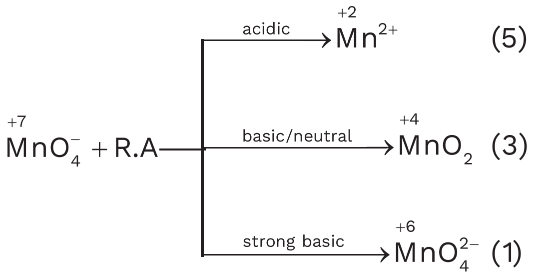
$$P_4 \longrightarrow PH_3 + H_2PO_2^-$$

$$\text{N–factor} - \frac{12 \times 4}{12 + 4} = \frac{48}{16} = (3)$$

Some commonly used agents

i) Permanganate ion $\left(MnO_4^-\right)$

Since (+7) is maximum oxidation numbers for Mn so in redox reactions, MnO_4^- always acts as an oxidizing agent.
The product depends upon the medium of reaction as following:



$$\overset{+7}{MnO_4^-} + R.A \xrightarrow{\text{acidic}} \overset{+2}{Mn^{2+}} \quad (5)$$
$$\overset{+7}{MnO_4^-} + R.A \xrightarrow{\text{basic/neutral}} \overset{+4}{MnO_2} \quad (3)$$
$$\overset{+7}{MnO_4^-} + R.A \xrightarrow{\text{strong basic}} \overset{+6}{MnO_4^{2-}} \quad (1)$$

ii) Dichromate ion ($Cr_2O_7^{2-}$)

It also acts as an oxidizing agent but only in acidic medium.

$$\begin{tikzcd} \overset{+6}{Cr_2O_7^{2-}} \arrow[r, "H^+"] \arrow[dr, "\text{Other medium}"'] & 2Cr^{3+} \\ & \text{Non-redox} \end{tikzcd}$$

$$n-\text{factor } Cr_2O_7^{-2} = \frac{6}{1} \text{ and } Cr^{3+} = \frac{6}{2}$$

iii) Oxalate ion ($C_2O_4^{2-}$)

In redox reactions, it always acts as reducing agent.

$$\overset{+3}{C_2O_4^{2-}} \xrightarrow[\text{any medium}]{\text{redox}} \overset{+4}{CO_2}$$

$$\Rightarrow \quad (n-\text{factor})_{C_2O_4^{2-}} = 2$$

iv) H_2O_2

With other reagent, will act as oxidizing and reducing agent

$$\left.\begin{array}{l} \underset{(O.A)}{H_2O_2} + R.A \longrightarrow H_2O \\ \underset{(R.A)}{H_2O_2} + O.A \longrightarrow O_2 \end{array}\right\} (\text{n-factor})_{H_2O_2} = 2$$

v) Mohr's salt(Ferrous Ammonium sulphate

$$FeSO_4.(NH_4)_2SO_4.6H_2O \xrightarrow{\text{Redox}} Fe^{3+} \text{ only}$$

$$\Rightarrow \quad (\text{n-factor})_{\text{Mohr's salt}} = 1$$

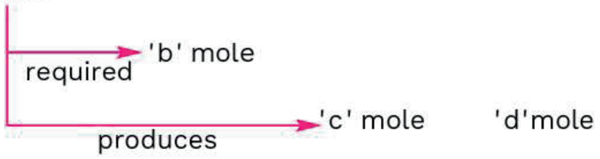
Law of equivalence

In a chemical reaction, all reactants react in equal number of equivalents and produce same number of equivalents of each product.

i.e.

For $aA + bB \longrightarrow cC + dD$

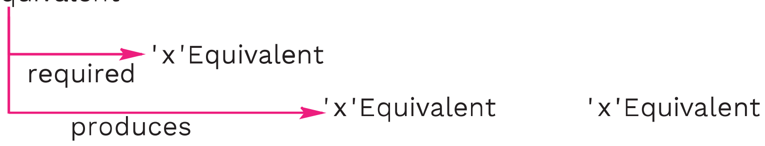
If 'a' mole



i.e. A:B:C:D by moles = a:b:c:d

But

If 'x' Equivalent



⇒ A:B:C:D by equivalent = 1:1:1:1

e.g.

	H_2SO_4 +	$2NaOH \longrightarrow$	Na_2SO_4 +	$2H_2O$
	1 mole	2 mole	1 mole	2 mole
n – factor	(2)	(1)	(2)	(1)
equivalent	2	2	2	2

Note: So, for a particular reaction,

$$\boxed{(\text{Equivalent})_{\text{given}} = (\text{Equivalent})_{\text{required}}}$$

where,

$$\boxed{\text{Equivalent}} = \begin{cases} \dfrac{\text{Mass}}{\text{Equivalent mass}} \\ \dfrac{\text{Mass}}{\text{Molar mass}} \times n-\text{factor} \\ \\ \text{Mole} \times n-\text{factor} \\ M \times V \times n-\text{factor} \\ N \times V \end{cases}$$

Illustration:

Q1 **To neutralize completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the volume of 0.1 M aqueous KOH solution required as:**

(A) 10 ml **(B) 20 ml**

(C) 40 ml **(D) 60 ml**

Q1 (C)

Given:

$H_3PO_3 + 2KOH \longrightarrow K_2HPO_3 + 2H_2O$

Volume of 0.1 M aqueous solution of phosphoric acid = 20 ml

We know from law of equivalence:

$$(\text{Equivalent})_{H_3PO_3} = (\text{Equivalent})_{KOH}$$

$M_1 \times V_1 \times$ n-factor = $M_2 \times V_2 \times$n-factor

$0.1 \times 20 \times 2 = 0.1 \times (V)_{KOH} \times 1$

$\Rightarrow \quad 4 = (V)_{KOH} \times 0.1$

$\Rightarrow \quad V_{KOH} = 40$ ml

Q2 **The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ions in acidic solution is:**

(A) 2/5 **(B) 3/5** **(C) 4/5** **(D) 1**

A2 A

$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

We know from law of equivalence:

$$(\text{Equivalent})_{KMnO_4} = (\text{Equivalent})_{SO_3^{-2}}$$

$$(\text{Mole} \times \text{n} - \text{factor})_{KMnO_4} = (\text{Mole} \times \text{n-factor})_{SO_3^{-2}}$$

$$n \times 5 = 1 \times 2$$

$$n = 2/5 \text{ moles}$$

Q3 **The mass of potassium dichromate crystals required to oxides 750 cm^3 of 0.6 M Mohr's salt solution is:**

(Given molar mass: potassium dichromate = 294 g/mol, Mohr's salt = 392 g/mol)

(A) 22.05 g **(B) 2.2 g** **(C) 0.49 g** **(D) 0.45 g**

A3 **(A)**

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

We know from law of equivalance:

$$(\text{Equivalent})_{K_2Cr_2O_7} = (\text{Equivalent})_{\text{Mohr's salt}}$$

$$\left(\frac{\text{Mole}}{\text{Molar mass}} \times n-\text{factor}\right) = (M \times V \times n-\text{factor})_{\text{Mohr's salt}}$$

$$\frac{w}{294} \times 6 = 0.6 \times \frac{750}{1000} \times 1$$

$$w = 0.6 \times \frac{75}{100} \times \frac{294}{6} = 22.05\,\text{gm}$$

Q4 **What weight of HNO$_3$ is needed to convert 62 gm of P$_4$ to H$_3$PO$_4$ in the reaction?**

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

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

A4 (B)

The balance chemical reaction:

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Molar mass of P_4 = 9/mol

Molar mass of HNO_3 = 63 9/mol

We know from law of equivalence:

$$(\text{Equivalent})_{P_4} = (\text{Equivalent})_{HNO_3}$$

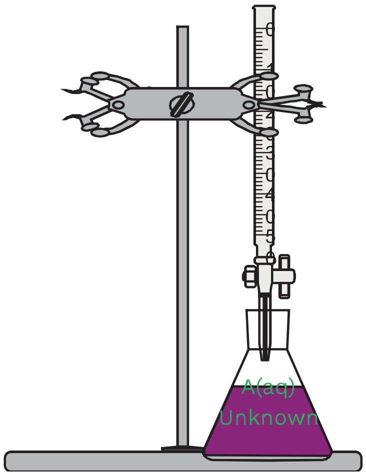
$$\left(\frac{\text{Mass}}{\text{Molar mass}} \times n-\text{Factor}\right)_{P_4} = \left(\frac{\text{Mass}}{\text{Molar mass}} \times n-\text{Factor}\right)_{HNO_3}$$

$$\Rightarrow \frac{62}{124} \times 20 = \frac{w}{63} \times 1$$

$$\Rightarrow w = \frac{62}{124} \times 20 \times 63 = 630\,\text{gm}$$

Titration ($A_{(aq)}$ vs $B_{(aq)}$)

Aim: Determination of the concentration of solution present in conical flask by titration with standard solution from burette.



B (aq). known : Standard Solution

At equivalence point

$(Eq.)_A = (Eq.)_B$

Illustration:

Q1 **It requires 40 ml of 1 M Ce^{4+} to titrate 20 ml of 1 M Sn^{2+} to Sn^{4+}. What is the oxidation state of the Cerium in the product?**

A1 $Ce^{4+} + Sn^{2+} \longrightarrow Sn^{4+} + Ce^{n+}$

$$(\text{Milli Equivalent})_{Ce^{4+}} = (\text{Milli Equivalent})_{Sn^{2+}}$$

$$(M \times V \times n - \text{factor})_{Ce^{4+}} = (M \times V \times n - \text{factor})_{Sn^{2+}}$$

$$1 \times 40 \times (4 - n) = 1 \times 20 \times 2$$

$$40 \times (4 - n) = 40$$

$$4 - n = 1$$

$$n = 4 - 1$$

$$\boxed{n = 3}$$

Q2 **6.7 gm sample of $Na_2C_2O_4$ is titrated with 40 ml, 0.02 M $KMnO_4$ solution in acidic medium. Calculate % purity of original sample.**

A2

$$Na_2\overset{+3}{C_2}O_4 + K\overset{+7}{Mn}O_4 \xrightarrow{H^+} \overset{+2}{Mn^{2+}} + \overset{+4}{C}O_2$$

$$(\text{Equivalent})_{Na_2C_2O_4} = (\text{Equivalent})_{KMnO_4}$$

$$\frac{x}{134} \times 2 = \left(0.02 \times \frac{40}{1000} \times 5\right)$$

$$\frac{x}{67} = 0.1 \times \frac{4}{100}$$

$$x = 0.1 \times \frac{4}{100} \times 67$$

$$x = \frac{26.8}{100}$$

$$x = 0.268$$

$$\text{Now, } \% \text{ purity} = \frac{0.268}{6.7} \times 100$$

$$\% \text{ purity} = 0.04 \times 100$$

$$\% \text{ purity} = 4\ \%$$

Q3 **An aqueous solution of H2O2 is diluted 20 times. If 100 ml of this diluted solution requires 200 ml, 0.1N K2Cr2O7 solution for complete titration in acidic medium, then calculate volume strength of the original H2O2 solution.**

A3 Molarity of original H_2O_2 solution is “x” M

Molarity of diluted H_2O_2 solution = $\frac{x}{20}$M

$$K_2Cr_2O_7 + H_2O_2 \longrightarrow Cr^{3+} + O_2$$

$$\therefore \text{Milli (Equivalent)}_{K_2Cr_2O_7} = (\text{Milli Equivalent})_{H_2O_2}$$

$$0.1 \times 200 = \frac{x}{20} \times 100 \times 2$$

$$x = 2\text{ M}$$

$\therefore$ Volume strength = 2×11.2 = 22.4 V

Different Types of Titration

Illustration:

Q1 **0.84 g iron ore containing ‘x’ percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required ‘x’ ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the normality of dichromatic solution.**

A1 $Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Fe^{3+} + Cr^{3+}$

$$(\text{Equivalent})_{Fe} = (\text{Equivalent})_{K_2Cr_2O_7} \text{ from law of equivalance}$$

$$\frac{0.84\times\frac{x}{100}}{56}\times 1=\frac{x\times N}{1000}$$

$$\Rightarrow N=\frac{0.84\times 100}{56\times 100}=0.15 \text{ eq / L}$$

Q2 **An equimolar mixture of $Na_2C_2O_4$ and $H_2C_2O_4$ required V_1 litre of 0.1 M $KMnO_4$ in acidic medium for complete oxidation. The same amount of the mixture required V_2 litre of 0.2 M NaOH for neutralization. The ratio of V_1 to V_2 (V_1/V_2) is:**

(A) 2:5 **(B) 1:2**

(C) 4:5 **(D) None of these**

A2 (A)

Case–I: Equimolar mixture of $Na_2C_2O_4$ and $H_2C_2O_4$ required V_1 L of 0.1M $KMnO_4$ in acidic medium.

As the mixture is equimolar, 1 mole of each are present.

∴ Eq. of $Na_2C_2O_4$ + Eq. of $H_2C_2O_4$ = Eq. of $KMnO_4$

$1\times2 + 1\times2 = 0.1\times V_1\times5$

(∴ equivalent = mole × valence factor)

$$V_1=\frac{4}{0.5}$$

$$V_1=8\,L$$

Case – II: Equimolar mixture of $Na_2C_2O_4$ and $H_2C_2O_4$ required V_2L of 0.2 M NaOH for neutralization.

$$(\text{Equivalent})_{Na_2C_2O_4} + (\text{Equivalent})_{H_2C_2O_4} = (\text{Equivalent})_{NaOH}$$

$$1\times2+1\times2=V_2\times0.2\times1$$

$$2+2=V_2\times0.2$$

$$V_2=20\,L$$

$$\therefore \quad \frac{V_1}{V_2}=\frac{8}{20}=2:5$$

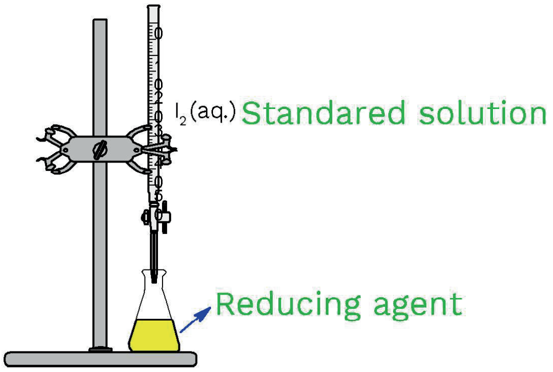
Iodimetric Titration:

- It is used to determine strength of a reducing agent by direct titration of it with standard solution of I_2
  i.e.

$$I_2 + \text{Reducing agent} \longrightarrow I^- + \text{product}$$

At equivalence point

$$(Eq)_{I_2} = (Eq.)_{\text{Reducing agent}}$$



Iodometric Titration:

- It is used to determine strength of an oxidizing agent
- It is a two–step process as following:

Step–I:

$$\text{Oxidising agent} + \underset{\text{(excess)}}{I^-(aq.)} \longrightarrow \text{Product} + I_2$$

Step–II:

$$\underset{\text{(evolved)}}{I_2} + \underset{\substack{\text{Sodium thiosulphate}\\ \text{(Hypo)}}}{2Na_2S_2O_3} \longrightarrow Na_2S_4O_6 + 2NaI$$

$$\left[(\text{Equivalent})_{O.A}\right] = \left[(\text{Equivalent})_{I_2}\right]_1 \qquad ...(1)$$

$$\left[(\text{Equivalent})_{I_2}\right]_2 = \left[(\text{Equivalent})_{\text{Hypo}}\right] \qquad ...(2)$$

∴ Moles of I_2 in both reactions are same.

$$\left(n - \text{factor}_{I_2}\right)_1 = 2$$

Also

$$\left(n - \text{factor}_{I_2}\right)_2 = 2$$

$$\Rightarrow \quad (Eq_{I_2})_1 = (Eq_{I_2})_2$$

So,

$$(Eq)_{O.A} = (Eq.)_{\text{hypo}}$$

Illustration:

Q1 **50 ml KMnO4 solution is mixed with excess of KI solution in acidic medium. The liberated I2 requires 200 ml of 0.25 M Na2S2O3 solution for complete titration. Calculate molarity of KMnO4 solution.**

A1 Given

$KMnO_4 + I^- \longrightarrow Mn^{2+} + I_2$

$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + NaI$

Volume of $KMnO_4$ solution = 50 ml

Volume of $Na_2S_2O_3$ solution = 200 ml

$$\therefore (\text{Mill Equivalent})_{KMnO_4} = (\text{Mill Equivalent})_{Na_2S}$$

$$M \times 50 \times 5 = 0.25 \times 200 \times 1$$

$$M = \frac{0.25 \times 200 \times 1}{50 \times 5}$$

$$\text{Molarity of } [KMnO_4] = 0.2\,M$$

Q2 **25 ml of household bleach solution was mixed with 30 ml of 0.50 M KI and 10 ml of 4 N acetic acid. In the titration of the liberated iodine, 48 ml of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is:**

(A) 0.48 M **(B) 0.96 M** **(C) 0.24 M** **(D) 0.024 M**

A2 **c**

$Cl_2 + I^- \longrightarrow I_2 + Cl^-$

$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + NaI$

$(n - \text{factor})_{I_2}$ is same in both steps

$$(\text{Molarity})_{\text{Bleach}} = \frac{x}{\text{Volume}} = \frac{6}{25} = 0.24\text{ M}$$

Note:

$A \longrightarrow B$

All $B \longrightarrow C$

If n – Factor of B in both are same

$(Eq.)_A = (Eq.)_C$

If n – Factor of B are different

$(Eq._B)_1 \neq (Eq._B)_2$,

then apply mole method for solving

Q3 **10 ml of $K_2C_2O_4$ solution is mixed with excess of KIO_3 solution. The evolved I_2 requires 20 ml, 0.5 M hypo solution for complete titration.**

Determine the molarity of $K_2C_2O_4$ solution.

A3 $K_2C_2O_4 + KIO_3 \longrightarrow I_2 + CO_2$

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

$$(\text{Milli Equivalent})_{I_2} = (\text{Milli Equivalent})_{Na_2S_2O_3}$$

$$n \times 2 = 0.5 \times 20 \times 1$$

$$n = \frac{10.0 \times 1}{2}$$

$$n = 5 \text{ m.mole}$$

$$(\text{Muilli Equivalent})_{K_2C_2O_4} = (\text{Milli Equivalent})_{I_2}$$

$$M \times 10 \times 2 = 5 \times 10$$

$$M = \frac{50}{20}$$

$$M = 2.5 \text{ M}$$

Q4 **To measure the quantity of $MnCl_2$ dissolved in an aqueous solution, it was completely converted to $KMnO_4$ using reaction,**

$MnCl_2 + K_2S_2O_8 + H_2O \rightarrow KMnO_4 + H_2SO_4 + HCl$ (Equation not balanced)

Few drops of concentration HCl were added to this solution and gently warmed. Further oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared.

The quantity of $MnCl_2$ (in mg) present in the initial solution is ____________. (Atomic weight in g mol⁻¹; Mn=55, Cl=35.5)

A4 $MnCl_2 \longrightarrow MnO_4^-$

$$MnO_4^- + H_2C_2O_4 \xrightarrow{H^+} Mn^{2+} + CO_2$$

$$(n - \text{Factor})_{MnO_4^-} \longrightarrow \text{same in both reaction}$$

$$(\text{Equivalent})_{C_2O_4^{2-}} = (\text{Equivalent})_{MnO_4^-}$$

$$2 \times \frac{0.225}{90} = \text{moles} \times 5$$

$$\Rightarrow \quad \text{moles}_{M_nO_4^-} = 0.001$$

$$(\text{Equivalent})_{MnCl_2} = (\text{Equivalent})_{MnO_4^-}$$

$$\text{Now,} \quad \frac{W_{MnCl_2}}{(55+71)} \times 5 = 0.001 \times 5$$

$$W_{MnCl_2} = 0.001 \times (55+71) \text{ gm}$$

$$W_{MnCl_2} = 126 \text{ mg}$$

Given quantity of $MnCl_2$ dissolved in an aqueous solution was completely converted to $KMnO_4$.

∴ Quantity of $MnCl_2$ present in the initial solution = 126 mg

Back Titration, Double Indicator Titration

Back Titration:

- A multistep process which can be used for both redox as well as non–redox reactions.

Step–I:

$$\underset{(L.R)}{A} + B \longrightarrow \text{product}$$

$$(Eq)_A = (Eq_B)_1$$

Step–II:

$$B + C \longrightarrow \text{product}$$
(remaining)

$$(Eq_B)_2 = (Eq)_C$$

$$(n_B)_1 + (n_B)_2 = \text{Initial moles of B (Given)}$$

- If n-factor of B in both are same:

$$\boxed{(Eq._B)_{Total} = (Eq.)_A + (Eq.)_C}$$

- If n-factor of B in both are different:
  First solve reaction in steps (2) and find $(n_B)_2$.
  Now, $(n_B)_1 = (n_B)_{given} - (n_B)_2$
  Now solve reaction in step (1) and find A.

Illustration:

Q1 **50 gm of a sample of $Ca(OH)_2$ is dissolved in 50 ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.3 N NaOH. The volume of NaOH used was 20 cc. Calculate % purity of $Ca(OH)_2$ sample.**

A1 $$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$$

$$\underset{(Remaining)}{HCl} + NaOH \longrightarrow NaCl + H_2O$$

Let ‘x’ gm of $Ca(OH)_2$ present in sample
n-factor of HCl is same in both.
So,

$$(Eq.)_{HCl} = (Eq.)_{Ca(OH)_2} + (Eq.)_{NaOH}$$

$$0.5 \times \frac{50}{1000} = \left(\frac{x}{74} \times 2\right) + \left(0.3 \times \frac{20}{1000}\right)$$

$$\frac{25}{1000} = \frac{x}{37} + \frac{6}{1000}$$

$$\Rightarrow \quad \frac{25}{1000} - \frac{6}{1000} = \frac{x}{37}$$

$$\frac{19}{1000} = \frac{x}{37}$$

$$\Rightarrow \quad x = \frac{19}{1000} \times 37$$

$$x = \frac{703}{1000} = 0.703 \text{ g}$$

Now,

$$\% \text{ purity} = \frac{\text{Mass of } Ca(OH)_2}{\text{Mass of sample}} \times 100 = \frac{0.703}{50} \times 100 = 1.406\%$$

Q2 **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?**

A2 Let mass of pure NH_3 = x gm

$$(Eq.)_{H_2SO_4} = (Eq.)_{NH_3} + (Eq.)$$

$$0.5 \times \frac{50}{1000} = \left(\frac{x}{17} \times 1\right) + \left(0.1 \times \frac{20}{1000}\right)$$

$$\frac{25}{1000} = \frac{x}{17} + \frac{2}{1000}$$

$$\Rightarrow \quad \frac{25}{1000} - \frac{2}{1000} = \frac{x}{17}$$

$$\Rightarrow \quad \frac{23}{1000} \times 17 = x$$

$$\Rightarrow \quad x = \frac{391}{1000} = 0.391 \text{gm}$$

$$\therefore \% \, NH_3 = \frac{0.391}{9} \times 100 = 4.34\%$$

Q3 **40 ml solution of $Na_2C_2O_4$ is treated with 100 ml, 0.1 M $KMnO_4$ in acidic medium, the excess of MnO_4^- solution requires 10 ml of 0.05 M H_2O_2 solution in basic medium for complete titration.**
Calculate molarity of $Na_2C_2O_4$.

A3

$$C_2O_4^{2-} + MnO_4^- \xrightarrow{H^+} Mn^{2+} + CO_2 \qquad \ldots(1)$$

$$MnO_4^- + H_2O_2 \xrightarrow{OH^-} MnO_2 + O_2 \qquad \ldots(2)$$

(Remaining)

n-factor of MnO_4^- is differed in both

For reaction 2,

$$(\text{m. eq.})_{MnO_4^-} = (\text{m. eq.})_{H_2O_2}$$

$$\text{m. moles} \times 3 = 0.05 \times 10 \times 2$$

$$\text{m. moles}_{MnO_4^1} = \frac{5 \times 10 \times 2}{100 \times 3}$$

$$\text{m. moles}_{MnO_4^1} = \frac{1}{3}$$

$$\text{m.moles of } \left(MnO_4^-\right)_{\text{Total}} = 0.1 \times 100 = 10\,\text{m.mole}$$

$$\text{m.moles of } MnO_4^- \text{ used in 1 reaction} = 10 - \frac{1}{3} = \frac{29}{3}\,\text{m.mole}$$

For reaction (1):

$$(\text{m. eq.})_{Na_2C_2O_4} = (\text{m. eq.})_{MnO_4^-}$$

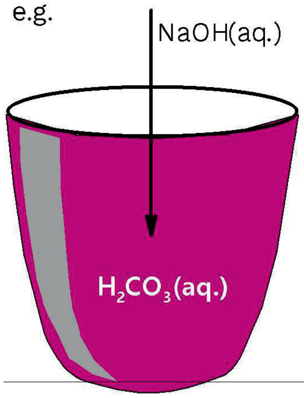
$$M \times 40 \times 2 = \frac{29}{3} \times 5$$

$$M = \frac{29}{3} \times \frac{5}{80} = \frac{145}{240} = \frac{29}{48}\,\text{mol / L}$$

Double Indicator Titration:

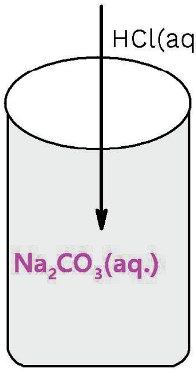
The titration consisting two equivalence points which are detected by two different indicators.

e.g.



$$H_2CO_3 + NaOH \longrightarrow NaHCO_3 + H_2O$$
$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

- Na_2CO_3(aq.) vs (HCl(aq.)



(i) Upon addition of HCl

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + \underset{\text{(Neutral)}}{NaCl}$$

i) When all Na_2CO_3 consume to give $NaHCO_3$,
$\Rightarrow$ **1st equivalence point is reached**
Suitable indicator = Phenolphthalein

ii) Now on further addition of HCl
$NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl$ (Neutral)
When all $NaHCO_3$ consumed to give H_2CO_3
$\Rightarrow$ **2nd equivalence point is reached**

Suitable indicator = Methyl orange

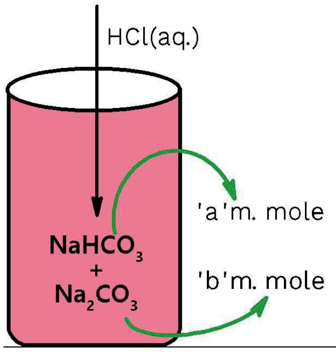
- If alone phenolphthalein is used then only 1st equivalence point in detected.
- If alone methyl orange is used then only 2nd equivalence point is detected.
- To detect both equivalence point, initially phenolphthalein is mixed and after 1st equivalence point, Methyl orange should be mixed.

Illustration:

Q1 **In the mixture of ($NaHCO_3$ + Na_2CO_3), volume of HCl required in ‘x’ ml with phenolphthalein indicator and y ml with methyl orange later in the same titration. Hence volume of HCl for complete reaction of Na_2CO_3 is:**

(A) 2x **(B) y** **(C) x/2** **(D) (y–x)**

A1 A



Phenolphthalein is added to detect 1st equivalence po

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

$$(Eq)_{HCl} = (Eq)_{Na_2CO_3}$$

$$N \times 'x' = b \times 1$$

Now, methyl orange is added to detect 2nd equivalence point

$$NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$$

$$(m.eq)_{HCl} = (m.eq)_{NaHCO_3}$$

$$N \times y = (a + b) \times 1$$

$$Na_2CO_3 \xrightarrow{HCl} H_2CO_3$$

$$\begin{aligned}(Eq)_{Na_2CO_3} &= (Eq)_{HCl}\\ b \times 2 &= N \times V\\ (Nx) \times 2 &= N \times V\\ V &= \frac{2Nx}{N}\\ V &= 2x\end{aligned}$$

∴ volume of HCl for complete reaction is 2x ml

Q2 **0.1 g of a solution containing Na_2CO_3 and $NaHCO_3$ requires 10 ml of 0.01 N HCl for neutralization using phenolphthalein as an indicator. Weight percent of Na_2CO_3 in solution is**

(A) 25 **(B) 32** **(C) 50** **(D) None of these**

A2 D

$$(\text{m.eq.})_{Na_2CO_3} = (\text{Eq})_{HCl}$$

$$\frac{x}{106} \times 1 = 0.01 \times \frac{10}{1000}$$

$$\Rightarrow \quad x = \frac{0.1}{1000} \times 106$$

$$\Rightarrow \quad x = 106 \times 10^{-4}\,\text{gm}$$

$$\therefore \quad \text{Wt. \% of } Na_2CO_3 = \frac{106 \times 10^{-4}}{0.1} \times 100 = 10.6\%$$

Q3 A mixture of NaOH and Na2CO3 required 25 ml of 0.1 M HCl using phenolphthalein as the indicator. However, the same amount of the mixture required 30 ml of 0.1 M HCl when methyl orange was used as the indicator. The molar ratio of NaOH and Na_2CO_3 in the mixture was:

A3 4:1

Let m.moles of NaOH = ‘x’ m.mole

and m.moles of Na_2CO_3 = ‘y’ m. mole

Phenolphthalein is added to detect 1st equivalence point ($NaHCO_3$)

First: All NaOH $\xrightarrow{HCl}$ NaCl; Then $Na_2CO_3 \xrightarrow{HCl} NaHCO_3$

$$(\text{m.eq.})_{HCl} = (\text{m.eq.})_{NaOH} + (\text{m.eq.})_{Na_2CO_3}$$

$$0.1 \times 25 \times 1 \times 1 = x(1) + y(1)$$

$$\Rightarrow \quad x + y = 2.5 \text{ m.mole} \quad \text{...(1)}$$

Titration with methyl orange is added to detect 2nd equivalence point direct

$$NaOH \xrightarrow{HCl} NaCl$$

$$NaCO_3 \xrightarrow{HCl} H_2CO_3$$

$$(\text{m.eq.})_{HCl} = (\text{m.eq.})_{NaOH} + (\text{m.eq})_{Na_2CO_3}$$

$$0.1 \times 30 \times 1 = x(1) + y(2)$$

$$\Rightarrow \quad x + 2y = 3 \text{ m.mole} \quad \text{...(2)}$$

⇒ x = 2 m mole and y = 0.5 m. mole, on solving (1) & (2).

Ratio of mole of NaOH & Na_2CO_3 = $\frac{2}{0.5} = 4 : 1$

Illustration:

Q1 **100 ml solution of NaOH and Na_2CO_3 was first titrated with N/10 HCl in presence of HPh, 17.5 ml is required to end point. After this MeOH was added and 2.5 ml of same HCl is required. The amount of NaOH in mixture is**

(A) 0.06 g per 100 ml **(B) 0.06 g per 200 ml**

(C) 0.05 g per 100 ml **(D) 0.012 g per 200 ml**

A1 **A**

Let ‘x’ m mole of NaOH in 100 ml solution and ‘y’ m.ole of Na_2CO_3 in 100 ml solution.

HPh ⇒ 1st equivalence point ($NaHCO_3$)

$$\Rightarrow \quad (\text{m.eq.})_{HCl} = (\text{m.eq.})_{NaOH} + (\text{m.eq.})_{Na_2CO_3}$$

$$\Rightarrow \quad \frac{1}{10} \times 17.5 = x(1) + y(1)$$

$$\Rightarrow \quad x + y = 1.75 \qquad \text{...(1)}$$

MeOH ⇒ 2nd equivalence point.

$$\Rightarrow \quad (\text{m.eq.})_{HCl} = (\text{m.eq.})_{NaHCO_3}$$

$$\Rightarrow \quad \frac{1}{10} \times 2.5 = y(1)$$

$$\Rightarrow \quad y = 0.25 \text{ m.mole}$$

$\Rightarrow$ x = 1.5 m.mole

$\therefore$ Weight of NaOH = $1.5 \times 40 \times 10^{-3}$ = 60 gm

Q2 **1 g of sample $CaCO_3$ was strongly heated and the CO_2 liberated was absorbed in 100 ml of 0.5 N NaOH solution. Assuming 90% purity for the sample. How many mL of 0.5 M HCl would be required to react with the resulting solution to reach the end point in presence of phenolphthalein?**

A2 **(A) 73 ml** **(B) 41 ml** **(C) 82 ml** **(D) 100 ml**

C

Weight of $CaCO_3 = 1 \times \frac{90}{100} = 0.9\,gm$

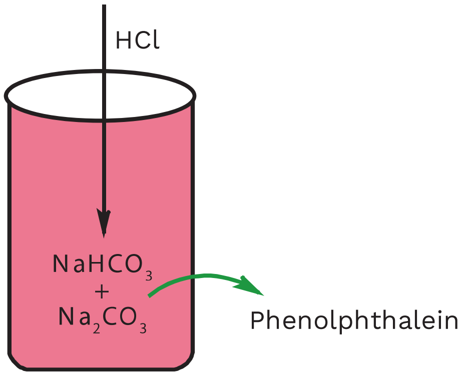
Mole of $CaCO_3 = \frac{0.9}{100}$ mole

$\therefore$ mole of CO_2 liberated $= \frac{0.9}{100}$ mole $= 9$ m.mole

$$\begin{array}{lcl} CaCO_3 & \longrightarrow & CaO + CO_2 \\ 9 \text{ m.mole} & & 9 \text{ m.mole} \end{array}$$

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + CO_2$$

$$\begin{array}{cccc} CO_2 & + \; 2NaOH & \longrightarrow & Na_2CO_3 + H_2 \\ 9 \text{ m.mole} & 50 \text{ m.mole} & & 9 \text{ m.mole} \\ \text{L.R} & (50\text{-}18) & & \\ & =32\text{m.mole(Remaining)} & & \end{array}$$



$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

1st equivalence point

$$\begin{aligned} (m.eq.)_{HCl} &= (m.eq.)_{NaOH} + (m.eq.)_{Na_2CO_3} \\ 0.5 \times V \times 1 &= 32(1) + 9(1) \\ V_{HCl} &= \frac{41}{0.5} \\ &= \frac{41}{5} \times 10 \\ V_{HCl} &= 82 \text{ ml} \end{aligned}$$

Hardness of water

Soft water: Water which produces lathers (foam) upon mixing of soap into it easily.
Hard water: Water which does not produce foam with soap due to presence of Ca^{2+}(aq.) or Mg^{2+}(aq.) in water.

Sodium stearate : $C_{17}H_{35}COONa$ (soap)

$$C_{17}H_{35}COO^-(aq.) + Ca^{2+}(aq.) \text{ or } Mg^{2+}(aq.) \longrightarrow \underset{\text{ppt.}}{(C_{17}H_{35}COO)_2Ca \text{ or } Mg(C_{17}H_{35}COO)_2}$$

- These Ca^{2+} or Mg^{2+} ions are furnished by their water soluble salts (bicarbonates, chlorides or sulphates only)

$$\text{i.e.} \quad \left.\begin{array}{l} Ca(HCO_3)_2 \\ Mg(HCO_3)_2 \\ CaCl_2 \\ MgCl_2 \\ CaSO_4 \end{array}\right\} \text{Hardness causing salt}$$

Degree of Hardness

- It is the measure of total hardness causing salt present in water.
- Measured in ppm as following:

* $CaCO_3$ is hardness causing.
For a water sample:

$$\sum (m.eq.)_{salts} = (m.eq.)_{CaCO_3}$$

$$\therefore n-\text{factor of all} = 2$$

$$\Rightarrow \sum (n)_{salts} = (n)_{CaCO_3}$$

Illustration:

Q1 **One litre of a sample of hard water contains 1 mg of CaCl2 and 1 mg of MgCl2 Then the total hardness in terms of parts of CaCO3 per 106 parts of water by mass is:**

(A) 1.954 **(B) 1.260** **(C) 0.946** **(D) None of these**

A1 (A)

1 litre water means 1000 gm

Given: Mass of $CaCl_2$= 1 mg

Moles of $CaCl_2$= $\frac{10^{-3}}{111}$ mole

Mass of $MgCl_2$= 1 mg

Moles of $MgCl_2$= $\frac{10^{-3}}{95}$ mole

$$\text{Hardness} = \frac{\left(\frac{10^{-3}}{111}+\frac{10^{-3}}{95}\right)}{1000\,g}\times 100gm\times 10^{6}$$

Hargness = 1.954 ppm

Q2 **A given sample of water containing the following impurities:**

$Mg(HCO_3)_2$ = 73 mg/L, $Ca(HCO_3)_2$ = 162 mg/L

$CaSO_4$ = 136 mg/L, $MgCl_2$ = 95 mg/L

$CaCl_2$ = 111 mg/L and NaCl = 100 mg / L

Then the total hardness (temporary and permanent) of above water sample is:

(A) 300 ppm **(B) 350 ppm** **(C) 450 ppm** **(D) 500 ppm**

A2 C

Let volume of water =1 L = 1000 ml

Mass of water = 1000 gm

$$\text{Hardness} = 10^{-3}\,\frac{\left[\frac{73}{146}+\frac{162}{162}+\frac{136}{136}+\frac{95}{95}+\frac{111}{111}\right]\times 100\times 10^{6}}{1000} = 450\text{ ppm}$$

Removal of Hardness:

$$\underset{\text{(Water soluble salts)}}{Ca^{2+}(aq.) \text{ or } Mg^{2+}(aq.)} \xrightarrow{\text{every method}} \underset{\text{(Precipitate)}}{\text{Water insoluble salt of Ca or Mg}}$$

- **Temporary hardness:**
  It is easily removed by following process:
  a) By boiling of water
  $M(HCO_3)_2(aq.) \rightarrow MCO_3(s) + H_2O(l) + CO_2(g)$

  b) By the addition of Na_2CO_3
  $M(HCO_3)_2(aq.) + Na_2CO_3(aq.) \rightarrow MCO_3^{(s)} + 2NaHCO_3(aq.)$

  c) Clarke's process:
  By the addition of exact amount of $Ca(OH)_2$, because excess will also impart hardness in water.
  $Ca(HCO_3)_2(aq.) + Ca(OH)_2(aq.) \rightarrow 2CaCO_3(s) + 2H_2O(l)$
  $Mg(HCO_3)_2(aq.) + Ca(OH)_2 \rightarrow MgCO_3(s) + CaCO_3(s) + 2H_2O(l)$

- **Permanent hardness**
  i) By adding Na_2CO_3 or Na_3PO_4.
  $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$
  $3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$

  ii) Ion exchange resins process.

$$\underset{\substack{\text{cation}\\\text{exchanger}}}{2RnH} + Ca^{2+} \longrightarrow (Rn)_2\,Ca + 2H^+$$

  iii) Permutit process
  $Ca^{2+}\ Na_2Z \rightarrow CaZ + 2Na^+ \rightarrow Ca^{2+}\ Na_2Z \rightarrow CaZ + 2Na^+$
  $Mg^{2+} + Na_2Z \rightarrow MgZ + 2Na^+$
  [Na_2Z is the sodium zeolite ($Na_2Al_2Si_2O_8H_2O$)]

  iv) Calgon (Calcium gone) process
  $Na_6(PO_3)_6$ is called Calgon which is written as $Na_2[Na_4(PO_3)_6]$
  $Na_4(PO_3)_6]^{2-} + M^{2+} \rightarrow Na_2M(PO_3)_6]^{2-} + 2Na^+$
  where $M = Ca^{2+}/Mg^{2+}$

Illustration:

Q1 **A sample of hard water contains 20 mg of Ca^{2+} ions per litre. How many milli equivalent of Na_2CO_3 would be required to soften 1 litre of the sample?**

(A) 0.5 **(B) 0.1** **(C) 0.2** **(D) 1**

A1 (D)

Given mass of Ca^{2+} ions = 20 mg

$$(\text{m.eq.})_{Na_2CO_3} = (\text{m.eq.})_{Ca^{2+}}$$

$$= \left(\frac{20}{40}\right) \times 2$$

$$= 1 \text{ milliequivalen}$$

Q2 **Consider the temporary hardness of water is due to the presence of $Ca(HCO_3)_2$ and specific gravity of hardwater is 1. Then the weight of CaO required for 10^6 litre of water to remove the temporary hardness of 1000 ppm is:**

(A) 3.6×10^4 gm **(B) 6.5×10^4 gm**

(C) 5.6×10^5 gm **(D) 8.5×10^5 gm**

A2 C Given Volume of water = 10^6L

$= 10^9$ ml

Mass of water = 10^9 gm

$$\text{Using, (in ppm) hardness} = \frac{\text{mass of } CaCO_3}{\text{mass of water}} \times 10^6$$

$$1000 = \frac{W_{CaCO_3} \times 10^6}{10^9}$$

$$W_{CaCO_3} = 10^6 \text{gm}$$

$$= 10^4 \text{mole}$$

i.e. ∴ mole of moe$CaCO_3$ = 10^4 mole

$$(\text{Eq.})_{\text{Salt}} = (\text{Eq.})_{CaO}$$

$$10^4 \times 2 = \frac{w}{56} \times 2$$

$$w = \frac{10^4 \times 2 \times 56}{2}$$

$$w = 56 \times 10^4$$

$$w = 5.6 \times 10^5 \text{gm}$$