Redox Reaction
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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**

<table>
<thead>
<tr>
<th>OXIDATION</th>
<th>REDUCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of oxygen or Removal of hydrogen</td>
<td>Addition of hydrogen or Removal of oxygen</td>
</tr>
</tbody>
</table>

**e.g.**

<table>
<thead>
<tr>
<th>OXIDATION</th>
<th>REDUCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of O</td>
<td>Reduction of Cl₂</td>
</tr>
</tbody>
</table>

2 Mg + O₂ → 2MgO

Oxidation of Mg

<table>
<thead>
<tr>
<th>OXIDATION</th>
<th>REDUCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of electronegative element or Removal of electropositive element</td>
<td>Addition of electropositive element or Removal of electronegative element</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>OXIDATION</th>
<th>REDUCTION</th>
</tr>
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<tbody>
<tr>
<td>Addition of electronegative element or Removal of electropositive element</td>
<td>Addition of electropositive element or Removal of electronegative element</td>
</tr>
</tbody>
</table>

Redox Reaction
## Oxidation Reduction

**Oxidation**

- Addition of electronegative atom
- Addition of electropositive
- Oxidation and reduction of HCl

**Reduction**

- Oxidation of Na and Reduction of Cl₂

---

<table>
<thead>
<tr>
<th>OXIDATION</th>
<th>REDUCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Oxidation Diagram" /></td>
<td><img src="image2.png" alt="Reduction Diagram" /></td>
</tr>
</tbody>
</table>

### Modern Concept

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

<table>
<thead>
<tr>
<th>OXIDATION</th>
<th>REDUCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>The process in which substance looses some electrons.</td>
<td>The process in which substance gains some electrons.</td>
</tr>
</tbody>
</table>
3. Oxidation of Zn and reduction of Cu$^{2+}$.

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.** H₂

\[
(O_{\text{oxidation number}})_H = \frac{\text{Total charge on H atoms}}{\text{Total number of H atoms}}
\]

\[
= \frac{0}{2} = 0
\]

Oxidation number of hydrogen in H₂ = zero

**e.g.**

i) HCl

\[
(O,N)_H = \left(\frac{+1}{1}\right) = +1
\]

\[
(O,N)_Cl = \left(\frac{-1}{1}\right) = -1
\]

ii) HCN

\[
(O,N)_H = \frac{+1}{1} = +1
\]

\[
(O,N)_C = \frac{-1 + 3}{1} = +2
\]

\[
(O,N)_N = \frac{-3}{1} = -3
\]

More electronegative

Order of electronegativity

H < C < N

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

i) \( \text{C}_2\text{O}_2 \) (carbon suboxide)

\[
\begin{align*}
\text{O} & \quad \text{C} \quad \text{O} \\
\end{align*}
\]

Now,

\[
\begin{align*}
(\text{O.N})_O & = \frac{-2 - 2}{2} = (-2) \\
(\text{O.N})_C & = \frac{+2 + 0 + 2}{3} = \left( \frac{+4}{3} \right)
\end{align*}
\]

ii) \( \text{Na}_2\text{S}_4\text{O}_6 \)

\[
\begin{align*}
\text{Na} & \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{O} \quad \text{S} \quad \text{S} \quad \text{O} \quad \text{Na} \\
\end{align*}
\]

\[
\begin{align*}
(\text{O.N})_{\text{Na}} & = \frac{+1 + 1}{2} = (+1) \\
(\text{O.N})_O & = \frac{-12}{6} = (-2) \\
(\text{O.N})_S & = \frac{+5 + 0 + 0 + 5}{4} \\
& = (+2.5)
\end{align*}
\]

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

e.g.

i) $\text{CO}_2$ and $\text{CH}_4$

\[
\begin{align*}
\text{O} = \text{C} = \text{O} \quad \text{and} \quad 
\text{H} \quad \text{C} \quad \text{H}
\end{align*}
\]

Oxidation number of carbon in $\text{CO}_2$ is +4 and in $\text{CH}_4$ is −4.

ii) $\text{H}_2$, $\text{HCl}$ and $\text{NaOH}$

Oxidation number of hydrogen in $\text{H}_2$, $\text{HCl}$ and $\text{NaOH}$ 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 $A_x B_y C_z$

- $x(p) + y(q) + z(r) = 0$
- $(A_x B_y C_z)_r$
- $x(p) + y(q) + z(r) = \phi$

**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.**

<table>
<thead>
<tr>
<th>$H$, $He$, $C$, $N_2$, $O_2$, $F_2$</th>
<th>Oxidation number = 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Na$, $Mg$, $S_8$, $P_4$, $Cl_2$</td>
<td></td>
</tr>
<tr>
<td>$Fe$, $Zn$, $Ag$, etc.</td>
<td></td>
</tr>
</tbody>
</table>

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

**i.e.**

| $Li$, $Na$, $K$, $Rb$, $Cs$     | In compounds, Oxidation number = (+1) always |

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

**i.e.**

| $Be$, $Mg$, $Ca$, $Sr$, $Ba$    | In compounds, Oxidation number = (+2) 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, (oxidation number)$_{Metal}$ = (-1)
  \[(Electronegativity)$_{Metal}$ < (Electronegativity)$_{H}\]
  
  **e.g.**
  
  - 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 = \((-\frac{1}{2})\)

<table>
<thead>
<tr>
<th>Na$_2$O</th>
<th>Na$_2$O$_2$</th>
<th>NaO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(+1)+ 1(x) = 0</td>
<td>2(+1) + 2(x) = 0</td>
<td>1(+1) + 2x = 0</td>
</tr>
<tr>
<td>x = (-2)</td>
<td>x = (-1)</td>
<td>[x = \left(-\frac{1}{2}\right)]</td>
</tr>
<tr>
<td>Oxide</td>
<td>Peroxide</td>
<td>Superoxide</td>
</tr>
</tbody>
</table>

- **Compounds of oxygen with fluorine**

<table>
<thead>
<tr>
<th>OF$_2$</th>
<th>O$_2$F$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(x) + 2(-1) = 0</td>
<td>2(x) + 2(-1) = 0</td>
</tr>
<tr>
<td>x = (+2)</td>
<td>x = +1</td>
</tr>
</tbody>
</table>
Where, 'n' is number of valence electrons.

- **For halogens (except F)**

  Oxidation Number Range = (-1) to (+7)

  \[
  \begin{bmatrix}
  -1 & 0 & +1 & +3 & +5 & +7 \\
  \text{Cl}^- & \text{Cl}_2 & \text{ClO}^- & \text{ClO}_2 & \text{ClO}_3^- & \text{ClO}_4^-
  \end{bmatrix}
  \]

- **Oxidation number of Chlorine**

<table>
<thead>
<tr>
<th>Case – I</th>
<th>Chlorine in chlorides</th>
<th>Cl(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1(x) = -1)</td>
<td>(x = -1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Case – II</th>
<th>Chlorine molecule</th>
<th>Cl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(2(x) = 0)</td>
<td>(x = 0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Case – III</th>
<th>Chlorine with more electronegative atom</th>
<th>ClO(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1(x) + 1(-2) = -1)</td>
<td>(x = +1)</td>
</tr>
</tbody>
</table>

- **For chalcogens except oxygen**

  Oxidation number range = (–2) to (+6)

  e.g. S\(^{2-}\), S\(^{2-}\), S\(^0\), S\(^{4-}\), S\(^{6+}\)

- **For Nitrogen family**

  Oxidation number = (–3) to (+5)

  e.g. N\(_3\), N\(_2\)H\(_4\), N\(_2\), N\(_2\)O, N\(_2\)O\(_3\), N\(_2\)O\(_4\), N\(_2\)O\(_5\)

- **d–block elements** show multiple but fixed oxidation number in their compounds.

  e.g. Fe = (+2), (+3)
  Tl = (+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 $+8$ which is for Osmium and Xenon in their particular compounds.

**e.g.**

$\text{CrO}_5$

Oxidation of Cr

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

$x = +10$

Not possible

i.e.

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

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

**e.g.**

$+1 \times -2$

$\text{H}_2\text{SO}_5$

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)  \( \text{Fe}_2\text{O}_3 \)
   \[ 3x + 4(-2) = 0 \]
   \[ 3x = 8 \]
   \[ x = \frac{8}{3} \]
   Oxidation number of Fe is \(+8/3\).
   
   ii)  \( \text{FeO} \)
   \[ x + (-2) = 0 \]
   \[ x = +2 \]
   Oxidation number of Fe is \(+2\).

   iii)  \( \text{Na}_2\text{S}_4\text{O}_6 \)
   Oxidation number of S in \( \text{Na}_2\text{S}_4\text{O}_6 \)
   \[ 2(+1) + 4x + 6(-2) = 0 \]
   \[ 2 + 4x -12 = 0 \]
   \[ 4x = 10 \]
   \[ x = \frac{10}{4} \]
   \[ x = +2.5 \]

   iv)  \( \text{C}_2\text{H}_5\text{OH} \)
   \[ 2x + 5(1) + (-2) + (1) = 0 \]
   \[ 2x + 5 -2 + 1 = 0 \]
   \[ 2x = -4 \]
   \[ x = -2 \]
   Oxidation number of C in \( \text{C}_2\text{H}_5\text{OH} \) is \(-2\).

   v)  \( \text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \)
   \( \text{FeSO}_4 \) \( \Rightarrow \) \( x+(-2) = 0 \) \( \Rightarrow x = +2 \)
   \( \text{NH}_4^+ \) \( \Rightarrow \) \( x + 4(1) = +1 \) \( \Rightarrow x = -3 \)
   Oxidation number of Fe in \( \text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} = +2 \)
   Oxidation number of N in \( \text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} = -3 \)

   vi)  \( \text{CO}_2 \)
   \[ x + 2(-2) = 0 \]
   \[ x = +4 \]
   Oxidation number of C in \( \text{CO}_2 \) is \(+4\).

   vii)  \( \text{FeS}_2 \)
   \[ (+2) + 2 \times x = 0 \]
   \[ 2x = -2 \]
\[ x = -1 \]
O.N. of S in FeS \(_2\) is (-1).

\text{viii) PbS}
\[ x + (-2) = 0 \]
\[ x = +2 \]
Oxidation number of Pb in PbS is +2.

\text{ix) CS}_2
\[ x + 2(-2) = 0 \]
\[ x - 4 = 0 \]
\[ x = +4 \]
Oxidation number of C in CS\(_2\) is +4.

\text{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. |

\text{xi) (N}_2\text{H}_5\text{SO}_4
\[ 2(2x + 5(1)) + (-2) = 0 \]
\[ 4x + 8 = 0 \]
\[ 4x = -8 \]
\[ x = -8/4 = -2 \]
Oxidation number of N in (N\(_2\)H\(_5\))\text{SO}_4 is (-2).

\text{xii) N}_2\text{O}_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\(_2\)O\(_5\) is +5.

\text{xiii) HCN}
Oxidation number of C:
\[ (1) + x + (-3) = 0 \]
\[ x = +2 \]
Oxidation number of N:
\[ 1 + (+2) + x = 0 \]
\[ x = -3 \]
Oxidation number of C in HCN is (+2).
Oxidation number of N in HCN is (-3).

xiv) \(\text{Ba}[\text{H}_2\text{PO}_2]_2\)

Oxidation number of Ba is +2

Oxidation number of P is:

\[(+2) + 2 [2(+1) + x+2(-2)] = 0\]
\[2 + 2 (2+x - 4) = 0\]
\[2 + 4 + 2x - 8 = 0\]
\[2x - 2 = 0\]
\[2x = 2\]
\[x = +1\]  \(\therefore\) O.N of P in \(\text{Ba}[\text{H}_2\text{PO}_2]_2\) is (+1)

xv) \(\text{OsO}_4\)

\[x+4(-2) = 0\]
\[x = 8\]
Oxidation number of Os in \(\text{OsO}_4\) is (+8).

xvi) \(\text{H}_2\text{S}_2\text{O}_3\)

\[2(+1) + 2(x) + 3(-2) = 0\]
\[2 + 2x - 6 = 0\]
\[2x - 4 = 0\]
\[2x = 4\]
\[x = 2\]
Oxidation number of S in \(\text{H}_2\text{S}_2\text{O}_3\) is (+2)

xvii) \(\text{CH}_3\text{SO}_3\text{H}\)

Oxidation number of C is (-2)
Oxidation number of S is (+4)

xix) \(\text{Ba}_2\text{XeO}_6\)

Oxidation number of Xe is +8.
\[2(+2) + x + 6(-2) = 0\]
\[x = +8\]

xx) \(\text{Ba}(\text{SCN})_2\)

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$_3$
\[(+1) + x + 3(-2) = 0\]
x = +5
O.N of Cl in HClO$_3$ is (+5).

c) HClO$_2$
\[(+1) + x + 2(-2) = 0\]
x = +3
O.N of Cl in HClO$_2$ is (+3).

d) HClO
\[(+1) + x + (-2) = 0\]
x = +1

Q2

The oxidation number of C in CH$_4$, CH$_3$Cl, CH$_2$Cl$_2$, 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$_4$
\[x + 4(1) = 0\]
x = −4

(ii) CH$_3$Cl
\[x + 3(1) + (-1) = 0\]
x = −2

(iii) CH$_2$Cl$_2$
\[x + 2 - 2 = 0\]
x = 0

(iv) CHCl$_3$
\[x + 1 + 3(-1) = 0\]
x = +2

(v) CCl$_4$
\[x + 4(-1) = 0\]
x = +4
Q1  The correct order of the increasing oxidation states of nitrogen in NO, N₂O, NO₂ and N₂O₃ is:

(A) N₂O < NO < N₂O₂ < NO₂  
(B) N₂O < N₂O₃ < NO < NO₂  
(C) NO₂ < NO < N₂O₃ < N₂O  
(D) NO₂ < N₂O₃ < NO < N₂O

A1  
Oxidation states of N in NO, N₂O, NO₂ and N₂O₃ are:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation State</th>
<th>Equation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>+2</td>
<td>x + (-2) = 0</td>
<td>x = +2</td>
</tr>
<tr>
<td>NO₂</td>
<td>+4</td>
<td>x + 2(-2) = 0</td>
<td>x = +4</td>
</tr>
<tr>
<td>N₂O</td>
<td>+1</td>
<td>2x + (-2) = 0</td>
<td>x = +1</td>
</tr>
<tr>
<td>N₂O₃</td>
<td>+3</td>
<td>2x + 3(-2) = 0</td>
<td>x = +3</td>
</tr>
</tbody>
</table>

Q2  Oxidation number of oxygen in K₂O, K₂O₂ and KO₂, 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)  

K₂O → Oxide  
K₂O₂ → Peroxide  
KO₂ → Superoxide
**Oxidation:**
The process in which oxidation number of element increases is known as *oxidation*.
e.g.

(i) $\text{Zn}^{0} \rightarrow \text{Zn}^{2+}$
(ii) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$
(iii) $\text{Cl}^{-} \rightarrow \text{Cl}_2$
(iv) $\text{MnO}_2 \rightarrow \text{MnO}_4^-$

**Reduction:**
The process in which oxidation number of element decreases is known as *reduction*.
e.g.

(i) $\text{Br}_2 \rightarrow \text{Br}^{-}$
(ii) $\text{Cl}_2 \rightarrow \text{Cl}^{-}$
(iii) $\text{Cu}^{2+} \rightarrow \text{Cu}^{-}$
(iv) $\text{Cr}_2 \text{O}_7^2- \rightarrow \text{Cr}^{3+}$

**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) $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$

Mg is oxidized.  
$\text{O}_2$ is reduced.

(ii) $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$

$\text{H}_2$ is oxidized.  
$\text{Cl}_2$ is reduced.

(iii) $\text{H}_2 \text{O} \rightarrow \text{H}_2 + \text{O}_2$

O is oxidised.  
H is reduced.
(iv) Oxidation

\[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \]

Zn is oxidized. 
Cu\(^{2+}\) is reduced.

(v) Oxidation

\[ \text{MnO}_{4}^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}^{2+} + \text{CO}_2 \]

\(\text{MnO}_4^-\) is reduced. 
\(\text{C}_2\text{O}_4^{2-}\) is oxidized.

(vi) Oxidation

\[ \begin{align*}
\text{HCl} + \text{NaOH} & \rightarrow \text{NaCl} + \text{H}_2\text{O} \\
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2
\end{align*} \]

′: No change in oxidation No. 
\(\Rightarrow\) 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) \[ \text{Fe}^0 + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2^0 \]

i.e. Fe = R.A (Reducing agent)
H\(^+\) = O.A (Oxidizing agent)

(ii) Oxidation

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O} \]

\(\text{Cr}_2\text{O}_7^{2-}\) is reducing agent.
I\(^-\) is oxidizing agent.
Illustration:

Q1  Which of the following is not a redox change?
(A) $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$  (B) $2\text{BaO} + \text{O}_2 \rightarrow 2\text{BaO}_2$
(C) $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$  (D) $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$

A1  (C)
Non redox reaction means no change in oxidation number.

Q2  In the following reaction
$3\text{Br}_2 + 6\text{CO}_3^2^- + 3\text{H}_2\text{O} \rightarrow 5\text{Br}^- + 3\text{BrO}_3^- + 6\text{HCO}_3^-$
(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)

Q3  In the reaction
$2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$,
$I_2$ 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 $\text{NaI}$. 
### Classification of redox reactions

<table>
<thead>
<tr>
<th>1. Intermolecular reactions</th>
<th>2. Intramolecular reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidation</strong></td>
<td><strong>Oxidation</strong></td>
</tr>
<tr>
<td>A + B → Products</td>
<td>A + B → Products</td>
</tr>
<tr>
<td>Reduction</td>
<td>Reduction</td>
</tr>
</tbody>
</table>

Reaction in which two different elements in different molecules undergo oxidation & reduction.

**(e.g.)**

- Reduction
  
  \[ \text{MnO}_4^- + \text{C}_2\text{O}_4^2- \rightarrow \text{Mn}^{2+} + 2\text{CO}_2 \]

**(i)**

- Oxidation
  
  \[ |+7| + |+3| + |+2| + |+4| \]

**(ii)**

- Reduction
  
  \[ \text{PH}_3 + 3\text{NaH}_2\text{PO}_4 \rightarrow \text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \]
Redox Reaction

Combination reactions

(i) At reactant side, at least one element in free state is present but no element in free state at product side.

Reactants \( \rightarrow \) Products
(At least one element \( \rightarrow \) No element in free state)

E.g.
(i) \( \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \)  
Combination Reaction (Intermolecular)

(ii) \( \text{P}_4 + 3\text{NaOH} \rightarrow 3\text{NaH}_2\text{PO}_3 + \text{P}_3\text{H}_3 \)  
Combination Reaction (Intramolecular)

(iii) \( \text{N}_2\text{H}_4\text{NO}_2 \rightarrow 4\text{N}_2 + 3\text{O}_2 + 2\text{H}_2\text{O} \)  
Decomposition Reaction (Intramolecular)

Decomposition reactions

(i) At reactant side, no element in free state but in product side, there is at least one element in free state i.e.

\[ \text{No element in free state} \rightarrow \text{At least one element in free state} \]

E.g.

(3) Redox Reaction

<table>
<thead>
<tr>
<th>Combination reactions</th>
<th>Decomposition reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) At reactant side, at least one element in free state is present but no element in free state at product side.</td>
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</tr>
<tr>
<td>Reactants ( \rightarrow ) Products</td>
<td>( \text{No element in free state} \rightarrow \text{At least one element in free state} )</td>
</tr>
<tr>
<td>(At least one element ( \rightarrow ) No element in free state)</td>
<td></td>
</tr>
</tbody>
</table>

E.g.

(i) \( \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \)  
Combination Reaction (Intermolecular)

(ii) \( \text{P}_4 + 3\text{NaOH} \rightarrow 3\text{NaH}_2\text{PO}_3 + \text{P}_3\text{H}_3 \)  
Combination Reaction (Intramolecular)

(iii) \( \text{N}_2\text{H}_4\text{NO}_2 \rightarrow 4\text{N}_2 + 3\text{O}_2 + 2\text{H}_2\text{O} \)  
Decomposition Reaction (Intramolecular)

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 \( \text{H}_2\text{O}_2 \)

\[
\text{Reduction} \quad 2\text{H}_2\text{O}_2 \quad \text{Oxidation} \quad 2\text{H}_2\text{O} + \text{O}_2
\]
i.e. disproportion reaction

(ii) Disproportion of $\text{KClO}_3$

$$2\text{KClO}_3 \rightarrow \text{KClO} + \text{KClO}_4$$

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

(iii) Disproportion of $\text{P}_4$

$$\text{P}_4 + 2\text{NaOH} + 3\text{H}_2 \rightarrow 3\text{PH}_3 + \text{NaH}_2\text{PO}_2$$

(iv) Disproportion of Halogens

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

(i) $2\text{H}_2\text{S} + \text{S}_2\text{O}_8 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$

(ii) $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
Illustration:

**Q1** White phosphorus reacts with NaOH as:

\[ P_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2 \]

is an example of:

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

**A1** B

\[ P_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{SO}_2 \]

**Q2** Which of the following chemical reactions does not depict the oxidizing behaviour of $\text{H}_2\text{SO}_4$?

(A) $\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$

(B) $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$

(C) $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \rightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$

(D) $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$

**Q2** A and C

Oxidising behaviour of $\text{H}_2\text{SO}_4$ means tendency to oxidise or reduction of self.

Example: $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$

In 1\textsuperscript{st} half: $2\text{HI} \rightarrow \text{I}_2$

Oxidation number of I is increases by one thus, oxidation reaction.

In 2\textsuperscript{nd} half: $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_2$

O.N of S decreases by 2, thus reduction reaction & $\text{H}_2\text{SO}_4$ 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 \( \text{H}_2\text{O} \).

   **Step-IV:** To balance hydrogen and oxygen.

<table>
<thead>
<tr>
<th>In acidic medium</th>
<th>by adding ( \text{H}^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>To balance O</td>
<td>add ( \text{H}_2\text{O} ) to side deficit of O and double number of ( \text{H}^+ ) ions on the opposite side. The number of ( \text{H}_2\text{O} ) molecules is equal to the number of O atoms deficit.</td>
</tr>
<tr>
<td>In basic medium</td>
<td>by adding ( \text{OH}^- )</td>
</tr>
<tr>
<td>To balance O</td>
<td>add ( \text{H}_2\text{O} ) to side excess of O and same number of ( \text{OH}^- ) ions on the opposite side. The number of ( \text{H}_2\text{O} ) molecules is equal to the number of O atoms deficit.</td>
</tr>
<tr>
<td>To balance H</td>
<td>add ( \text{H}_2\text{O} ) to side deficit of H and same number of ( \text{OH}^- ) ions on the opposite side. The number of ( \text{H}_2\text{O} ) molecules is equal to the number of O atoms deficit.</td>
</tr>
</tbody>
</table>

   **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) \( \text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}^{2+} + \text{CO}_2 \)

   **Step-I:**
   
   \( \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \)
   
   \( \text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2 \)

   **Step − II**
   
   \( \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \)
   
   \( \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 \)

   **Step-III**
   
   \( \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \)
   
   \( \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 \)

   **Step-IV**

   |
\[ 8\text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \]
\[ \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 \]

**Step – V**
\[ 5\text{e}^- + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \]
\[ \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{e}^- \]

**Step – VI**
\[
(\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}) \times 2 \\
(\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{e}^-) \times 5
\]

**Step – VII**

After adding above two reactions we get:
\[
2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}
\]

ii) \[ \text{NO}_3^- + \text{Br}^- \xrightarrow{\text{H}^+} \text{NO} + \text{Br}_2 \]

\[ 3\text{e}^- + 4\text{H}^+ + \text{NO}_3^- \rightarrow \text{NO} + 2\text{H}_2\text{O}) \times 2 \]

\[ 2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^- \times 3 \]

After adding above two reactions we get
\[
2\text{NO}_3^- + 6\text{Br}^- + 8\text{H}^+ \rightarrow 2\text{NO} + 3\text{Br}_2 + 4\text{H}_2\text{O}
\]

iii) \[ \text{Zn} + \text{NO}_3^- \xrightarrow{\text{OH}^-} \text{ZnO}_2^{2-} + \text{NH}_3 \]

\[ 1\times(4\text{OH}^- + 2\text{H}_2\text{O} + \text{Zn} \rightarrow \text{ZnO}_2^{2-} + 4\text{H}_2\text{O} + 2\text{e}^-) \]

\[ 8\text{e}^- + 9\text{H}_2\text{O} + \text{NO}_3^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O} + 9\text{OH}^- \]

After adding above two reactions we get
\[
4\text{Zn} + \text{NO}_3^- + 7\text{OH}^- \rightarrow 4\text{ZnO}_2^{2-} + \text{NH}_3 + 2\text{H}_2\text{O}
\]

iv) \[ \text{AsO}_3^{3-} + \text{NO}_3^- \xrightarrow{\text{OH}^-} \text{AsO}_4^{3-} + \text{NO}_2 \]

\[ 2\text{OH}^- + \text{H}_2\text{O} + \text{AsO}_3^{3-} \rightarrow \text{AsO}_4^{3-} + 2\text{H}_2\text{O} + 2\text{e}^- \]

\[ 2\times(e^- + 2\text{H}_2\text{O} + \text{NO}_3^- \rightarrow \text{NO}_2 + \text{H}_2\text{O} + 2\text{OH}^-) \]

After adding above two reactions we get
\[
\text{AsO}_3^{3-} + 2\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{AsO}_4^{3-} + 2\text{NO}_2 + 2\text{OH}^-
\]

v) \[ \text{BrO}_4^- + \text{Br}^- \xrightarrow{\text{H}^+} \text{BrO}_3^- \]

\[ 3\times(2\text{e}^- + 2\text{H}^+ + \text{BrO}_4^- \rightarrow \text{BrO}_3^- + \text{H}_2\text{O}) \]

\[ 1\times(3\text{H}_2\text{O} + \text{Br}^- \rightarrow \text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^-) \]

After adding above two reactions we get
\[
3\text{BrO}_4^- + \text{Br}^- \rightarrow 4\text{BrO}_3^- 
\]

(vi) \[ \text{Cl}_2 \xrightarrow{\text{OH}^-} \text{Cl}^- + \text{ClO}_3^- \]

\[ 2\text{e}^- + \text{Cl}_2 \rightarrow 2\text{Cl}^- \]

\[ 12\text{OH}^- + 6\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{ClO}_3^- + 12\text{H}_2\text{O} + 10\text{e}^- \]
After adding above two reactions we get
\[ 6\text{Cl}_2 + 12\text{OH}^- \rightarrow 10\text{Cl}^- + 2\text{ClO}_3^- + 6\text{H}_2\text{O} \]

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

\[
\begin{align*}
\text{KCl} &= \text{K}^+ + \text{Cl}^- \\
\text{H}_2\text{SO}_4 &= 2\text{H}^+ + \text{SO}_4^{2-} \\
&= \text{H}^+ + \text{HSO}_4^{-} \\
\text{KMnO}_4 &= \text{K}^+ + \text{MnO}_4^{-}
\end{align*}
\]

**Example:**

i) \(\text{KMnO}_4 + \text{KI} + \text{HCl} \rightarrow \text{MnCl}_2 + \text{I}_2 + \text{KCl} + \text{H}_2\text{O}\)

If all spectator ions are removed, we get

\[\text{MnO}_4^- + \text{I}^- + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{I}_2\]

Balancing the equation

\[2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}\]

Final equation:

\[2\text{KMnO}_4 + 10\text{KI} + 16\text{HCl} \rightarrow 2\text{MnCl}_2 + 5\text{I}_2 + 8\text{H}_2\text{O} + 12\text{KCl}\]

ii) \(\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{CO}_2 + \text{K}_2\text{SO}_4\)

If all spectator ions are removed, we get

\[2\text{Cr}_2\text{O}_7^{2-} + 6\text{C}_2\text{O}_4^{2-} + 28\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 12\text{CO}_2 + 14\text{H}_2\text{O}\]

Balancing,

\[2\text{Cr}_2\text{O}_7^{2-} + 6\text{C}_2\text{O}_4^{2-} + 28\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 12\text{CO}_2 + 14\text{H}_2\text{O}\]

Final equation:

\[2\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{K}_2\text{C}_2\text{O}_4 + 14\text{H}_2\text{SO}_4 \rightarrow 2\text{Cr}_2(\text{SO}_4)_3 + 12\text{CO}_2 + 14\text{H}_2\text{O} + 8\text{K}_3\text{SO}_4\]
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 H₂O.

vi) Balance remaining H by H⁺ or OH⁻ and H₂O (discussed in ion electron method).

Examples:

i) \[ \text{HN}_3 + \overset{+1}{\text{S}}_2 \overset{-2}{\text{O}}_2 \rightarrow \overset{+4}{\text{N}}_2 \overset{+1}{\text{O}}_2 + \overset{-1}{\text{S}}_4 \]

Step: \[ \text{HN}_3 + \overset{+5}{\text{S}}_2 \overset{-2}{\text{O}}_2 \rightarrow \overset{+4}{\text{N}}_2 \overset{+6}{\text{O}}_2 + \overset{-1}{\text{S}}_4 \]

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

\[ 2\text{HNO}_3 + 1\text{SO}_2 \rightarrow 2\text{NO}_2 + 1\text{H}_2\text{SO}_4 \]

ii) \[ \overset{+1}{\text{N}}_2 + \overset{0}{\text{Br}}_2 \rightarrow \overset{+5}{\text{NO}}_3 + \overset{-1}{\text{HBr}} \]

There is 3 increase in N and 2 decrease in Br₂.

So,

\[ 2\text{NO} + 3\text{Br}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + 6\text{HBr} \]

iii) \[ \overset{+2}{\text{Na}}_2\overset{0}{\text{S}_2\text{O}_3} + \overset{0}{\text{I}}_2 \rightarrow \overset{+2.5}{\text{Na}}_2\overset{-1}{\text{S}_4\text{O}_6} + \overset{+1}{\text{Na}} \]

\[ 2\text{Na}_2\overset{+2}{\text{S}_2\text{O}_3} + \overset{0}{\text{I}}_2 \rightarrow 1\text{Na}_2\overset{+2.5}{\text{S}_4\text{O}_6} + 2\overset{+1}{\text{Na}} \]

iv) \[ \overset{+6}{\text{Cr}_2}\overset{-2}{\text{O}_7^2} + \overset{+3}{\text{C}_2\text{O}_4^2} \rightarrow \overset{+3}{\text{Cr}^3+} + \overset{+4}{\text{CO}_2} \]

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

\[ 1\text{Cr}_2\overset{+6}{\text{O}_7^2} + 3\text{C}_2\overset{+3}{\text{O}_4^2} + 14\overset{+1}{\text{H}^+} \rightarrow 2\text{Cr}^3+ + 6\text{CO}_2 + 7\text{H}_2\text{O} \]
Practice questions

v) \[ \begin{align*}
\text{CrO}_4^{2-} & \quad + \quad I^- & \quad \xrightarrow{\text{H}^+} & \quad \text{Cr}^{3+} & \quad + \quad I_2 \\
1\text{CrO}_4^{2-} & \quad + \quad 3I^- & \quad + \quad 8\text{H}^+ & \quad \rightarrow & \quad 1\text{Cr}^{3+} & \quad + \quad 3/2 I_2 & \quad + \quad 4\text{H}_2\text{O} \\
\end{align*} \]

vi) \[ \begin{align*}
\text{AsO}_3^{-} & \quad + \quad \text{NO}_3^{-} & \quad \xrightarrow{\text{OH}^-} & \quad \text{AsO}_4^{3-} & \quad + \quad \text{NO}_2 \\
1\text{AsO}_3^{3-} & \quad + \quad 2\text{NO}_3^{-} & \quad + \quad \text{H}_2\text{O} & \quad \rightarrow & \quad 1\text{AsO}_4^{3-} & \quad + \quad 2\text{NO}_2 & \quad + \quad 2\text{OH}^- \\
\end{align*} \]

vii) \[ \begin{align*}
\text{FeS}_2 & \quad + \quad \text{O}_2 & \quad \rightarrow & \quad \text{Fe}_2\text{O}_3 & \quad + \quad \text{SO}_2 \\
2\text{FeS}_2 & \quad + \quad 11/2 \text{O}_2 & \quad \rightarrow & \quad \text{Fe}_2\text{O}_3 & \quad + \quad 4\text{SO}_2 \\
\end{align*} \]

viii) \[ \begin{align*}
\text{As}_2\text{S}_3 & \quad + \quad \text{HNO}_3 & \quad \rightarrow & \quad \text{H}_3\text{AsO}_4 & \quad + \quad \text{H}_2\text{SO}_4 & \quad + \quad \text{NO} \\
3\text{As}_2\text{S}_3 & \quad + \quad 28\text{HNO}_3 & \quad + \quad 4\text{H}_2\text{O} & \quad \rightarrow & \quad 6\text{H}_3\text{AsO}_4 & \quad + \quad 9\text{H}_2\text{SO}_4 & \quad + \quad 28\text{NO} \\
\end{align*} \]

ix) \[ \begin{align*}
\text{Cl}_2 & \quad \xrightarrow{\text{OH}^-} & \quad \text{Cl}^- & \quad + \quad \text{ClO}_3^- \\
3\text{Cl}_2 & \quad + \quad 6\text{OH}^- & \quad \rightarrow & \quad 5\text{Cl}^- & \quad + \quad \text{ClO}_2^- & \quad + \quad 3\text{H}_2\text{O} \\
\end{align*} \]

x) \[ \begin{align*}
\text{KMnO}_4 & \quad + \quad \text{H}_2\text{C}_2\text{O}_4 & \quad + \quad \text{H}_2\text{SO}_4 & \quad \rightarrow & \quad 2\text{MnSO}_4 & \quad + \quad \text{CO}_2 & \quad + \quad \text{K}_2\text{SO}_4 \\
2\text{KMnO}_4 & \quad + \quad 5\text{H}_2\text{C}_2\text{O}_4 & \quad + \quad 3\text{H}_2\text{SO}_4 & \quad \rightarrow & \quad 2\text{MnSO}_4 & \quad + \quad 10\text{CO}_2 & \quad + \quad \text{K}_2\text{SO}_4 & \quad + \quad 8\text{H}_2\text{O} \\
\end{align*} \]

xi) \[ \begin{align*}
\text{K}_2\text{Cr}_2\text{O}_7 & \quad + \quad \text{Fe(NO}_3)_2 & \quad + \quad \text{HNO}_3 & \quad \rightarrow & \quad \text{Cr(NO}_3)_3 & \quad + \quad \text{Fe(NO}_3)_3 & \quad + \quad \text{KNO}_3 & \quad + \quad \text{H}_2\text{O} \\
1\text{K}_2\text{Cr}_2\text{O}_7 & \quad + \quad 6\text{Fe(NO}_3)_2 & \quad + \quad 14\text{HNO}_3 & \quad \rightarrow & \quad 2\text{Cr(NO}_3)_3 & \quad + \quad 6\text{Fe(NO}_3)_3 & \quad + \quad 2\text{KNO}_3 & \quad + \quad 7\text{H}_2\text{O} \\
\end{align*} \]

xii) \[ \begin{align*}
\text{KMnO}_4 & \quad + \quad \text{HCl} & \quad \rightarrow & \quad \text{MnCl}_2 & \quad + \quad \text{H}_2\text{O} & \quad + \quad \text{Cl}_2 & \quad + \quad \text{KCl} \quad \text{oxidation no. is not} \\
\text{All HCl is not converting into Cl}_2. \\
\text{KMnO}_4 & \quad + \quad 8\text{HCl} & \quad \rightarrow & \quad 1\text{MnCl}_2 & \quad + \quad 5/2 \text{Cl}_2 & \quad + \quad \text{KCl} & \quad + \quad 4\text{H}_2\text{O} \\
\end{align*} \]

xiii) \[ \begin{align*}
\text{Cu} & \quad + \quad \text{HNO}_3 & \quad \rightarrow & \quad \text{Cu(NO}_3)_2 & \quad + \quad \text{NO}_2 & \quad + \quad \text{H}_2\text{O} \\
\text{Cu} & \quad + \quad 4\text{HNO}_3 & \quad \rightarrow & \quad \text{Cu(NO}_3)_2 & \quad + \quad 2\text{NO}_2 & \quad + \quad 2\text{H}_2\text{O} \\
\end{align*} \]
Consider the following reaction: \( x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + z\text{ H}^+ \rightarrow x\text{MnO}^{2+} + 2y\text{CO}_2 + \frac{z}{2}\text{H}_2\text{O} \)

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

(B)

Balanced chemical reaction:

\[ 2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \]

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

For the reaction:

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

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

(A) Stoichiometric coefficient of \( \text{HSO}_4^- \) is 6  
(B) Iodide is oxidized  
(C) Sulphur is reduced  
(D) \( \text{H}_2\text{O} \) is one of the products

(A), (B) & (D)

The balanced equation is:

\[ \text{ClO}_3^- + 6\text{I}^- + 6\text{H}_2\text{SO}_4 \rightarrow 3\text{I}_2 + \text{Cl}^- + 6\text{HSO}_4^- + 3\text{H}_2\text{O} \]

So, stoichiometric coefficient of \( \text{HSO}_4^- \) 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

\[
\text{Equivalent mass} = \frac{\text{Molar mass}}{n \text{- factor}}
\]

**Number of gm – equivalent**
- Equivalents is similar property as moles but its value of not fixed.
  i.e. 1 mole = \(N_A\) particles

  \[
  \text{But, 1 equivalent} = \begin{cases} 
  \frac{N_A \text{ particles}}{} & \text{All are possible} \\
  \frac{2N_A \text{ particle}}{} \\
  \frac{N_A / 3 \text{ particles etc.}}{} 
  \end{cases}
  \]

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

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

  \[
  = \text{Moles} \times n \text{-factor}
  \]

**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 \(\rightarrow\) equivalent/L or Normal

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

\[
\text{Normality} = \text{Molarity} \times n \text{- factor}
\]

\[
N \times V = (\text{Equivalent})_{\text{Solute}}
\]

**Calculation of n-factor**
- \(n\)-factor is the property of a substance which have a positive value only.
Redox Reaction

Case I: When no reaction is provided

i) For atom

\[ n - \text{factor} = \text{General valency} \]

\[ n - \text{Factor} \neq 0 \neq \text{negative} \]

e.g.

<table>
<thead>
<tr>
<th>Atom</th>
<th>n-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
</tr>
<tr>
<td>Fe</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
</tr>
</tbody>
</table>

\[ \text{etc.} \]

- **For ions:**

  \[ [n-\text{factor} = |\text{magnitude of charge on ion}| \]

  e.g. \[ \text{H}^+ = 1 \]

  \[ \text{Ba}^{2+} = 2 \]

  \[ \text{OH}^- = 1 \]

  \[ \text{CO}_3^{2-} = 2 \]

  \[ \text{PO}_4^{3-} = 3 \text{ etc.} \]

- **For acids:**

  \[ n - \text{factor} = \text{Maximum basicity} \]

  Basicity = number of replaceable H\(^+\) per molecule of acid.

  \[ \text{HCl, HBr, HI, HNO}_3, \text{ HCN,} \]

  e.g. \[ \text{HCOOH, CH}_3\text{COOH, H}_3\text{PO}_2, \]

  \[ \text{H}_3\text{BO}_3 \text{ etc.} \]

  \[ n - \text{factor} = 1 \]

  \[ \text{H}_2\text{SO}_4, \text{ H}_2\text{C}_2\text{O}_4, \text{ H}_2\text{CO}_4, \text{ H}_3\text{PO}_4 \text{ etc.} \]

  \[ n - \text{factor} = 2 \]

  \[ \text{H}_3\text{PO}_4, \text{ H}_3\text{AsO}_4 \text{ etc.} \]

  \[ n - \text{factor} = 3 \]

- **For bases:**

  \[ n - \text{factor} = \text{Maximum acidity} \]
Acidity = \( \frac{\text{No. of replacable OH}^-}{\text{No. of acceptable H}^+} \) 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:**
  \[ n – \text{factor} = \text{Total charge on cation or Total charge on anions} \]

<table>
<thead>
<tr>
<th>Salt</th>
<th>Ions</th>
<th>n-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>1 Na(^+) and 1 Cl(^-)</td>
<td>1</td>
</tr>
<tr>
<td>K(_2)SO(_4)</td>
<td>2 K(^+) and 1 SO(_4^{2-})</td>
<td>2</td>
</tr>
<tr>
<td>MgBr(_2)</td>
<td>1 Mg(^{2+}) and 2 Br(^-)</td>
<td>2</td>
</tr>
<tr>
<td>Ba(_3)(PO(_4))(_2)</td>
<td>3 Ba(^{2+}) and 2 PO(_4^{3-})</td>
<td>6</td>
</tr>
</tbody>
</table>

**Illustration:**

**Q1** Determine \( n – \text{factor} \) of K\(_2\)SO\(_4\).Al\(_2\)(SO\(_4\))\(_3\).24H\(_2\)O

**A1**
From cation: \( 2K^+ + 2Al^{3+} \)  
\( n – \text{factor} = 2 \times 1 + 2 \times 3 = 8 \)  
From anion: \( 1SO_4^{2-} + 3SO_4^{2-} \)  
\( n – \text{factor} = 4 \times 2 = 8 \)

**Q2** Calculate no. of gram equivalents in following:
i) 54 gm Al

Equivalent = \( \frac{54}{27} \times 3 = 6 \)

ii) 98 mg H₃PO₄

\( \frac{98}{98} \times 3 = 3 \)

iii) 2 mole CO₃²⁻ = 2×2 = 4

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

v) 12.04×10²² ions of SO₄²⁻ = \( \frac{12.04 \times 10^{22}}{N_A} \) \times 2 = 0.4

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

**A2** Using No. of equivalent = \( \frac{\text{Mass}}{\text{Molar mass}} \times n\text{-factor} \)

**Q3** Calculate normality of solution prepared by mixing 24.5 gm H₂SO₄ in its 500 ml solution.

**A3** Given 24.5 gm of H₂SO₄

\[ M = \frac{24.5}{\frac{98}{5000}} = 0.5 \]

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

or, No. of equivalents = \( \frac{\text{Mass}}{\text{Molar mass}} \times n\text{-factor} = \frac{24.5}{98} \times 2 = 0.5 \)
**n-factor (Valency Factor)**

**n-factor in non-redox reaction**

\[
\text{n-factor} = \frac{\text{Charge}}{\text{Exchanged per molecule}}
\]

Or

It is the magnitude of charge per molecule

\[
\begin{align*}
\text{Ag}^{+}\text{NO}_3^- + \text{Na}^+\text{Cl}^- & \rightarrow \text{Ag}^{+}\text{Cl}^- + \text{Na}^+\text{NO}_3^- \\
\text{n-factor} & \begin{array}{c}
1 \\
1 \\
1 \\
2
\end{array} \\
\text{Ag}^+\text{NO}_3^- + \text{Ba}^+\text{Cl}_2 & \rightarrow \text{Ag}^{+}\text{Cl}^- + \text{Ba}^\text{NO}_3^- \\
\text{n-factor} & \begin{array}{c}
1 \\
2 \\
1 \\
2
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + \text{HCl} & \rightarrow \text{H}_2\text{CO}_3 + \text{NaCl} \\
\text{n-factor} & \begin{array}{c}
2 \\
1 \\
1 \\
1
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + \text{HCl} & \rightarrow \text{NaHCO}_3 + \text{NaCl} \\
\text{n-factor} & \begin{array}{c}
1 \\
1 \\
1 \\
1
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{H}^+\text{Cl}^- + \text{Na}^+\text{OH} & \rightarrow \text{Na}^+\text{Cl}^- + \text{H}_2\text{O} \\
\text{n-factor} & \begin{array}{c}
1 \\
1 \\
1 \\
1
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{SO}_4 + \text{NaOH} & \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \\
\text{n-factor} & \begin{array}{c}
2 \\
1 \\
1 \\
1
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{SO}_4 + \text{NaOH} & \rightarrow \text{NaHSO}_4 + \text{H}_2\text{O} \\
\text{n-factor} & \begin{array}{c}
1 \\
1 \\
1 \\
1
\end{array}
\end{align*}
\]

**Note:**

\[
\begin{align*}
\text{Acid} + \text{Base} & \rightarrow \text{Salt} + \text{H}_2\text{O} \\
\downarrow & \downarrow & \downarrow & \downarrow \\
\text{n-factor} & \text{Basicity} & \text{Acidity} & \text{|Charge|} & (1)
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{PO}_4 + \text{NaOH} & \rightarrow \text{Na}_3\text{PO}_4 + \text{H}_2\text{O} \\
\text{n-factor} & \begin{array}{c}
3 \\
1 \\
3 \\
1
\end{array}
\end{align*}
\]
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:

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

**Example:**

\[
\begin{align*}
\text{H}_3\text{PO}_4 + \text{NaOH} & \rightarrow \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O} \\
n\text{-factor} & \quad (2) \quad (1) \quad (2) \quad (1)
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{PO}_4 + \text{NaOH} & \rightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O} \\
n\text{-factor} & \quad (1) \quad (1) \quad (2) \quad (1)
\end{align*}
\]

**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:

\[
\begin{align*}
\text{HNO}_3 + \text{SO}_2 & \rightarrow \text{NO}_2 + \text{H}_2\text{SO}_4 \\
n\text{-factor} & \quad (1) \quad (2) \quad (1) \quad (2)
\end{align*}
\]

\[
\begin{align*}
\text{NO} + \text{Br}_2 & \rightarrow \text{HIO}_3 + \text{HBr} \\
n\text{-factor} & \quad (3) \quad (2) \quad (3) \quad (1)
\end{align*}
\]

\[
\begin{align*}
\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 & \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + \text{NaI} \\
n\text{-factor} & \quad (1) \quad (2) \quad (2) \quad (1)
\end{align*}
\]

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{O}_4^{2-} & \rightarrow \text{Cr}^{3+} + \text{CO}_2 \\
n\text{-factor} & \quad (6) \quad (2) \quad (3) \quad (1)
\end{align*}
\]

\[
\begin{align*}
\text{CrO}_4^{2-} + \text{I}^- & \rightarrow \text{Cr}^{3+} + \text{I}_2 \\
n\text{-factor} & \quad (6) \quad (1) \quad (3) \quad (2)
\end{align*}
\]

\[
\begin{align*}
\text{AsO}_3^{3-} + \text{NO}_3^- & \rightarrow \text{AsO}_4^{3-} + \text{NO}_2 \\
n\text{-factor} & \quad (2) \quad (1) \quad (2) \quad (1)
\end{align*}
\]
Redox Reaction

\[
2\text{KMnO}_4 + 5\text{H}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{MnSO}_4 + 10\text{CO}_2 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O}
\]

\[
\begin{array}{cccccccc}
\text{n-factor} & \frac{10}{2} & \frac{10}{5} & \frac{10}{3} & \frac{10}{2} & \frac{10}{10} & \frac{10}{1} & \frac{10}{8} \\
\end{array}
\]

\[
\text{H}_3\text{AsO}_4^5^- + 2\text{K}^+ + 2\text{HCl} \rightarrow \text{H}_3\text{AsO}_4^3^- + \text{I}_2 + 2\text{KCl} + \text{H}_2\text{O}
\]

\[
\begin{array}{cccccccc}
\text{n-factor} & \frac{2}{1} & \frac{2}{2} & \frac{2}{2} & \frac{2}{1} & \frac{2}{2} & \frac{2}{2} \\
\end{array}
\]

\[
\text{KMnO}_4 + 8\text{HCl} \rightarrow \text{MnCl}_2 + \frac{5}{2}\text{H}_2\text{O} + \text{Cl}_2 + 4\text{KCl}
\]

\[
\begin{array}{cccccccc}
\text{n-factor} & \frac{5}{1} & \frac{5}{8} & \frac{5}{1} & \frac{5}{5/2} & \frac{5}{1} & \frac{5}{4} \\
\end{array}
\]

\[
\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + 2\text{NO}_3^- + 2\text{H}_2\text{O}
\]

\[
\begin{array}{cccccccc}
\text{n-factor} & \frac{2}{1} & \frac{2}{4} & \frac{2}{1} & \frac{2}{2} & \frac{2}{2} \\
\end{array}
\]

\[\text{n-factor for disproportionation} = \frac{xy}{x+y}\]

where
\[
x \rightarrow \text{n-factor for alone oxidation}
\]
\[
y \rightarrow \text{n-factor for alone reduction}
\]

\[\text{e.g.} \quad x = 1 \times 2 = 2 \uparrow \]
\[\text{Oxidation} \quad \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]
\[y = 1 \times 2 = 2 \downarrow \]
\[\text{Reduction} \quad \text{Cl}_2 \rightarrow \text{Cl}^- + \text{ClO}_3^- \]
\[\text{(n-factor)}_{\text{H}_2\text{O}_2} = \frac{2 \times 2}{2 + 2} = 1 \]
\[\text{(n-factor)}_{\text{Cl}_2} = \frac{2 \times 10}{2 + 10} = \frac{5}{3} \]

36.
Redox Reaction

\[ \text{KMnO}_4 + \text{MnSO}_4 \rightarrow \text{MnO}_2 \]

Reduction Oxidation Disproportion

\[ (n - \text{factor})_{\text{MnO}_2} = \frac{3 \times 2}{3 + 2} = \frac{6}{5} \]

**Note:** \( A_{x}B_{y} \rightarrow \text{Product} \)

\( n \)-Factor \( \neq 0 \)

\( \neq (-\text{ve}) \)

e.g., \( \text{NH}_3 \rightarrow \text{N}_2 + \text{H}_2 \)

\[ (n - \text{Factor})_{\text{NH}_3} \neq 0 \]

\[ = 3 \]

\[ \therefore 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \]

\[ \begin{pmatrix} 6 \\ 2 \end{pmatrix} \quad \begin{pmatrix} 6 \\ 1 \end{pmatrix} \quad \begin{pmatrix} 6 \\ 3 \end{pmatrix} \]

\( \text{H}_2 \quad \text{O}_2 \quad \rightarrow \quad \text{H}_2\text{O} \quad \text{(2)} \quad \text{(4)} \quad \text{(2)} \)

\( \text{P}_4 \rightarrow \text{PH}_3 + \text{H}_2\text{PO}_2^- \)

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

**Some commonly used agents**

i) **Permanganate ion** \( (\text{MnO}_4^-) \)

Since (+7) is maximum oxidation numbers for Mn so in redox reactions, \( \text{MnO}_4^- \) always acts as an oxidizing agent.

The product depends upon the medium of reaction as following:

- **Acidic**
  \[ \text{MnO}_4^- + \text{R.A} \rightarrow \text{Mn}^{2+} \quad \text{(5)} \]

- **Basic/Neutral**
  \[ \text{MnO}_4^- + \text{R.A} \rightarrow \text{MnO}_2 \quad \text{(3)} \]

- **Strong Basic**
  \[ \text{MnO}_4^- + \text{R.A} \rightarrow \text{MnO}_4^{2-} \quad \text{(1)} \]
ii) **Dichromate ion (Cr$_2$O$_7^{2-}$)**
It also acts as an oxidizing agent but only in acidic medium.

\[
\text{Cr}_2\text{O}_7^{2-} + 10\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 5\text{H}_2\text{O}
\]

\[
n - \text{factor Cr}_2\text{O}_7^{2-} = \frac{6}{1} \quad \text{and Cr}^{3+} = \frac{6}{2}
\]

\[
\text{Other medium} \quad \text{Non-redox}
\]

iii) **Oxalate ion (C$_2$O$_4^{2-}$)**
In redox reactions, it always acts as reducing agent.

\[
\text{C}_2\text{O}_4^{2-} \xrightarrow{\text{redox}} \text{any medium} \rightarrow \text{CO}_2
\]

\[
\Rightarrow (n - \text{factor})_{\text{C}_2\text{O}_4^{2-}} = 2
\]

iv) **H$_2$O$_2$**
With other reagent, will act as oxidizing and reducing agent

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{R.A} & \rightarrow \text{H}_2\text{O} \\
(\text{O.A}) & \\
\text{H}_2\text{O}_2 + \text{O.A} & \rightarrow \text{O}_2 \\
(\text{R.A}) & \end{align*}
\]

\[
(n - \text{factor})_{\text{H}_2\text{O}_2} = 2
\]

v) **Mohr's salt (Ferrous Ammonium sulphate)**

\[
\text{FeSO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O} \xrightarrow{\text{Redox}} \text{Fe}^{3+} \text{ only}
\]

\[
\Rightarrow (n - \text{factor})_{\text{Mohr's salt}} = 1
\]
**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 $aA + bB \rightarrow cC + dD$

If 'a' mole

required

`b` mole

produces

`c` mole

'd' mole

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

But

If 'x' Equivalent

required 'x' Equivalent

produces 'x' Equivalent

'x' Equivalent

$\Rightarrow A:B:C:D$ by equivalent = $1:1:1:1$

**e.g.**

\[
\begin{align*}
H_2SO_4 + 2NaOH & \rightarrow Na_2SO_4 + 2H_2O \\
1 \text{ mole} & \rightarrow 2 \text{ mole} \\
1 \text{ mole} & \rightarrow 2 \text{ mole} \\
\end{align*}
\]

$n$-factor \(2\) \(1\) \(2\) \(1\)

Equivalent \(2\) \(2\) \(2\) \(2\)

**Note:** So, for a particular reaction,

\[
\frac{(\text{Equivalent})_{\text{given}}}{(\text{Equivalent})_{\text{required}}} = 1
\]

where,

\[
\text{Equivalent} = \frac{\text{Mass}}{\text{Molar mass}} \times n \text{ - factor}
\]

\[
= \frac{\text{Mole} \times n \text{ - factor}}{M \times V \times n \text{ - factor}}
\]

\[
= \frac{N \times V}{M \times V}
\]
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:
$H_3PO_3 + 2KOH \rightarrow K_2HPO_3 + 2H_2O$
Volume of 0.1 M aqueous solution of phosphoric acid = 20 ml
We know from law of equivalence:
\[
\text{(Equivalent)}_{H_3PO_3} = \text{(Equivalent)}_{KOH}
\]
\[M_1 \times V_1 \times n\text{-factor} = M_2 \times V_2 \times n\text{-factor}\]
\[0.1 \times 20 \times 2 = 0.1 \times (V_{KOH}) \times 1\]
\[4 = (V_{KOH}) \times 0.1\]
\[V_{KOH} = 40 \text{ ml}\]

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
\[2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O\]
We know from law of equivalence:
\[
\text{(Equivalent)}_{KMnO_4} = \text{(Equivalent)}_{SO_3^{2-}}
\]
\[\text{(Mole} \times n\text{-factor})_{KMnO_4} = \text{(Mole} \times n\text{-factor})_{SO_3^{2-}}\]
\[n \times 5 = 1 \times 2\]
\[n = 2/5 \text{ moles}\]
**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)

\[
K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O
\]

We know from law of equivalence:

\[
\text{(Equivalent)}_{K_2Cr_2O_7} = \text{(Equivalent)}_{\text{Mohr’s salt}}
\]

\[
\left( \frac{\text{Mole}}{\text{Molar mass}} \times n - \text{factor} \right)_{K_2Cr_2O_7} = \left( \frac{\text{Mole}}{\text{Molar mass}} \times n - \text{factor} \right)_{\text{Mohr’s salt}}
\]

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

\[
w = \frac{0.6 \times 75 \times 294}{100 \times 6} = 22.05 \text{ gm}
\]

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

\[
P_4 + \text{HNO}_3 \rightarrow \text{H}_3\text{PO}_4 + \text{NO}_2 + \text{H}_2\text{O}
\]

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

**A4**  (B)

The balance chemical reaction:

\[
P_4 + 20\text{HNO}_3 \rightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}
\]

Molar mass of P$_4$ = 9/mol

Molar mass of HNO$_3$ = 63 9/mol

We know from law of equivalence:

\[
\text{(Equivalent)}_{P_4} = \text{(Equivalent)}_{\text{HNO}_3}
\]

\[
\left( \frac{\text{Mass}}{\text{Molar mass}} \times n - \text{Factor} \right)_{P_4} = \left( \frac{\text{Mass}}{\text{Molar mass}} \times n - \text{Factor} \right)_{\text{HNO}_3}
\]

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

\[
w = \frac{62}{124} \times 20 \times 63 = 630 \text{ gm}
\]
**Titration (A\(_{aq}\) vs B\(_{aq}\))**

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

![Titration setup with a conical flask and burette]

At equivalence point
\[(\text{Eq.})_A = (\text{Eq.})_B\]

**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**

\[\text{Ce}^{4+} + \text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + \text{Ce}^{n+}\]

\[
\begin{align*}
(\text{Milli Equivalent})_{\text{Ce}^{4+}} &= (\text{Milli Equivalent})_{\text{Sn}^{4+}} \\
(M \times V \times n - \text{factor})_{\text{Ce}^{4+}} &= (M \times V \times n - \text{factor})_{\text{Sn}^{4+}} \\
1 \times 40 \times (4 - n) &= 1 \times 20 \times 2 \\
40 \times (4 - n) &= 40 \\
4 - n &= 1 \\
n &= 4 - 1 \\
&= 3
\end{align*}
\]

**Q2** 6.7 gm sample of Na\(_2\)C\(_2\)O\(_4\) is titrated with 40 ml, 0.02 M KMnO\(_4\) solution in acidic medium. Calculate % purity of original sample.
A2 \[ \text{Na}_2\text{C}_2\text{O}_4 + \text{KMnO}_4 + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 \]

\[
\frac{x}{134} \times 2 = 0.02 \times \frac{40}{1000} \times 5
\]

\[
\frac{x}{67} = 0.1 \times \frac{4}{100}
\]

\[
x = 0.1 \times 4 \times 67
\]

\[
x = \frac{26.8}{100}
\]

\[
x = 0.268
\]

Now, \( \% \) purity = \( \frac{0.268}{6.7} \) \times 100

\( \% \) 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 \( \text{H}_2\text{O}_2 \) solution is “x” M

Molarity of diluted \( \text{H}_2\text{O}_2 \) solution = \( \frac{x}{20} \) M

\[ \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}_2 \rightarrow \text{Cr}^{3+} + \text{O}_2 \]

\[ \text{Milli } (\text{Equivalent})_{\text{K}_2\text{Cr}_2\text{O}_7} = (\text{Milli Equivalent})_{\text{H}_2\text{O}_2} \]

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

\[ x = 2 \text{ M} \]

\[ \text{Volume strength} = 2 \times 11.2 = 22.4 \text{ V} \]
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-} → Fe^{3+} + Cr^{3+}

(Equivalent)_{Fe} = (Equivalent)_{Cr_2O_7}, from law of equivalence

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

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

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.

\[ \therefore \text{ Eq. of } Na_2C_2O_4 + \text{ Eq. of } H_2C_2O_4 = \text{ Eq. of } KMnO_4 \]
\[ 1\times2 + 1\times2 = 0.1\times V_1 \times 5 \]
\[ (\because \text{ equivalent } = \text{ mole } \times \text{ valence factor}) \]
\[ V_1 = \frac{4}{0.5} \]
\[ V_1 = 8 \text{ L} \]

Case − II: Equimolar mixture of Na_2C_2O_4 and H_2C_2O_4 required V_2 L of 0.2 M NaOH for neutralization.

\[ \text{(Equivalent) } Na_2C_2O_4 + \text{(Equivalent) } H_2C_2O_4 = \text{(Equivalent) } NaOH \]
\[ 1\times2 + 1\times2 = V_2 \times 0.2 \times 1 \]
\[ 2 + 2 = V_2 \times 0.2 \]
\[ V_2 = 20 \text{ L} \]
\[ \therefore \frac{V_1}{V_2} = \frac{8}{20} = 2 : 5 \]
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.

\[
\text{I}_2 + \text{Reducing agent} \rightarrow \text{I}^- + \text{product}
\]

At equivalence point
\[
(Eq)_b = (Eq)_{\text{reducing agent}}
\]

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

**Step-I:**

\[
\text{Oxidising agent} + \Gamma (\text{aq})_{(\text{excess})} \rightarrow \text{Product} + \text{I}_2
\]

**Step-II:**

\[
\text{I}_2 (\text{evolved}) + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}
\]

\[
\begin{align*}
[(\text{Equivalent})_{\text{OA}}] &= [(\text{Equivalent})_{\text{I}_2}]_1 \quad \cdots (1) \\
[(\text{Equivalent})_{\text{I}_2}]_2 &= [(\text{Equivalent})_{\text{Hypo}}] \quad \cdots (2)
\end{align*}
\]

\[\therefore \text{Moles of I}_2 \text{ in both reactions are same.} \]

\[
(\text{n-factor})_1 = 2 \\
(\text{n-factor})_2 = 2
\]

\[\Rightarrow (Eq)_1 = (Eq)_2 \]

\[\text{So,} \quad (Eq)_{\text{OA}} = (Eq)_{\text{Hypo}}\]
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

\[ \text{KMnO}_4 + I^- \rightarrow \text{Mn}^{2+} + I_2 \]

\[ I_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + \text{NaI} \]

Volume of KMnO₄ solution = 50 ml

Volume of Na₂S₂O₃ solution = 200 ml

\[ \text{Mill Equivalent}_{\text{KMnO}_4} = \text{Mill Equivalent}_{\text{Na}_2\text{S}_2\text{O}_3} \]

\[ M \times 50 \times 5 = 0.25 \times 200 \times 1 \]

\[ M = \frac{0.25 \times 200}{50 \times 5} \]

Molarity of KMnO₄ = 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 Na₂S₂O₃ 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** 0.24 M

\[ \text{Cl}_2 + I^- \rightarrow I_2 + \text{Cl}^- \]

\[ I_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + \text{NaI} \]

\( n \) - factor \( I_2 \) is same in both steps

\[ \text{Molarity}_{\text{Bleach}} = \frac{x}{\text{Volume}} = \frac{6}{25} = 0.24 \text{ M} \]

**Note:**

All \( B \rightarrow C \)

If \( n \) - Factor of \( B \) in both are same

\( \text{Eq.}_A = (\text{Eq.})_C \)

If \( n \) - Factor of \( B \) are different

\( (\text{Eq.}_A)_1 \neq (\text{Eq.}_B)_2 \)

then apply mole method for solving

**Q3** 10 ml of K₂C₂O₄ solution is mixed with excess of KIO₃ solution. The evolved I₂ requires 20 ml, 0.5 M hypo solution for complete titration. Determine the molarity of K₂C₂O₄ solution.
A3 \[ \text{K}_2\text{C}_2\text{O}_4 + \text{KIO}_3 \rightarrow \text{I}_2 + \text{CO}_2 \]

\[ \text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]

(Milli Equivalent) \(_b\) = (Milli Equivalent) \(_{\text{Na}_2\text{S}_2\text{O}_3}\)

\[
\begin{align*}
n & = \frac{0.5 \times 20 \times 1}{2} \\
 & = 5 \text{ m.mole} \\
&= (\text{Milli Equivalent}) \(_{\text{K}_2\text{C}_2\text{O}_4}\) = (\text{Milli Equivalent}) \(_b\)
\end{align*}
\]

\[
\begin{align*}
M & = \frac{50}{20} \\
&= 2.5 \text{ M}
\end{align*}
\]

Q4 To measure the quantity of MnCl\(_2\) dissolved in an aqueous solution, it was completely converted to KMnO\(_4\) using reaction,

\[ \text{MnCl}_2 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{HCl} \] (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 \[ \text{MnCl}_2 \rightarrow \text{MnO}_4^- \]

\[ \text{MnO}_4^- + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Mn}^{2+} + \text{CO}_2 \]

\[
\begin{align*}
(\text{Factor})_{\text{MnO}_4^-} & \quad \text{same in both reaction} \\
\text{(Equivalent)}_{\text{C}_2\text{O}_4^2^-} & = \text{(Equivalent)}_{\text{MnO}_4^-} \\
2 \times \frac{0.225}{90} & = \text{moles} \times 5 \\
\Rightarrow & \quad \text{moles}_{\text{MnO}_4^-} = 0.001 \\
\text{(Equivalent)}_{\text{MnCl}_2} & = \text{(Equivalent)}_{\text{MnO}_4^-} \\
\text{Now}, \quad \frac{W_{\text{MnCl}_2}}{(55 + 71)} \times 5 & = 0.001 \times 5 \\
W_{\text{MnCl}_2} & = 0.001 \times (55 + 71) \text{ gm} \\
W_{\text{MnCl}_2} & = 126 \text{ mg}
\end{align*}
\]

Given quantity of MnCl\(_2\) dissolved in an aqueous solution was completely converted to KMnO\(_4\).

\[
\therefore \quad \text{Quantity of MnCl}_2 \text{ present in the initial solution} = 126 \text{ mg}
\]
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:**
\[ A + B \rightarrow \text{product} \]
\[ (\text{Eq})_A = (\text{Eq})_B \]

**Step–II:**
\[ B + C \rightarrow \text{product} \]
\[ \text{(remaining)} \]
\[ (\text{Eq})_B = (\text{Eq})_C \]
\[ (n_B)_1 + (n_B)_2 = \text{Initial moles of } B \text{ (Given)} \]

- If n-factor of B in both are same:
  \[ (\text{Eq})_B = (\text{Eq})_A + (\text{Eq})_C \]

- If n-factor of B in both are different:
  First solve reaction in steps (2) and find \((n_B)_1\).
  Now, \((n_B)_1 = (n_B)_{\text{given}} - (n_B)_2\)
  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**
\[ \text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} \]
\[ \text{HCl (Remaining)} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \]

Let ‘x’ gm of Ca(OH)$_2$ present in sample
n-factor of HCl is same in both.
So,
\[ (\text{Eq.)}_{\text{HCl}} = (\text{Eq.)}_{\text{Ca(OH}_2\text{)}} + (\text{Eq.)}_{\text{NaOH}} \]

\[
0.5 \times \frac{50}{1000} = \left( \frac{x}{74} \times 2 \right) + \left( 0.3 \times \frac{20}{1000} \right) \\
\frac{25}{1000} = \frac{x}{37} + \frac{6}{1000} \\
\Rightarrow \frac{25}{1000} \times \frac{6}{1000} = \frac{x}{37} \\
\frac{19}{1000} = \frac{x}{37} \\
\Rightarrow x = \frac{19}{1000} \times 37 \\
x = \frac{703}{1000} = 0.703 \text{ g} \\
\]

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

Q2 9.0 g of an ammonia solution is treated with 50 ml 0.5 N \( \text{H}_2\text{SO}_4 \) 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 \( \text{NH}_3 \) = \( x \) gm

\[
(\text{Eq.)}_{\text{H}_2\text{SO}_4} = (\text{Eq.)}_{\text{NH}_3} + (\text{Eq.)}} \\
0.5 \times \frac{50}{1000} = \left( \frac{x}{17} \times 1 \right) + \left( 0.1 \times \frac{20}{1000} \right) \\
\frac{25}{1000} = \frac{x}{17} + \frac{2}{1000} \\
\Rightarrow \frac{25}{1000} - \frac{2}{1000} = \frac{x}{17} \\
\Rightarrow \frac{23}{1000} \times 17 = x \\
\Rightarrow x = \frac{391}{1000} = 0.391\text{gm} \\
\therefore \% \text{NH}_3 = \frac{0.391}{9} \times 100 = 4.34\% \\
\]
40 ml solution of \( \text{Na}_2\text{C}_2\text{O}_4 \) 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 \( \text{H}_2\text{O}_2 \) solution in basic medium for complete titration.

Calculate molarity of \( \text{Na}_2\text{C}_2\text{O}_4 \).

\[
\begin{align*}
\text{C}_2\text{O}_4^{2–} + \text{MnO}_4^– & \rightarrow \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 \quad \ldots(1) \\
\text{MnO}_4^– + \text{H}_2\text{O}_2 & \rightarrow \text{OH}^- \rightarrow \text{MnO}_2 + \text{O}_2 \quad \ldots(2)
\end{align*}
\]

(Remaining)

\( n \)-factor of MnO\(_4^–\) is differed in both

For reaction 2,

\[
\begin{align*}
\text{m. moles} \times 3 &= 0.05 \times 10 \times 2 \\
\text{m. moles}_{\text{MnO}_4} &= \frac{5 \times 10 \times 2}{100 \times 3} \\
\text{m. moles}_{\text{MnO}_4} &= \frac{1}{3} \\
\text{m.moles of (MnO}_4^–)_{\text{Total}} &= 0.1 \times 100 = 10 \text{m.mole} \\
\text{m.moles of MnO}_4^– \text{ used in 1 reaction} &= 10 \times \frac{1}{3} = \frac{29}{3} \text{ m.mole}
\end{align*}
\]

For reaction (1):

\[
\begin{align*}
\text{(m. eq.)}_{\text{Na}_2\text{C}_2\text{O}_4} &= \text{(m. eq.)}_{\text{MnO}_4} \\
M \times 40 \times 2 &= \frac{29}{3} \times 5 \\
M &= \frac{29 \times 5}{3 \times 80} = \frac{145}{240} = \frac{29}{48} \text{ mol / L}
\end{align*}
\]
Double Indicator Titration:
The titration consisting two equivalence points which are detected by two different indicators.

- $\text{Na}_2\text{CO}_3(\text{aq.})$ vs (HCl(\text{aq.})

\begin{align*}
\text{i)} & \quad \text{When all } \text{Na}_2\text{CO}_3\text{ consume to give } \text{NaHCO}_3, \\
& \Rightarrow \quad \text{1st equivalence point is reached} \\
& \text{Suitable indicator = Phenolphthalein}
\end{align*}

\begin{align*}
\text{ii)} & \quad \text{Now on further addition of HCl} \\
& \quad \text{\text{NaHCO}_3 + HCl } \rightarrow \text{NaHCO}_3 + \text{NaCl} \quad \text{(Neutral)} \\
& \quad \text{When all } \text{NaHCO}_3\text{ consumed to give } \text{H}_2\text{CO}_3 \\
& \Rightarrow \quad \text{2nd equivalence point is reached} \\
& \text{Suitable indicator = Methyl orange}
\end{align*}

- 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.
Q1  In the mixture of (NaHCO₃ + Na₂CO₃), 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 Na₂CO₃ is:
(A) 2x  (B) y  (C) x/2  (D) (y−x)

A1 A

Now, methyl orange is added to detect 2nd equivalence point
NaHCO₃ + HCl → H₂CO₃ + NaCl

\[ (\text{m.eq})_{\text{HCl}} = (\text{m.eq})_{\text{NaHCO₃}} \]
\[ N \times y = (a + b) \times 1 \]

Na₂CO₃ + HCl → H₂CO₃

\[ (\text{Eq})_{\text{Na₂CO₃}} = (\text{Eq})_{\text{HCl}} \]
\[ b \times 2 = N \times V \]
\[ (N) \times 2 = N \times V \]
\[ V = \frac{2Nz}{N} \]
\[ V = 2x \]

∴ volume of HCl for complete reaction is 2x ml

Q2 0.1 g of a solution containing Na₂CO₃ and NaHCO₃ requires 10 ml of 0.01 N HCl for neutralization using phenolphthalein as an indicator. Weight percent of Na₂CO₃ in solution is
(A) 25  (B) 32  (C) 50  (D) None of these
A2

\[
\frac{m.\text{eq.}}{Na_2CO_3} = (\text{Eq})_{HCl}
\]

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

\[x = \frac{0.1 \times 106}{1000}\]

\[x = 106 \times 10^{-4} \text{ gm}\]

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

Q3

A mixture of NaOH and Na_2CO_3 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 1\textsuperscript{st} equivalence point (NaHCO_3)

First: All NaOH \[\text{HCl} \rightarrow NaCl; \text{ Then Na}_2CO_3 \text{HCl} \rightarrow NaHCO_3\]

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

\[0.1 \times 25 \times 1 \times 1 = x(1) + y(1)\]

\[\Rightarrow \quad x + y = 2.5 \text{ mmole} \quad \ldots(1)\]

Titration with methyl orange is added to detect 2\textsuperscript{nd} equivalence point direct

NaOH \[\text{HCl} \rightarrow NaCl\]

NaCO_3 \[\text{HCl} \rightarrow H_2CO_3\]

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

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

\[\Rightarrow \quad x + 2y = 3 \text{ mmole} \quad \ldots(2)\]

\[\Rightarrow x = 2 \text{ m. mole and } y = 0.5 \text{ m. mole, on solving (1) & (2).}\]

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

Q1

100 ml solution of NaOH and Na$_2$CO$_3$ 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

A

Let ‘x’ m mole of NaOH in 100 ml solution and ‘y’ m.ole of Na$_2$CO$_3$ in 100 ml solution.

HPh $\rightarrow$ 1$^{st}$ equivalence point (NaHCO$_3$)

$\Rightarrow$ \[(\text{m.eq.})_{\text{HCl}} = (\text{m.eq.})_{\text{NaOH}} + (\text{m.eq.})_{\text{Na}_2\text{CO}_3}\]

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

$\Rightarrow$ \[x + y = 1.75\] \hspace{1cm} (1)

MeOH $\Rightarrow$ 2$^{nd}$ equivalence point.

$\Rightarrow$ \[(\text{m.eq.})_{\text{HCl}} = (\text{m.eq.})_{\text{NaHCO}_3}\]

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

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

$\Rightarrow$ \[x = 1.5 \text{ m.mole}\]

\[\therefore\] Weight of NaOH $= 1.5 \times 40 \times 10^{-3} = 60 \text{ gm}\]
Q2

1 g of sample CaCO₃ was strongly heated and the CO₂ 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 CaCO₃ = 1×\(\frac{90}{100}\) = 0.9 gm

Mole of CaCO₃ = \(\frac{0.9}{100}\) mole

\[\therefore \text{ mole of CO}_2 \text{ liberated} = \frac{0.9}{100} \text{ mole} = 9 \text{ m.mole}\]

\[\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2\]

9 m.mole 9 m.mole

\[\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2\]

\[\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\]

9 m.mole 50 m.mole 9 m.mole

L.R (50-18)

=32 m.mole (Remaining)

\[\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}\]

\[\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl}\]

1st equivalence point

\[(\text{m.eq.})_{\text{HCl}} = (\text{m.eq.})_{\text{NaOH}} + (\text{m.eq.})_{\text{Na}_2\text{CO}_3}\]

\[0.5 \times V \times 1 = 32(1) + 9(1)\]

\[V_{\text{HCl}} = \frac{41}{0.5}\]

\[= \frac{41}{5} \times 10\]

\[V_{\text{HCl}} = 82 \text{ ml}\]
**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.) or Mg$^{2+}$(aq.) $\rightarrow$ (C$_{17}$H$_{35}$COO)$_2$Ca or Mg(C$_{17}$H$_{35}$COO)$_2$ ppt.

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

\[
\begin{align*}
\text{i.e.} & \quad \text{Ca(HCO}_3\text{)}_2 \\
& \quad \text{Mg(HCO}_3\text{)}_2 \\
& \quad \text{CaCl}_2 \\
& \quad \text{MgCl}_2 \\
& \quad \text{CaSO}_4 \\
\end{align*}
\]

**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:

\[
\sum (\text{m.eq.) salts}) = (\text{m.eq.)CaCO}_3 \\
\therefore n\text{ factor of all} = 2 \\
\Rightarrow \sum (n)_{\text{salts}} = (n)_{\text{CaCO}_3}
\]

**Illustration:**

Q1 One litre of a sample of hard water contains 1 mg of CaCl$_2$ and 1 mg of MgCl$_2$ Then the total hardness in terms of parts of CaCO$_3$ 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

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

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

Hardness = \( 10^{-3} \left[ \frac{73}{146} + \frac{162}{162} + \frac{136}{136} + \frac{95}{95} + \frac{111}{111} \right] \times 100 \times 10^6 \)

Hardness = 450 ppm
Removal of Hardness:

\[ \text{Ca}^{2+}(aq.) \text{ or Mg}^{2+}(aq.) \xrightarrow{\text{every method}} \text{Water insoluble salt of Ca or Mg} \]

\((\text{Water soluble salts}) \xrightarrow{\text{Precipitate}}\)

- **Temporary hardness:**
  It is easily removed by following process:
  a) By boiling of water
     \[ \text{M(HCO}_3\text{)}_2(aq.) \rightarrow \text{MCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \]
  b) By the addition of Na\(_2\)CO\(_3\)
     \[ \text{M(HCO}_3\text{)}_2(aq.) + \text{Na}_2\text{CO}_3(aq.) \rightarrow \text{MCO}_3(s) + 2\text{NaHCO}_3(aq.) \]
  c) Clarke’s process:
     By the addition of exact amount of Ca(OH)\(_2\), because excess will also impart hardness in water.
     \[ \text{Ca(HCO}_3\text{)}_2(aq.) + \text{Ca(OH)}_2(aq.) \rightarrow 2\text{CaCO}_3(s) + 2\text{H}_2\text{O}(l) \]
     \[ \text{Mg(HCO}_3\text{)}_2(aq.) + \text{Ca(OH)}_2 \rightarrow \text{MgCO}_3(s) + \text{CaCO}_3(s) + 2\text{H}_2\text{O}(l) \]

- **Permanent hardness**
  i) By adding Na\(_2\)CO\(_3\) or Na\(_3\)PO\(_4\).
     \[ \text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3↓ + \text{Na}_2\text{SO}_4 \]
     \[ 3\text{CaCl}_2 + 2\text{Na}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2↓ + 6\text{NaCl} \]
  ii) Ion exchange resins process.
     \[ 2\text{RnH}^+ + \text{Ca}^{2+} \xrightarrow{\text{cation exchanger}}(\text{Rn})_2\text{Ca} + 2\text{H}^+ \]
  iii) Permutit process
     \[ \text{Ca}^{2+} \text{Na}_2Z \rightarrow \text{CaZ} + 2\text{Na}^+ \rightarrow \text{Ca}^{2+} \text{Na}_2Z \rightarrow \text{CaZ} + 2\text{Na}^+ \]
     \[ \text{Mg}^{2+} + \text{Na}_2Z \rightarrow \text{MgZ} + 2\text{Na}^+ \]
     \[ \text{[Na}_2Z \text{is the sodium zeolite (Na}_2\text{Al}_2\text{Si}_2\text{O}_8\text{H}_2\text{O)]} \]
  iv) Calgon (Calcium gone) process
     \[ \text{Na}_3(\text{PO}_4)_6 \text{ is called Calgon which is written as Na}_3[\text{Na}_2(\text{PO}_4)_6] \]
     \[ \text{Na}_3(\text{PO}_4)_6]^{2+} + \text{M}^{2+} \rightarrow \text{Na}_2\text{M(PO}_3\text{)}_6^{2+} + 2\text{Na}^+ \]
     where \( \text{M} = \text{Ca}^{2+}/\text{Mg}^{2+} \)
Illustration:

Q1 A sample of hard water contains 20 mg of Ca^{2+} ions per litre. How many milli equivalent of Na_{2}CO_{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
\[
(m.equiv.)_{Na_{2}CO_{3}} = (m.equiv.)_{Ca^{2+}}\]
\[
= \left(\frac{20}{40}\right) \times 2
\]
\[
= 1 \text{ milliequivalent}
\]

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 \times 10^{4} gm  (B) 6.5 \times 10^{4} gm  (C) 5.6 \times 10^{5} gm  (D) 8.5 \times 10^{5} gm

A2  
C  
Given Volume of water = 10^{6} L
\[
= 10^{9} \text{ ml}
\]
Mass of water = 10^{9} gm

Using, (in ppm) hardness = \frac{\text{mass of CaCO}_{3} \times 10^{6}}{\text{mass of water}}
\[
1000 = \frac{W_{\text{CaCO}_{3}} \times 10^{6}}{10^{9}}
\]
\[
W_{\text{CaCO}_{3}} = 10^{4} \text{ gm}
\]
\[
= 10^{4} \text{ mole}
\]
i.e. \[ \text{mole of moeCaCO}_{3} = 10^{4} \text{ mole} \]
\[
\text{(Eq.)}_{\text{salt}} = (\text{Eq.)}_{\text{CaO}}
\]
\[
10^{4} \times 2 = \frac{W}{56}
\]
\[
w = \frac{10^{4} \times 2 \times 56}{2}
\]
\[
w = 56 \times 10^{4}
\]
\[
w = 5.6 \times 10^{5} \text{ gm}